6th INTERNATIONAL CONFERENCE ON

BROADBAND DIELECTRIC SPECTROSCOPY AND ITS APPLICATIONS

CONFERENCE CHAIRS

Tiberio A. Ezquerra
Aurora Nogales
Instituto de Estructura de la Materia

madrid
7-10 september
2010

CSIC
CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

6th International Conference
on
BROADBAND DIELECTRIC SPECTROSCOPY
and its APPLICATIONS.

Joint Meeting of
The 6th Conference of the
INTERNATIONAL DIELECTRIC SOCIETY

The 11th Conference on
DIELECTRIC AND RELATED PHENOMENA

September 7-10, 2010
Madrid (Spain)

BOOK OF ABSTRACTS

CSIC
Consejo Superior de Investigaciones Científicas

IEM INSTITUTO DE ESTRUCTURA DE LA MATERIA

GOBIERNO DE ESPAÑA

MINISTERIO DE CIENCIA E INNOVACIÓN

CSIC
CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

MODELICO
Modelización y Simulación de Sistemas Complejos (S2009ESP-1691),
Programa de Actividades I+D entre Grupos de Investigación de la Comunidad de Madrid 2010-2013

SEDOPTICA
SOCIEDAD ESPAÑOLA DE ÓPTICA

¡MADRID! MADRID CONVENTION BUREAU
Con la colaboración de
Comunidad de Madrid
MADRID about you

novocontrol Technologies

solartron analytical

Depósito Legal: M-31153-2010
Dirección y coordinación: Tiberio A. Ezquerra y Aurora Nogales
Edita: Consejo Superior de Investigaciones Científicas
Instituto de Estructura de la Materia
C/ Serrano 121
http://www.iem.csic.es/
Diseño de cubierta y maquetación: Aurora Nogales y Tiberio A. Ezquerra
Fotografía de portada: Isabel Nogales
Impresión: Gráficas MAFRA
Impreso en España (Printed in Spain)

ORGANIZING COMMITTEE

CONFERENCE CHAIRS

Tiberio A. Ezquerra. IEM-CSIC, Spain
Aurora Nogales. IEM-CSIC, Spain

LOCAL COMMITTEE

Alejandro Sanz. IEM-CSIC, Spain
Mari Cruz García Gutierrez. IEM-CSIC, Spain
Jaime J. Hernández. IEM-CSIC, Spain
Amelia Linares. IEM-CSIC, Spain
Daniel R. Rueda. IEM-CSIC, Spain
Santiago Sánchez Cortés. IEM-CSIC, Spain
Cristina Álvarez. ICTP-CSIC, Spain
Carlos León. UCM, Spain
Alberto Rivera-Calzada. UCM, Spain

INTERNATIONAL ADVISORY BOARD

K. Asami (Japan)
I. Alig (Germany)
G. Bąk (Poland)
M.C. Bellissent-Funel (France)
J.G. Berberian (USA)
G. Boiteux (France)
P. Cebe (USA)
J. Colmenero (Spain)
R. Díaz-Calleja (Spain)
M. Dionísio (Portugal)
Y. Feldman (Israel)
G. Floudas (Greece)
K. Fukao (Japan)
R. Gerhard (Germany)
R. González-Rubio (Spain)
B. Hilczer (Poland)
J.M. Kenny (Spain)
F. Kremer (Germany)
J. Klafter (Israel)
C. Lacabanne (France)
J.J. Martinez-Vega (France)
J. Mijovic (USA)
M. Paluch (Poland)
P. Pissis (Greece)
R. Richert (USA)
Mike Roland (USA)
B. Roling (Germany)
P. Rolla (Italy)
J. Runt (USA)
J.M. Saiter (France)
A. Schönhals (Germany)
J. Swenson (Sweden)
J. Ulański (Poland)
A. Vassilikou-Dova (Georgia)
K. Weron (Poland)
G. Williams (UK)
M. Wübbenhorst (Belgium)
S. Yagihara (Japan)

Preface

Broadband Dielectric Spectroscopy (BDS) is a technique that relies on the interaction of electromagnetic waves with matter in a frequency range that goes from 10^{-6} Hz to 10^{12} Hz. This extremely wide frequency range allows the study of both molecular fluctuations and collective phenomena, charge and polarization effects and the characterization of dielectric properties of a great variety of materials in both liquid and solid phase. This versatility has made BDS to become a fundamental tool in useful in the multidisciplinary design, characterization and application of advanced functional materials and systems applied in such diverse fields as those ranging from nanotechnology to biology.

The development of modern techniques of Broadband Dielectric Spectroscopy (BDS) during the mid-nineties inspired Yuri Feldman, John Berberian and Friedrich Kremer to organize a series of international conferences in Dielectric Spectroscopy beginning in 2001 in Jerusalem. Previously, a series of conferences on Dielectric and Related Phenomena (DRP) were initiated in Poland in 1990 by Aleksander Szymanski and Andrew K. Jonscher to meet demands of both academic and industrial researchers to discuss different aspects of investigations and applications of dielectrics, insulators, electrets etc.

Since then four BDS conferences have been organized: 2nd BDS-2002 in Liepzig, Germany, 3rd BDS-2004 in Delft, Holland; 4th BD-S2006 in Poznan, Poland and finally the 5th BDS-2008 in Lyon, France.

In 2010 the group of Structure and Dynamics of Condensed Matter, Institute of Structure of Matter (CSIC) (http://www.iem.cfmac.csic.es/fmacro/softmatpol/) is committed to organize in Madrid the BDS-2010.

6th International Conference on Broad Band Dielecric Spectroscopy

Monday 6/09/2010

	Room A
18:00-20.00	Welcome Party

Tuesday 07/09/2010

9:00-9:30	Opening Ceremony

Room A	MD_GT (J. Berberian)
9:30-10:00	**K.L.Ngai**
10:00-10:15	D. Cangialosi
10:15-10:30	Y. Matsumiya
10:30-10:45	D. Fragiadakis
10:45-11:15	**C.M. Roland**

11:15-11:45	Coffee Break (Room A)	
	Room A	Room B
	S_GR (K. Ngai)	HM_1(J. Kenny)
11:45-12:15	**R. Richert**	**C. Lacabanne**
12:15-12:30	L. Delbreilh	F. Aliev
12:30-12:45	M. Shahin-Thayyil	A. Lyaschenko
12:45-13:00	K. Grzybowska	B. Ishai
13:00-13:15	P. Frübing	T. Blochowicz

13:15-15:00	Lunch	
	Room A	Room B
	IL_CT_1 (A. Rivera)	BM_1(S. Cerveny)
15.15:15:45	**B. Roling**	**J. Swenson**
15:45-16:00	C. León	S. Capaccioli
16:00-16:15	R.J. Sengwa	Y. Katsumoto
16:15-16:30	M. Drüschler	Y. Hayashi
16:30-16:45	A. Mogus-Milankovic	I. Ermolina

16:45-17:15	Coffe Break (Room A)	
	Room A	Room B
	IL_CT_2 (C. León)	BM_2 (F. Bruni)
17:15-17:45	**J. Ulanski**	**Y. Feldman**
17:45-18:00	C. Filipic	V. Samouillan
18:00-18:15	L.I. Trakhtengerg	I. Stroe
18:15-18:30	G.F. Novikov	R.B. Talware
18:30-18:45	J.R. Sangoro	

Wednesday 08/09/2010

	NCS_1		HB_AM_1
Room A	(A. Sanz)	Room B	(T. Blochowicz)
9:00-9:30	**F. Kremer**	9:00-9:30	**G. Williams**
9:30-9:45	S. Napolitano	9:30-9:45	R. Nozaki
9:45-10:00	K.H. Nguyen	9:45-10:00	R. Casalini
10:00-10:15	K. Verkhovskaya	10:00-10:15	J. Bartos
10:15-10:30	C. Rotella	10:15-10:30	K. Kaminski
10:30-11:00	**K.Fukao**	10:30-10:45	R. Pelster
		10:45-11:00	Z. Chen

11:00-13:30	Coffee Break (Cloister) Poster_1

13:30-15:30	Lunch (Cloister)		
	HB_AM_2		HM_2
Room A	(D. Cangialosi)	Room B	(G. Bolteux)
15:30-16:00	**M. Wübbenhorst**	15:30-16:00	**A. Schönhals**
16:00-16:15	M. Dionisio	16:00-16:15	O.I.H. Dimitry
16:15-16:30	E. Dantras	16:15-16:30	V. Boucher
16:30-16:45	S. Ancherbak	16:30-16:45	A. Kyritsis
16:45-17:00	M.C. Lanca	16:45-17:00	J.L. Wojkiewicz
17:00-17:15	A.V. Adejanov	17:00-17:15	J.M. Kenny

Thursday 09/09/2010

	NCS_2	P_FM_1
	(S. Napolitano)	(G. Schwartz)
9:00-9:30	**E. Laredo**	**D. Prevosto**
9:30-9:45	I. Royaud	V. Bovtun
9:45-10:00	A. Serghei	V.A. Stephanovic
10:00-10:15	A. Sanz	A. Levstik
10:15-10:30	N.T. Correia	N. Seleznev
10:30-10:45	A. Naberezhnov	H. Haspel
10:45-11:15	**A. Alegria**	**E.A. Rossler**
	Room A	Room B

11:15-13:30	Coffee Break (Cloister) Poster_2

13:30-15:30	Lunch(Cloister)	
	Room A	Room B
	P_FM_2(I. Royaud)	S_T (J. Colmenero)
15:30-16:00	**G. Floudas**	**G.D. Smith**
16:00-16:15	S. Arrese-Igor	F. Affouard
16:15-16:30	M. Hernandez	Z. Ghallabi
16:30-16:45	A. Bernes	J. Trzmiel
16:45-17:00	R. Kisiel	R.R. Nigmatulin
17:00-17:15	S. Jurga	M. Yu Balakina
17:15-17:45	**J. Runt**	**J. Dyre**

21:00-24:00	Conference Dinner

Friday 10/09/2010

Room A	DD (F. Kremer)
9:00-9:30	**R. Böhmer**
9:30-9:45	G.A. Schwartz
9:45-10:00	V.V. Meriakri
10:00-10:15	N. Axelrod
10:15-10:30	B.A. Mazzeo
10:30-10:45	B. Martin
10:45-11:00	M. Abdelguerfi
11:00-11:30	**M. Paluch**

11:30-12:00	Coffee break(Room A)

Room A	BM_3 (Y. Feldman)
12:00-12:15	F. Bruni
12:15-12:30	M. Vogel
12:30-12:45	A. Caduff
12:45-13:00	S. Cerveny
13:00-13:30	**A.P. Sokolov**

13:30-13:45	Closing Ceremony
13:45-16:00	Farewell Party Cloister

MD_GT	Molecular Dielectric and Glass Transition
S_GR	Secondary and Glassy Relaxations
IL_CT	Ionic Liquids/Charge Transport
BM	Biological materials
NCS	Nanoconfined Systems

HB_AM	Hydrogen Bonded/Aqueous Materials
HM	Heterogeneous Materials
P_FM	Polymers/Funcional Materials
S_T	Simulation and Theory
DD	Dielectric Developments

Room A	Serrano 117
Room B	Serrano 119
Cloister	Serrano 123

Conference Dinner: Restaurant Pedro Larrumbe
Serrano 61,level 4th

6TH INTERNATIONAL CONFERENCE ON
BROADBAND DIELECTRIC
SPECTROSCOPY AND ITS APPLICATIONS

www.dielectric2010.com
07 - 10 MADRID
SEPTEMBER 2010

List of contributions

ORAL CONTRIBUTIONS

Molecular Dielectric And Glass Transition

MDGT-1: *Universal relaxation and diffusion in many-body interacting systems.*
K. L. Ngai

MDGT-2: *Effect of environment on the dynamics of a polychlorinated biphenyl in 1-4 polybutadiene.*
D. Cangialosi, A. Alegría, J. Colmenero

MDGT-3: *Viscoelastic and dielectric investigation of segmental dynamics of Polystyrene.*
Y.Matsumiya, H.Watanabe

MDGT-4: *Dynamics of liquid crystals at their phase transitions.*
D. Fragiadakis, R.B. Bogoslovov, J. Czub, S. Urban, C.M. Roland

MDGT-5: *Dielectric Isosbestic Points.*
G. Williams.

Secondary And Glassy Relaxations

SGR-1: *The heterogeneous nature of physical aging.*
R. Richert

SGR-2: *Temperature dependence of the characteristic length scale for glassy dynamics: Combination of dielectric and specific heat spectroscopy.*
L. Debreilh, A. Saiter, H. Couderc, K. Arabeche, E. Dantras, A. Schönhals, J.-M. Saiter

SGR-3: *Universality of Johari-Goldstein relaxation: Crucial evidences from flexible dipolar molecules.*
M. Shahin Thayyil, S. Capaccioli, D. Prevosto, S. Ancherbak, M. Lucchesi, P.A. Rolla, K. L. Ngai.

SGR-4: *Molecular dynamics and physical stability of amorphous anti-inflammatory drug – celecoxib.*
K. Grzybowska, Z. Wojnarowska, M. Paluch, A. Grzybowski, K. Adrjanowicz, P. Wlodarczyk, and K. L. Ngai.

SGR-5: *Relaxation processes and structural transitions in stretched films of poly(vinylidene fluoride) and its copolymer with hexafluoropropylene.*
P. Frübing, F. Wang, R. Gerhard, and M. Wegener.

Ionic Liquids And Charge Transport

ILCT-1: *Characterisation of nonlinear ion transport in solid and liquid electrolytes.*
B. Roling, H. Staesche, J. Kirchberg.

ILCT-2: *AC conductivity and nearly constant loss in oxide-ion conductors* $Gd_2(Zr_yTi_{1-y})_2O_7$.
M.R. Díaz-Guillén, J.A. Díaz-Guillén, A.F. Fuentes, J. Santamaría, C. León.

ILCT-3: *Dielectric relaxation and ionic conduction behaviour of melt compounded PEO-blend salt-MMT nanocomposite electrolytes.*
R.J. Sengwa, S. Sankhla, S. Choudhary.

ILCT-4: *Temperature-dependent measurements of differential capacitance at Pt / RTIL interfaces.*
M. Drüschler, B. Huber, B. Roling.

ILCT-5: *Correlation between electrical properties and microstructure of crystallized* $ZnO\text{-}Fe_2O_3\text{-}P_2O_5$ *glass.*
A. Moguš-Milankovic, K. Sklepic, Ž. Skoko, S.T. Reis.

ILCT-6: *Charge carrier transport in organic p-n junctions as seen by impedance spectroscopy.*
J. Jung, K. Kisiel, J. Ulanski

ILCT-7: *Polarons in Magnetoelectric* $K_3Fe_5F_{15}$ *and* $K_3Fe_2Cr_3F_{15}$.
C. Filipič, V. Bobnar, G. Tavčar, B. Žemva, and A. Levstik.

ILCT-8: *Non-phenomenological description of complex dielectric permittivity of metal oxide nanocrystals films.*
L.I. Trakhtenberg, M.A. Kozhushner, V.F. Gromov, G.N. Gerasimov, A. Greenbaum (Gutina)

ILCT-9: *Broadband photodielectric spectroscopy: history, progress and near prospects.*
G. F. Novikov.

Heterogeneous materials

HM-1: *Dielectric relaxations and Electrical behaviour in polyamide matrix nanocomposites: PA 11 / NTC and PA 11 /* $BaTiO_3$.
J.- F. Capsal, D. Carponcin, E. Dantras, C. Lacabanne.

HM-2: *Dynamic and thermodynamic properties of dry and hydrated novel networks from ring-opening metathesis polymerization.*
F. Aliev, V. Dolidze, Ke Zhang, Gregory N. Tew.

HM-3: *Dielectric spectroscopy of aqueous electrolyte solutions in all orientation frequency range.*
A. Lyashchenko, A.Lileev, T.Novskova.

HM-4: *Exposing the dielectric behaviour of 'exotic' gels.*
P. Ben Ishai, D. Libster, A. Aserin, N. Garti, Yu. Feldman

HM-5: *Intrinsic Confinement Effects in the Blend Dynamics of Binary Glass-Forming Systems*
T. Blochowicz, S. Schramm, E. Gouirand, P. Gutfreund, B. Stühn ,B. Frick

HM-6: *Structure-Property Relationships of Polymeric Nanocomposites with Layered Nanofillers. Interplay between Matrix and Interfacial Effects.*
A. Schönhals.

HM-7: *Studies of some polyurethane/organically modified montmorillonite nanocomposites.*
O. I.H. Dimitry, A.I.Abdeen E.A. Ismail, A.L.G.Saad

HM-8: *Application of dielectric spectroscopy to the study of physical aging in PMMA/silica nanocomposites.*
V. Boucher, D. Cangialosi, A. Alegrìa, J. Colmenero, I. Pastoriza-Santos, L. M. Liz-Marzan.

HM-9: *Thermal transitions of solvent and polymer dynamics in binary poly(ethyl acrylate) /p-xylene mixtures.*
A. Kyritsis, A. Stathopoulos, F. Romero Colomer, A. Sanchez Alcazar, J.L. Gómez Ribelles, N. Shinyashiki.

HM-10: *Dielectric properties of polyaniline hybrid nanocomposites.*
JLWojkiewicz, N.El Kamchi, C.Saravanan, N.Redon, T.Lasri.

HM-11: *Dielectric and Chemorheological Behavior of Carbon Nanotube Epoxy Nanocomposites.*
F. Scarponi, M. Leonardi, D. Fioretto, L.Valentini, J.M. Kenny.

Biological Materials

BM-1: *Slow relaxations in liquids and the role of solvent for the protein glass transition.*
J. Swenson, H. Jansson, R. Bergman.

BM-2: *Slow and fast dynamics of hydrated proteins: the pivotal role of secondary β-relaxation of water.*
S. Capaccioli, M. Bertoldo, P.A. Rolla, N. Shinyashiki, K.L. Ngai

BM-3: *Dielectric spectroscopy on flowing single lymphocytes.*
Y. Katsumoto, S. Omori, K. Sato, T. Umetsu, Y. Hayashi, H. Soma, T. Hayakawa, M. Saito, S. Lee, A. Yasuda, M. Nagasawa, T. Morio, S. Mizutani.

BM-4: *Venous thrombosis risk assessment by dielectric spectroscopy.*
Y. Hayashi, Y. Katsumoto, M-A. Brun, S. Omori, M. Kaibara, I. Uchimura.

BM-5: *Investigating temperature-induced phase transition in aqueous solutions of poly(vinyl methyl ether) by dielectric, terahertz and microscopic techniques.*

I. Ermolina, V. Khutoryanskiy .

BM-6: *Dielectric properties of bound water in biological systems; The Beauty of Nature.*
Y. Feldman, A. Puzenko and P. Ben Ishai.

BM-7: *Scanning of the hydrogen bond network of hydrated elastin by dielectric spectroscopy.*
D. Tintar, V. Samouillan, J. Dandurand, I. Bocchichio and C. Lacabanne.

BM-8: *Detection of Amyloid Precursors by Dielectric Relaxation Spectroscopy.*
I. Stroe, D. Barry, F. Prifti.

BM-9: *Dielectric relaxation study of biomolecules using time domain reflectometry (TDR) technique.*
R. B. Talware, P. G. Hudge, A. C. Kumbharkhane.

BM-10: *Two dynamic crossovers in protein hydration water.*
F. Bruni, M. G. Mazza, K. Stokely, S. E. Pagnotta, H. E. Stanley, G. Franzese.

BM-11: *Comparison of results from nuclear magnetic resonance and dielectric spectroscopy on the temperature-dependent dynamics of protein hydration waters.*
M. Vogel, S.A. Lusceac

BM-12: *Chronobiology, dielectric characterisation and the relevance to non invasive in vivo monitoring of biophysical parameters.*
A. Caduff , P. Zakharov, A. Megej, F. Dewarrat, M. Talary

BM-13: *Hydration water dynamics in cement based materials and deoxyribonucleic acid (DNA).*
S. Cerveny, S. Arrese-Igor, J, Dolado, A. Alegría, J. Colmenero.

BM 14: *Dynamics of biomolecules: Combining dielectric and neutron scattering spectroscopy.*
A. P. Sokolov.

Nanoconfined systems

NCS-1: *Dielectric relaxations at nanometric length-scales.*
F. Kremer, E. Mapesa, M. Tress and A. Serghei.

NCS-2: *Adsorption and deviations from bulk behavior, from dead to self-accelerated layers.*
S. Napolitano, M. Wübbenhorst.

NCS-3: *Relaxation dynamics of ultrathin polymer films investigated on the nanoscale by local dielectric spectroscopy.*
K. H. Nguyen, D. Prevosto, M. Labardi, S. Capaccioli, M. Lucchesi, P.A. Rolla

NCS-4: *Dielectric relaxation spectra in ultrathin ferroelectric polymer films and nanocrystals.*

K.Verkhovskaya, A.Plakseev, A.Lotonov and N. Gavrilova.

NCS-5: *Dielectric relaxation spectroscopy signature of polymer adsorption at a solid surface.*
C. Rotella, S. Napolitano, M. Wübbenhorst.

NCS-6: *Glass transition dynamics of single and stacked thin films of polymers.*
K. Fukao, Y. Oda, T. Terasawa, K. Nakamura, D. Tahara.

NCS-7: *Bionanocomposites based on poly(ε-caprolactone), poly(lactide) and their blend.*
E. Laredo.

NCS-8: *Molecular mobility at the interfaces of nanostructured systems.*
E. Nikaj, I. Royaud, G. Seytre, L. David, E. Espuche, A. Jonquières, M. Billy, S. Etienne.

NCS-9: *Nanofluidics by Broadband Dielectric Spectroscopy.*
A. Serghei, and T. P. Russell.

NCS-10: *Confined dynamics in semicrystalline polymers: A Dielectric Spectroscopy and Neutron Spin Echo Study.*
A. Sanz, A. Nogales, M. Soccio, N. Lotti and T.A. Ezquerra

NCS-11: *Confinement effects in the molecular dynamics of ibuprofen studied by DRS.*
A. R. Brás, I. M. Fonseca, F. Affouard, A.Schönhals, M. Dionísio, N.T. Correia

NCS-12: *Dielectric response and crystal structure of nanocomposites* KNO_3 *- porous glasses.*
A. Naberezhnov, E. Koroleva, A. Sysoeva, S.Vakhrushev, E. Rysiakiewicz-Pasek, M.Tovar.

NCS-13: *Dielectric relaxation in nano-structured diblockcopolymers: obtaining specific structural information*
A.Alegría.

Hydrogen Bonded and Aqueous Materials

HBAM-1: *Dynamic heterogeneity and relaxation properties of supercooled liquids.*
C.M. Roland, D. Fragiadakis, R. Casalini, K.L. Ngai, and S. Capaccioli

HBAM-2: *Dielectric spectroscopy of alcohols up to 2.5THz.*
Y. Yomogida, R. Nozaki

HBAM-3: *Insights On The Origin Of The Debye Process In Monoalcohols From Dielectric Spectroscopy Under Extreme Pressure Conditions.*
D. Fragiadakis, C.M. Roland and R. Casalini.

HBAM-4: *On the mutual relationships between atomistic and molecular probe dynamics and broad-band dielectric spectroscopy.*
J Bartoš, H.Švajdlenková, O.Šauša, J.Krištiak, P.Lunkenheimer, A.Loidl

HBAM-5: *Dynamic of the clusters in monosaccharides followed by dielectric spectroscopy.*
K. Kaminski, K. Adrjanowicz, Z Wojnarowska, P. Wlodarczyk, K. Grzybowska, R. Wrzalik, M. Paluch.

HBAM-6: *Crystallization and induced glass transition of n-alcohols confined in silicon-nanochannels.*
R. Pelster, R. Berwanger, Ch. Schumacher.

HBAM-6: *Phase transition of 5CB/DDAB/Water microemulsion as a function of temperature and time: detected by dielectric spectroscopy*
Z. Chen, R. Nozaki.

HBAM-8: *Dynamics in H-bonding glass forming liquids: From ultrathin films to ultrastable glasses.*
M.Wübbenhorst, S. Capponi, S. Napolitano, S. Rozanski, G. Couderc, N-R. Behrnd, J. Hulliger.

HBAM-9: *Physico-Chemical and Dynamical Characterization of a Cellulose Acetate Membrane.*
M.Sousa, A. R. Brás, F. C. Ferreira, M. N. de Pinho, N.T. Correia, M. Dionísio

HBAM-10: *Dielectric analysis of water/polymer interactions: from synthetic to natural polymers.*
E. Dantras, F. Roig, N. Caussé, M. Chevalier, C. Tonon, P. Guigue, C. Puig, C. Durin, C. Lacabanne.

HBAM-11: *Dynamics of aqueous mixtures at low T and high P.*
S. Ancherbak, S. Capaccioli, D. Prevosto, K. Grzybowska, M. Paluch.

HBAM-12: *Controlling the electrical and dielectric properties of a cork derivative and their relation to humidity.*
M. C. Lança, I. Cunha, J. P. Marques, E. R. Neagu, C. Dias, L.Gil, J. N. Marat-Mendes

HBAM-13: *Dielectric and electric properties of nanodiamonds water suspensions.*
A.V. Adeljanov, O.A. Gorobchenko, E. M. Mamotyuk, O.T. Nikolov, V. N. Ivaschenko, S.V. Gatash

Polymers and funcional materials

PFM-1: *Relaxation properties of polymer nanocomposites: a dielectric spectroscopy insight at the nanometric scale.* D. Prevosto, M. Labardi, Kim H. Nguyen, S. Capaccioli, M. Lucchesi, P. Rolla.

PFM-2: *Broadband dielectric spectroscopy of relaxor ferroelectrics with and without ferroelectric transition*
V. Bovtun, S. Kamba, D. Nuzhnyy, J. Petzelt.

PFM-3: *Non - perovskite disordered ferroelectrics: relaxor vs mixed ferroelectric - dipole glass behavior.*
V.A.Stephanovich, E.V. Kirichenko.

PFM-4: *Magnetoelectric Relaxor* $0.8Pb(Fe_{1/2}Nb_{1/2})O_3$-$0.2Pb(Mg_{1/2}W_{1/2})O_3$ *and Burns temperature in ferroelectric relaxors.*
A. Levstik, C. Filipič, V. Bobnar, and Z. Kutnjak.

PFM-5: *Dielectric properties of dry rocks.*
N. Seleznev

PFM-6: *Dielectric spectroscopic studies on 1D titanate nanostructures.*
H. Haspel, A. Sápi, Á. Kukovecz, Z. Kónya, I. Kiricsi.

PFM-7: *Protracted crossover to full entanglement dynamics revealed by dielectric spectroscopy and field cycling 1H NMR.*
A. Abou Elfadl, R. Kahlau, A. Herrmann, D. Kruk, V. N. Novikov, E.A. Rössler.

PFM-8: *Effect of pressure on the dynamic heterogeneity of miscible polymer blends.*
G. Floudas

PFM-9: *Effect of Blending on the Chain Dynamics of the "Low-Tg" component in non-entangled polymer blends.*
S. Arrese-Igor, A. Alegría, J. Colmenero

PFM-10: *Effects of strain induced crystallization on the dielectric behavior of natural rubber.*
M. Hernández, R. Verdejo, M.A. López-Manchado, T.A. Ezquerra.

PFM-11: *Storage effects in an adhesive system studied by dielectric relaxations*
E. Carsalade, A. Bernès, S. Perraud, C. Lacabanne

PFM-12: *Molecular dynamics in PVME hydrogels at sub-zero temperatures.*
R. Kisiel, M. Kozanecki, A. Schoanhals, M. Pastorczak, K. Koynov, L. Okrasa1, H.J. Butt, K. Krysiak, J. Ulanski.

PFM-13: *Molecular dynamics of miktoarm star block copolymers based on poly(butyl acrylate) and poly(ethylene oxide)*
M. Makrocka-Rydzyka, A. Wypycha, M. Jancelewicza, S. Jurga

PFM-14: *Dynamics of Polyurethane Block Copolymers in the Undeformed and Deformed States*
J. Runt, H. Lee, D. Fragiadakis, A. Castagna, D. Martin.

Simulation and theory

ST-1: *Dynamics and Relaxation in Room Temperature Ionic Liquids: Molecular Dynamics Simulation Studies Using High Quality Polarizable Force Fields.* G. D. Smith*, D. Bedrov and O. Borodin.

ST-2: *Debye process in ibuprofen glass-forming liquid: insight from molecular dynamics simulation.* F. Affouard, N.T. Correia.

ST-3: *Theoretical and experimental study of the composite based polyfluoride of vinylidene P(VDF)/barium titanate.*
Z. Ghallabi , M. Arous, A. Kallel, I. Stevenson-Royaud, G. Boiteux and G. Seytre.

ST-4: *Two-power-law relaxation processes in semiconductors possessing metastable defects.*
J. Trzmiel, K. Weron.

ST-5: *Evidences of the fractional kinetics in temperature region: evolution of extreme points in dielectric spectra.*
R. R. Nigmatullin.

ST-6: *Modeling of Quadratic Response and its RelaxationStability for Nonlinear Optical Polymer Electret*
M.Yu. Balakina

ST-7: *Modeling ion conduction in disordered solids and other funda*mental challenges.
Jeppe C. Dyre.

Dielectric developments

DD-1: *Electrical cleaning of dielectric materials: Experimental method for spectral resolution enhancement and recent applications.*
C. Gainaru, R. Böhmer.

DD-2: *nanoDielectric Spectroscopy (nDS) of polymeric systems by using Electric Force Microscopy.*
G.A. Schwartz, R. Arinero, C. Riedel, P. Tordjeman, A. Alegria and J. Colmenero.

DD-3: *Beam Waveguide spectroscopy of Materials in Millimeter and Submillimeter Waves Ranges.*
V.V. Meriakri, E.E. Chigrai, M.P. Parkhomenko.

DD-4: *Analyte Detection in Solutions Using Coupled Antennae Impedance Spectroscopy (AIS).*
A. Lichtenstein, A. Konevsky, N. Ferrera, D. Nuttman, J. Schreiber, N. Axelrod.

DD-5: *Overcoming electrode polarization by magnetic induction spectroscopy.*
B.A. Mazzeo, P. Getz.

DD-6: *Kohlrausch relaxations by interacting and non-interacting dipoles in PVDF copolymer.*

B. Martin, H. Kliem.

DD-7: *New dielectric techniques developed by time domain reflectometry.*
M.Abdelguerfi, A.Soualmia.

DD-8: *Study of Kinetics of Tautomerization Process in some Pharmaceutically Important Molecules – New Application of BDS.*
M. Paluch, Ż.Wojnarowska, P. Włodarczyk, K. Kamiński.

Poster contributions

P-1: *Dielectric study in methacrylate-endcapped caprolactone/poly(ethylene glycol) methacrylate copolymer networks.*
R. Sabater i Serra, J.L. Escobar Ivirico, A. Andrio Balado, M. Monleón Pradas, M. Salmerón-Sánchez, J.L. Gómez Ribelles

P-2 *Dielectric Spectroscopy and Phase Behavior of Side Chain Liquid Crystalline Copolymers.*
Y.Hepuzer Gursel, H. Cinkaya, O.Kamer, F.Salehli.

P-3: *Effect of gamma-irradiation on the electret properties of poly-L-lactid*
T.Yovcheva, M. Marudova, A. Viraneva, E. Gencheva, N. Balabanov, G. Mekishev

P-4: *Pressure effect on the polymer electrets films behaviour.*
A.Viraneva, T.Yovcheva, E. Gencheva, G. Mekishev

P-5: *Influence of the gas media on the stability of corona charged polypropylene films stored at low pressures.*
G. Mekishev, T. Yovcheva, A. Viraneva, E. Gencheva

P-6: *Influence of fragility on polymer cold crystallization.*
A. Sanz, A. Nogales, T.A. Ezquerra

P-7: *Influence of the Crystalline Structure in the Segmental Mobility of Semicrystalline Polymers: Poly(triethylene terephthalate).*
I. Martín-Fabiani, A. Linares, A. Sanz, A. Nogales, T.A. Ezquerra

P-8: *Phase behaviour and dynamics in a symmetric Polystyrene-block-Poly(ethyl methacrylate) Copolymer*
A. Sanz, D. R. Rueda, T.A. Ezquerra and A. Nogales

P-9: *On the use of insulating electrodes in dielectric spectroscopy measurements*
S.E. Pagnotta, S. Cerveny, A. Alegría, J. Colmenero, F. Bruni

P-10: *Dielectric properties of poly(2- hydroxyethoxyethylmethacrylamide-cooxyethylenemethacrylate)s*
M.B. Redondo, M. Carsí, P. Ortiz-Serna, M.J. Sanchis, R. Díaz-Calleja, E. Riande, J. Guzmán ,F. García

P-11: *Dipolar and Ionic Relaxations of Poly(methacrylate)s Containing Dimethoxy-Phenyl Side Groups*

M.J. Sanchis, M. Carsí, P. Ortiz-Serna, G. Domínguez-Espinosa, R. Díaz-Calleja, E. Riande, L. Alegría, L. Gargallo, D. Radic´

P-12: *Broadband Dielectric Spectroscopy of Poly(methyl methacrylate-co-(1,4,7,10-tetraoxacyclododecan-2-yl) methyl methacrylate) membranes*
M.B. Redondo, P. Ortiz-Serna, M. Carsí, M.J. Sanchis, R. Díaz-Calleja, E. Riande, J. Guzmán, F. García, J.M. García

P-13: *Molecular dynamics of 2,2,2-trifluoroethylacrylate polymers investigated by dielectric spectroscopy*
M. Raihane, E. G. Merino, S. Atlas, A. Belfkira, M. Dionísio, N. Correia

P-14: *Crystal growth in low density poly(ethelene) observed by use of ion motion*
Y. Anada

P-15: *Low k dielectric materials in electronic interconnect devices*
I. Abuetwirat

P-16: *Dielectric Properties of Poly (2-ethoxyethyl methacrylate-co-2,3 dihydroxypropyl methacrylate) Membranes.*
M. Carsí, P. Ortiz-Serna, M. B. Redondo, R. Díaz-Calleja, M. J. Sanchis, E. Riande, J. Guzmán

P-17: *Assessment of mechanical and dielectric characteristics of polyethylene/polar seed hair systems*
S. Aradoaei, R. Darie, I. Spiridon, R. Ciobanu

P-18: *Morphology and dielectric properties of some LDPE/PA blendes in present of compatibilizers*
R. Darie, S. Aradoaei, R. Ciobanu, C. Vasile,

P-19: *Study of the nanostructure of phase-separated polymer mixtures by using Electrostatic Force Microscopy*
M.M. Kumali, G.A. Schwartz, A. Alegría, J. Colmenero

P-20: *Combined DDS and TSC studies of dipolar relaxations in PEEK*
A. Leonardi, E. Dantras, C. Lacabanne

P-21: *Relation between the electromechanical response and the dielectric breakdown of Poly(ethylene naphthalene 2,6-dicarboxylate) (PEN) films under high DC electrical field*
N. Lahoud, B. Zegnini, J. Martinez-Vega

P-22: *Influence of the nature of the solvent on the secondary and structural relaxations of PMMA*
N. Suárez, N. Salazar Serge, J. L. Feijoo, and M. Hernández

P-23: α- *and* β- *Dielectric Relaxations in Fluorinated Methacrylate Polymers and Copolymers of Vinylidene Cyanide*
S. Capaccioli, V. Castelvetro, P.A. Rolla, M. Raihane, S. Atlas and A. Meskini

P-24: *Molecular motion of mechanically degradated poly(ethylene terephthalate) PET studied by offresonance NMR techniques*
M. Baranowski, A. Woźniak-Braszak, K. Jurga, J. Jurga, K Hołderna-Natkaniec

P-25: *On the influence of the space charge on the characteristics of the phase transition in ferroelectric polymers*
V. Kochervinskii, I. Malyshkina, M. Shcherbina, N. Bessonova

P-26: *Study on molecular motions and phase separation in polyEGDM/LBH semi-interpenetrating network*
M. Makrocka-Rydzyk, K. Wegner, A. Wypych, S. Jurga, E. Andrzejewska

P-27: *Polymer functionalization as a tool to selectively study component dynamics in miscible polymer blends by dielectric spectroscopy*
S. Plaza-García, R. Lund, A. Alegría, J. Colmenero, J. Janoski, R. P. Quirk.

P-28: *Kinetics of curing reaction for selected epoxy resins described in terms of changes in ionic conductivity.*
M. Włodarska

P-29: *Dielectric response of cured epoxy resins based on biphenyl group in wide range of temperature.*
M. Włodarska, B. Mossety-Leszczak, A Maj, G. W. Bąk, H. Galina, M. Izdebski

P-30: *Molecular dynamics and structure of poly(styrene-b-isoprene) diblock copolymers*
studied by BDS and NMR
J. Jenczyk, M. Makrocka-Rydzyk, A. Wypych, S. Głowinkowski, S. Jurga

P-31: *Sub-glass relaxations in novel aromatic polyimides with application on gas separation process.*
C. Álvarez, C. García, M. Calle, A. E. Lozano, J. G. de la Campa, J. de Abajo

P-32: *Origin of the β relaxation in PVDF based ferroelectric polymers. Confinement effects?*
A. Nogales, A. Sanz, T.A. Ezquerra

P-33: *The study of space charge relaxation in polyethylene terephthalate by using the final thermally stimulated discharge current method*
E. R. Neagu, C. J. Dias, M. C. Lança, R. Igreja, P. Inácio, J.N. Marat-Mendes

P-34: *Electro-thermal poling of silver ion conducting glasses with antibacterial properties*
J. Kruempelmann, B. Roling

P-35: *Investigations of the nonlinear ionic conductivity in mixtures of*

ionic liquids with molecular solvents.
J. Kirchberg, B. Roling.

P-36: *Colloidal Dispersions of Nanoparticles in Ionic Liquid*
C. Roesser, R. Roling

P-37: *Ammonia-hydrates: Ionic liquids and solids.*
H. Didzoleit, C. Gainaru, R. Böhmer

P-38: *Dielectric properties of Zn-ZnO multilayer systems deposited on non-woven substrate.*
M. Jaroszewski, J. Pospieszna, J. Ziaja

P-39: *Temperature-dependent cyclic voltammetry on different RTIL based on FAP-anions*
T. Jänsch, M. Drüschler, B. Roling

P-40: *Polymeric Lithium Electrolytes based on Ionic Liquids.*
B. Huber, B. Roling.

P-41: *A dielectric spectroscopy study on ionic liquid microemulsions*
Z. Chen, R. Nozaki

P-42: *The dielectric and transport properties of anisotropic polymer electrolytes*
A. Greenbaum (Gutina), Yu. Feldman, K. Shvartsman, D. Golodnitsky, E. Peled, S. Khatun, P. Stallworth, S. Greenbaum

P-43: *Dielectric relaxation in double potassium yttrium orthophosphate $K_3Y(PO_4)_2$ doped by ytterbium ions*
S. Szulia, H.A. Kołodziej, M. Kosmowska, G. Czupińska

P-44: *Dielectric relaxation of aqueous salts solutions with negative hydration of ions.*
A. Kobelev, A. Lileev, A. Lyashchenko

P-45: *Characteristic hopping lengths and molecular volumes of imidazolium-based ionic liquids*
J. R. Sangoro, C. Iacob, and F. Kremer

P-46: *Dielectric Strength of Polaron Process as Effective Dipole Correlation Factor in Ferroelectric $KTaNbO_3$*
S. E. Lerner, P. Ben Ishai, M. Mierzwa, M. Paluch, A. J. Agranat, and Y. Feldman

P-47: *Behavior Dielectric Properties of Ceramic System (SiO2-Fe2O3-MoO3) Added to V2O5 with Temperature Variation.*
C.C.Silva, T. S. M. Fernandes, M. A. S. Silva, M.M. Costa, A.S.B. Sombra.

P-48: *Slow molecular mobility and calorimetric studies in the amorphous solid state of some imidazolium ionic liquids derivatives*
H. P. Diogo, J. J. Moura-Ramos, S. S. Pinto

P-49: *Dielectric Spectroscopy of the $C0_2Y$, Y-type hexaferrite $Ba_2Co_2Fe_{12}O_{22}$ added with Bi_2O_3*
M.M. Costa, G.F.M. Pires Júnior, A.M. Walterley, C.C Silva, A.S.B. Sombra.

P-50: *Nb_2O_5 nanopowders - structural, morphology and dielectric properties.*
M.P.F Graça ,A. Meireles, C. Nico and M.A. Valente

P-51: *Dielectric properties of the glasses and related crystalline phases issued from the $BaNb_2O_6$-$NaNbO_3$- WO_3-P_2O_5 system.*
M.A. Valente, M.P.F. Graça and L. Bih

P-52: *Explaining the dielectric behavior of poly- and singlecrystalline CCTO using a polaronic stacking fault defect model*
F. Amaral, M. Valente, L. Costa, F. Costa, A. Fernandes

P-53: *AC conductivity of zirconia doped with rare earth oxides.*
Z. Benali Z. , B. Ziane, H. Belarbi, A. Haouzi.

P-54: *Electric and dielectric response of nanosize zinc-ferrites crystallites incorporated in a glass network*
M.G. Ferreira da Silva, M.P.F. Graça

P-55: *Effect of adding TeO_2 in $CaCu_3Ti_4O_{12}$ on the dielectric losses*
F. Amaral, B. Ferreira, M.A. Valente, M.P.F. Graça, L.C. Costa

P-56: *Dielectric studies on antimony tellurite glasses doped with titanium.*
T. Satyanarayana, M.A. Valente, M.P.F. Graça and N. Veeraiah

P-57: *Dynamics of ionic liquids based on different cations.*
A. Rivera-Calzada, K. Kaminski, C. Leon, M. Paluch

P-58: *Dielectric properties of aqueous $Ca(NO_3)_2.4H_2O$ Solution*
D B Suryawanshi, A C Kumbharkhane

P-59: *The Evaluating of the activation parameters in the transition region of parylene C by thermally stimulated techniques.*
A. Kahouli, A.Sylvestre, J. Legrand, F. Jomni, B. Yangui

P-60: *Dielectric properties and hydration of DNA complexes with some intercalators.*
D.A. Pesina, V.A. Kashpur, O.V. Khorunzhaya and V.Ya. Maleev

P-61: *Finite-difference calculations for effects of T-tubules on dielectric spectra of skeletal muscle.*
K. Sekine, A. Yamada, H. Kageyama, T. Igarashi, K. Asami

P-62: *Dielectric modeling of biological cells using three-dimensional finite-element method.*
K. Asami

P-63: *Time Domain Dielectric Study of Mouse spleen B and T cell suspensions.*
A. Shendrik, G. Elikin, I. Resnick, Y. Feldman

P-64: *Dielectric Influence of the Glutaraldehyde in the Galactomannan Films.*
A.A.M. Macêdo, C.C.Silva, M.M. Costa, ,A.S.B. Sombra,S.E. Mazzetto,

P-65: *Thermally stimulated currents study on the amorphous state of two disaccharides: cellobiose and gentiobiose.*
H. P. Diogo, J. J. Moura-Ramos, S. S. Pinto,2, T. G. Nunes

P-66: *Dielectric properties of the Collagen_Chitosan membrane in the temperature range.*
M.M. Costa, J.C. Góes, S. D. Figueirô, A.S.B. Sombra.

P-67: *Glass transitions in aqueous solution of protein (hen egg lysozyme).*
A.Panagopoulou, M.Aravantinou, D.Nanopoulos, P.Pissis

P-68: *Design and performance test of a Coaxial waveguide for measurement of dielectric constant in a broad microwave region (1GHz to 6GHz)*
J. Monteiro, S.K. Mendiratta, J. C. Pedro

P-69: *Analysis of dielectric spectra of human subjects during glucose excursions.*
F. Dewarrat, M. Talary, Y. Feldman, A. Caduff

P-70: *Segmental dynamics of semicrystalline poly(vinylidene fluoride) nanorods.*
J. Martín, C. Mijangos, A. Sanz, T. A. Ezquerra, A. Nogales

P-71: *Impact of surface interactions on the glassy dynamics of thin layers of PMMA*
M. Tress, M. Erber, E.U. Mapesa, K.-J. Eichhorn, A. Serghei, B. Voit, F. Kremer.

P-72: *Charge transport in confined ionic liquids.*
C. Iacob, J. R. Sangoro, P. Papadopoulos, J. Kärger, F. Kremer

P-73: *Restricted Segmental Relaxation in Oriented Semicrystalline Poly(vinilydene fluoride) as Revealed by Broad Band Dielectric Spectroscopy.*
A. Linares, A. Nogales, A. Sanz, T.A. Ezquerra, M. Pieruccini

P-74: *Dynamics in ultrathin liquid films studied by simultaneous dielectric spectroscopy (DRS) and organic molecular beam deposition (OMBD).*
S. Capponi, S. Napolitano, M. Wübbenhorst

P-75: *Behavior of dielectric properties of thin conductive polymers film.*
M. Olariu, R. Ciobanu, S. Aradoaei

P-76: *Glassy dynamics in nanometer thin layers of polystyrene.*
E.U. Mapesa, M.Erber, M. Tress, K.-J. Eichhorn, A. Serghei, B. Voit, F. Kremer

P-77: *Dielectric spectrum and water activity of swine skin gelatin-gel.*
R. Shirakashi, R. Sakane, J. Yamada

P-78: *Destabilizing hydrogen-bonded structures in monohydroxy alcohols.*

C. Gainaru, M. Preuß, A. Reiser, R. Böhmer

P-79: *Changing the dielectric properties of insulating oil under the influence of water content..*
M. Jaroszewski, J. Pospieszna

P-80: *Study of the Molecular Dynamics under crystallization of Triton X-100.*
E. G. Merino, J. Sotomayor, M. Dionísio, N. Correia

P-81: *Dynamics of Orientationally Disordered Mixed Crystals composed of CN-cyclohexane and Cyclohexane.*
J. C. Martinez-Garcia, J. Ll. Tamarit, M. Barrio, L. C. Pardo, N. Veglio, P. Lunkenheimer, A. Loidl

P-82: *Dynamics of Orientationally Disordered Mixed Crystals composed of Cycloheptanol and Cyclooctanol.*
J. C. Martinez-Garcia, J. Ll. Tamarit, L. C. Pardo, M. Barrio, N. Veglio, A. Drozd-Rzoska, S.J. Rzoska

P-83: *Statistical Disorder Effects on the Dynamics of 2-Adamantanone.*
M. Romanini, J. C. Martinez-Garcia, J. Ll. Tamarit, M. Barrio, L. C. Pardo, Ph. Negrier, D. Mondieig.

P-84 *Dominant Parameter for Dielectric α -relaxation Time of Polyhydric Alcohols.*
M. Nakanishi, R. Nozaki

P-85 *Microwave dielectric properties and relaxation in alkali metals and ammonium fluoride aqueous solutions.*
A. Lileev, A.Lyashchenko

P-86: *Dielectric Relaxation in ATP and AMP aqueous solutions.*
E. Levy, A. Puzenko, A. Shendrik, I. Segev, M. Talary, A. Caduff, Y. Feldman

P-87: *Monitoring changes during network formation by dielectric measurements.*
M.T. Viciosa, M. Dionísio, J.L. Gómez Ribelles

P-88: *Dynamics of water in poly(propylene glycol) studied by BDS and low temperature ATR-FTIR.*
L. P. Singh, S. Cerveny, A. Alegría, J. Colmenero.

P-89: *Dielectric relaxation and ac conductivity of poly(Nvinylcaprolactam)-water systems.*
I. Malyshkina, N. Gavrilova, E. Makhaeva, G. Markin

P-90: *Dielectric permittivity and electrical conductivity of ionic mixtures soil/rainwater.*
A.Soualmia, M.Abdelguerfi

P-91: *Multiple phase diagram in supercooled ethanol studied by Simultaneous Dielectric Spectroscopy and Neutron Diffraction.*
A. Sanz, I. Puente-Orench, M. Jiménez-Ruiz, A. Nogales and T. A. Ezquerra.

P-92: *Dielectric studies of sodium carboxymethylcellulose.*

V. Holcman, T. Palai-Dany, K. Liedermann

P-93: *Infrared dispersion of dipropyl ethers.*
J.P. Hawranek, W. Wrzeszcz, M. Pajdowska and H.A. Kołodziej

P-94: *Infrared dispersion of intramolecularly H-Bonded o-Hydroxybenzylidenemethylimine.*
J.P. Hawranek, W. Wrzeszcz, M. Matusiak-Kucharska, M. Pajdowska

P-95: *Molecular dynamics in PVME hydrogels at sub-zero temperatures.*
R. Kisiel, M. Kozanecki, A. Schoanhals, M. Pastorczak, K. Koynov, L. Okrasa, H.J. Butt, K. Krysiak, J. Ulanski

P-96: *Influence of Gemini surfactant on phase behaviour of phosphocholine DMPC water suspension.*
K. Szpotkowski, A. Wypych, M. Kozak and S. Jurga

P-97: *Dielectric and electric properties of nanodiamonds water suspensions.*
A.V. Adeljanov, O.A. Gorobchenko, E.M. Mamotyuk, O.T. Nikolov1, V.N. Ivaschenko, S.V. Gatash.

P-98: *Role of counterions on thermal behavior of aqueous phospholipid-surfactant systems.*
M. Kozak, A. Wypych, K. Szpotkowski and S. Jurga

P-99: *Influence of selected technological parameters on the dielectric properties of carbon-unwoven fabric composite systems.*
M. Jaroszewski, J. Pospieszna

P-100: *Dielectric properties and structures of melt compounded poly(ethylene oxide)-montmorillonite nanocomposites*
S. Choudhary, R.J. Sengwa

P-101: *Structural investigation of nanocomposites based on Poly(methyl methacrylate) and Methacryl Polyhedral Oligomeric Silesquioxanes.*
P. J. Purohit, Andreas Schönhals

P-102: *Molecular mobility at the interfaces of nanostructured polymers filled by functional nanofillers.*
H. Rekik, M. Arous, A. Kallel I. Stevenson-Royaud, G. Boiteux, G. Seytre

P-103 *Dielectric studies of segmental and global chain dynamics in intercalated poly (propylene oxide) amines/layered silicate nanocomposites.*
S. Kripotou, A, Kyritsis, K. S. Triantafyllidis, P. I. Xidas, P. Pissis

P-104 *Activation energy of conductivity at glass transitions of hybrid organic-inorganic polymer systems.*
M. Iurzhenko, G. Boiteux, Ye. Mamunya, E. Nikaj, E. Lebedev.

P-105 *Dielectric spectroscopy of a new metal-containing polymer structure.*
V.T. Avanesyan , E. G. Vodkailo

P-106 *Dynamic dielectric study of carbon nanotubes dispersion in polyamide 11*
D. Carponcin, E. Dantras, C. Lacabanne

P-107 *Domain size and internal dynamics of poly(butylene terephthalate)/decylamine/fullerene nanocomposite.*
A. Woźniak-Braszak, M. Baranowski, W. Grzesiak, B. Brycki, K. Jurga, J. Jurga, K. Hołderna-Natkaniec

P-108: *The influence of concentration of TCNEO/C60 adduct on the molecular dynamics and domain size in PBT/TCNEO/C60.*
A. Woźniak-Braszak, W. Grzesiak, B. Brycki, K. Jurga, J. Jurga, K. Hołderna-Natkaniec1

P-109: *Electric Characterization of poly(lactide)/MWCNT nanocomposites*
A. Bello, M. Grimau, E. Laredo, D. Wu

P-110: *Dielectric dispersion and conductivity analysis in piezoelectric composite materials*
H. Hammami, A. kallel

P-111: *Dielectric study on polyaniline/polymethylmetacrylathe composite films near the percolation threshold.*
Z. Ben Othmen, A. Fattoum, M. Arous

P-112: *Influence of preparation procedure on the conductivity and transparency of SWCNT-polymer nanocomposites.*
J.J. Hernández, M.C. García-Gutiérrez, A. Nogales, D.R. Rueda, M. Kwiatkowska, Z. Roslaniec, A. Sczymzyk, T.A. Ezquerra

P-113: *Polyimide nanocomposite thin films based on a nitrile-containing polyimide and* $BaTiO_3$
L. Okrasa, E. Hamciuc, C. Hamciuc, I. Bacosca

P-114: *Polymer nanocomposite films based on silica and a polyimide-polydimethylsiloxane copolymer.*
L. Okrasa, C. Hamciuc, E. Hamciuc

P-115: *Dielectric analysis of natural nanocellulosic fibers filled polymer nanocomposites. Influence of surface treatments.*
M. Bouchhima, M. Arous, S. Boufi, A. Kallel

P-116: *Influence of orientation of molecules on photodielectric properties nematic of the liquid crystal with impurity fullerene and dyes.*
V.E. Vovk, A.V Koval'chuk

P-117: *Self-assembly and molecular dynamics of nanographenes*
C. Grigoriadis, N. Haase, G. Floudas, K. Müllen

P-118: *Dielectric and magnetic analysis of dispersed particles in composites of unknown microstructure.*

R. Pelster, B. Hallouet.

P-119 *BDS study of sols and films of silver nanoparticles capped by alkyl carboxylate ligands.*
G.F. Novikov

P-120: *Study of the Electrical Conductivity of Polyamide 66 and Carbon Nanofibers Composites by Dielectric Spectroscopy.*
J.C. Canalda, A. Linares, M.E. Cagiao, T.A. Ezquerra

P-121: *Development of an experimental approach to detect phase transitions in dilute solution.*
B. Vanroy, S. Napolitano, I Monnaie, E Nies, I K. Robeyns, B. Goderis, M. Wübbenhorst

P-122: *Characterisation of biomimetic nano-structures using low frequency impedance spectroscopy.*
H. G. L. Coster, T. C. Chilcott, M. Baudouin

6TH INTERNATIONAL CONFERENCE ON
BROADBAND DIELECTRIC
SPECTROSCOPY AND ITS APPLICATIONS

www.dielectric2010.com
07 - 10 MADRID
SEPTEMBER 2010

Molecular dielectrics & Glass Transition

Tuesday 7/Sept
Room A

9:00 - 9:30	OPENING CEREMONY
9:30 - 10:00	**K. L. Ngai**
10:00 - 10:15	D. Cangiasoli
10:15 - 10:30	Y. Matsuyima
10:30 - 10:45	D. Fragiadakis
10:45 - 11:15	**G. Williams**

Universal relaxation and diffusion in many-body interacting systems

K. L. Ngai

polyLab & Dipartimento di Fisica, Universita di Pisa - Pisa, Italy
*Email address: Ngai@df.unipi.it

Using the template to submit this abstract, I was thrilled to see text of the article by M. Cardona *et al.*[1] on the history of the stretched exponential function of R. Kohlrausch[2]. These authors pointed out that his original paper was forgotten until it was cited by Palmer et al.[3] in 1984, but Palmer et al. refer incorrectly to his 1847[4] paper and not the correct 1854 paper[3]. Actually I and coworkers have to share the blame for citing the 1847 paper in our 1983 Phys.Rev.B paper[5]. This might have misled Palmer et al. to cite the wrong reference, and by the talks I gave at Princeton U. in 1981 and Aspens Center for Physics in 1982 all invited by P.W. Anderson, as well as the interaction with Palmer and Stein during the Workshop on Relaxation in Disordered Systems at Virginia Tech in July 1983. Incidentally, the Workshop and its Proceedings were quoted by Palmer et al.[3] as well as my first publication of the Coupling Model (CM)[6] in 1979. I was not aware of the works of R.[2,4] or F. Kohlrausch[7] in 1979[6], only years later[5]. In his 1854 paper, R. Kohlrausch actually started with the time dependent relaxation rate equation, $d(pQ_t - r_t)/dt = - bt^m(pQ_t - r_t)$, where m is a negative fraction of unity. Integrating from $t=0$ to $t=t$ and with $Q_t(t=0)=Q_0$ and $r_t(t=0)=0$, he then arrived at $\log[(pQ_t - r_t)/pQ_0] = -[b/(m+1)]t^{m+1}$, or $(pQ_t - r_t)/pQ_0 = \exp(-Bt^{m+1})$, the Kohlrausch function where $B=b/(m+1)$. Using his own data he deduced $m=-0.5744$, and $b=0.4289$. F. Kohlrausch[7] wrote down a similar equation, $dx/dt=-g\cdot x/t^n$. Now in my 1979 paper[6], the primary result of the theory is the time dependent relaxation rate, $W(t)=W_0(t/t_c)^{-n}$, exactly the same as bt^m of Kohlrausch with $m=-n$, and $b=W_0(t_c)^n$. From the rate equation, $d\phi/dt = -W(t)\phi$, I obtained not only the Kohlrausch function, $\exp[-(t/\tau)^{1-n}]$, but also the 2nd relation $\tau=[(1-n)(t_c)^{-n}\tau_0]^{1/(1-n)}$, where $\tau_0\equiv 1/W_0$. This 2nd relation introduces new physics and immensely enhances the applications of the Kohlrausch function beyond an empirical function to fit data. In the CM, n is indicator of the extent of the many-body relaxation. The 2nd relation has explained the experimentally observed anomalous and universal properties of τ from the normal properties of the primitive relaxation time τ_0. These advances in various fields can be found in a forthcoming book[8]. None of these would be possible without the $W(t)=W_0(t/t_c)^{-n}$, originally proposed as bt^m, $-1<m<0$, by R. Kohlrausch. Therefore when paying homage to Kohlrausch, one should cite Kohlrausch's fractional power time dependent rate, bt^m, instead of his stretched exponential function. My talk will use examples to show the existence of universal properties of relaxation and diffusion in totally different interacting systems, and not just glassforming systems. The book[8] with about 400 figures and 1,800 references is a useful tool for research.

References

[1] M. Cardona, R.V. Chamberlin, W. Marx. Ann. Phys. (Leipzig) **16**(12), 842 (2007).
[2] R. Kohlrausch, Pogg. Ann. Phys. Chem. **91**, 179 (1854).
[3] R. G. Palmer, D. L. Stein, E. Abrahams, P. W. Anderson. Phys. Rev. Lett. **53**, 958 (1984).
[4] R. Kohlrausch, Pogg. Ann. Phys. Chem. **72**, 353 (1847).
[5] K. L. Ngai, A.K. Rajagopal, R.W. Rendell, S. Teitler, Phys.Rev.B **28**, 6073 (1983).
[6] K. L. Ngai, Comments Solid State Phys. **9**, 127 (1979).
[7] F. Kohlrausch, Pogg. Ann. Phys. Chem. **119**, 337 (1863).**128**, 1, 207, 399 (1866).
[8] K. L. Ngai, *Relaxation and Diffusion in Complex Systems*, Springer, Berlin (in press)

Effect of environment on the dynamics of a polychlorinated biphenyl in 1-4 polybutadiene

D. Cangialosi[1*], **A. Alegrìa**[1,2], **J. Colmenero**[1,2,3]
[1]Centro de Física de Materiales Centro Mixto (CSIC-UPV/EHU), Apartado 1072, 20080 San Sebastián, Spain
[2]Departamento de Física de Materiales, Universidad del País Vasco (UPV/EHU), Apartado 1072, 20080 San Sebastián, Spain
[3]Donostia International Physics Center, Paseo Manuel de Lardizabal 4, 20018 San Sebastián, Spain
*Email address: swxcacad@sw.ehu.es

The mobility of isolated polychlorinated biphenyl (PCB54) in 1,4-polybutadiene (PB) has been investigated by means of broadband dielectric spectroscopy (BDS). The aim was to provide new insights about the effect of the environment on the dynamics of PCB54 [1]. Our results indicate that PCB54 structural dynamics is neither independent of the PB matrix nor slaved to the matrix itself. We interpret these results as a consequence of the limited size of cooperatively rearranging regions (CRR) involved in PCB54 structural relaxation possessing an effective concentration different from the macroscopic one. This implies a non-negligible influence of "self-concentration", already proven for the component segmental dynamics in polymer blends [2, 3], also in the relaxation of binary mixtures involving low molecular weight glass formers. Starting from these premises, the size of CRR was determined in two ways: i) estimating the PCB54 threshold concentration above which the dynamics of PCB54 deviates from the infinitely diluted regime. In this case the threshold concentration marks the involvement of a PCB54 molecule in the cooperative relaxation of another PCB54 molecule; ii) incorporating the self-concentration concept in the Adam-Gibbs (AG) theory of the glass transition that explicitly relates the size of CRR to the configurational entropy [4]. The two approaches provide comparable sizes of CRR. These are of about 1 nm. This means that the cooperativity extends over the first shell around PCB54 molecules.

References

[1]D. Cangialosi, A. Alegrìa, J. Colmenero. J. Chem. Phys. 126, 204904 (2007).
[2] D. Cangialosi, G.A. Schwartz, A. Alegrìa, J. Colmenero. J. Chem. Phys. 123, 144908 (2005).
[3] G.A. Schwartz, D. Cangialosi, A. Alegrìa, J. Colmenero. J. Chem. Phys. 124, 154904 (2006).
[4] G. Adam and J. H. Gibbs, J. Chem. Phys. 43, 139 (1965).

Viscoelastic and Dielectric Investigation of Segmental Dynamics of Polystyrene

Y.Matsumiya, H.Watanabe
[1]Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011 Japan
*Email address: matsmiya@scl.kyoto-u.ac.jp

Segmental dynamics of polystyrene (PS) chains with molecular weight M = 500 – 100,000 g/mol is studied via viscoelastic and dielectric spectroscopy. Viscoelastic and dielectric measurements were conducted at various temperatures form glass transition temperature of respective polystyrene chain to the temperature where the terminal relaxation behavior was observed. Dielectric terminal relaxation was exclusively attributed to a-relaxation mode for all PS samples, while viscoelastic terminal relaxation was assigned to glassy mode (segmental mode) for PS samples with M < 2500, and to rubbery mode (global mode) for those with M > 2500. Time-temperature superposition held for segmental relaxation of viscoelastic and dielectric data, and their shift factors coincided with each other for each PS sample. Viscoelastic and dielectric relaxation times of each PS sample were compared, and dielectric relaxation time was longer than viscoelastic relaxation time for all PS samples. Interestingly, the relaxation time ratio and the dielectric relaxation intensity decreased with increasing M up to 2500 but leveled off for larger M. This result suggested that effective size of the dielectrically detected segment (motional unit) was M~2500, which was larger than the whole chain size for PS with M < 2500, and thereby activating the change of the relaxation time ratio and dielectric relaxation intensity. We also noted that viscoelastic and dielectric relaxation spectra for the glassy mode of each PS sample agreed well. The mechanism of this coincidence will be discussed.

Dynamics of liquid crystals at their phase transitions

D. Fragiadakis[1*], R.B. Bogoslovov[1], J. Czub[2], S. Urban[3], C.M. Roland[1]
[1]Naval Research Laboratory, Code 6120, Washington DC 20375-5342, USA
[2] Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, Al.Mickiewicza 30, 30-059 Krakow, Poland
[3] Institute of Physics, Jagiellonian University, Reymonta 4, 30-059 Krakow, Poland
*Email address: daniel.fragiadakis.ctr@nrl.navy.mil

We study dielectric relaxation as a function of temperature and pressure for a variety of thermotropic liquid crystals. While the transition temperatures depend on pressure, the longitudinal relaxation time at the transition is found to be essentially constant, independent of temperature and pressure [1,2]. This is the case for the transition from the crystal to the ordered nematic or smectic phase, transitions between different mesogenic phases, and from the ordered to the isotropic liquid phase (clearing point). This result suggests a relationship between the thermodynamic conditions that determine the transition temperatures (reflecting the competition between the anisotropic interaction energy of the molecules and the orientational entropy) and the dynamics in the ordered state.

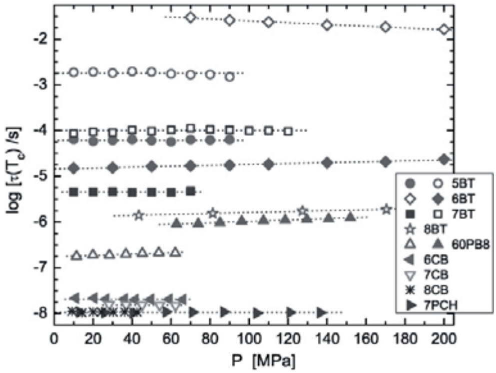


Fig.1. Longitudinal relaxation times as a function of pressure at the phase transitions of various liquid crystals (from [2])

References

[1] C.M. Roland; R.B. Bogoslovov; R. Casalini; A.R. Ellis; S. Bair; S.J. Rzoska; K. Czuprynski; S. Urban, J. Chem. Phys. 128, 224506 (2008).
[2] C.M. Roland, Soft Matter 4, 2316 (2008).

Dielectric Isosbestic Points

Graham Williams
Swansea University, Singleton Park, Swansea SA2 8PP, United Kingdom
*Email address: g.williams6013@ntlworld.com

Isosbestic Points, where two absorption spectra cross in the frequency domain, are well-known in the UV/visible spectra of dye-molecules that have two inter-connected structures that depend on the pH of the medium. Such features can also be observed in broadband dielectric-relaxation spectra for dipolar systems in which the molecules may (i) exist in two forms A↔B, (ii) undergo chemical reaction A→B or (iii) be organized to give different macroscopic orientations. Examples of (i) include liquid↔rotator-phase crystal and amorphous polymer↔partially-crystalline polymer while (iii) include nematic liquid crystals and LC polymers that are macroscopically-aligned with respect to a measuring E-field. If the molecular dynamics are sufficiently-different, individual dipolar loss peaks will occur at different frequencies, giving an isosbestic point (IP) in each case. While the locations and contours of the individual spectra of dyes in chemical equilibria change little with temperature (T) and pressure (P), dielectric relaxation times for species in (i) and (ii) change considerably with these variables so, in order to observe dielectric IPs, the chosen (T,P) condition must be carefully maintained and the dielectric measurements be made to a high precision, both of which are now possible with modern BDS equipment.

In the present work we outline the theory for multiple dielectric relaxations in coupled [A,B] systems and in liquid crystalline systems that lead to IPs and give examples, taken from the literature, of their observation. These include :-

(*a*) the original observation of IPs in LC side chain polymers[1,2] where the macroscopic alignment was varied continuously from planar (**E**⊥**n**), to unaligned (**n** random**)** to homeotropic (**E**//**n**), where **n** is the nematic director, (*b*) low molar mass liquid crystals, especially in flow[3], (*c*) supercooled liquid↔rotator-phase crystal[4], (*d*) a glass-forming binary mixture[5], (*e*) real-time BDS studies of the cold-crystallization of amorphous polymers.[6-8]

The information provided by isosbestic points will be discussed briefly, especially in determining (i) the relative amounts of species in the [A,B] systems, (ii) the director order parameter S_d for partially-aligned LC polymers and for low molar mass liquid crystals in flow[5] (''rheodielectrics'') and (iii) the development with time, and the nature of, the constrained amorphous regions within the crystalline phase during bulk polymer crystallizations.[6-8]

References

[1] K. Araki, G.S. Attard, Liq. Cryst.1, 301 (1986).
[2] G.S. Attard, K. Araki, J.J. Moura-Ramos, G. Williams. Liq. Cryst. 3, 861 (1988).
[3] S. Capaccioli, D. Prevesto, A. Best, A. Hanewald, T. Pakula. J. Non-Cryst. Solids, 355, 4267 (2007).
[4] S. Benkhof, A. Kudlik, T. Blochowicz, E. Rossler. J. Phys. Cond. Matter, 10, 8155 (1998).
[5] K. Kessairi, S.Capaccioli, D. Prevesto, M. Lucchesi, P. Rolla. J. Chem. Phys. 127, 174502 (2007).
[6] T.A. Ezquerra, F.J. Balta-Calleja, H. Zachmann. Polymer, 35, 2600 (1994).
[7] M. Mierzwa, G. Floudas. IEEE Trans. Diel. Electr. Insul. 8, 359 (2001).
[8] R. Lund, A.Alegria, L. Goitandia, J. Colmonero, M.A. Gonzalez, P. Lindner. Macromolecules, 41, 1364 (2008).

6TH INTERNATIONAL CONFERENCE ON
BROADBAND DIELECTRIC
SPECTROSCOPY AND ITS APPLICATIONS

www.dielectric2010.com
07-10 SEPTEMBER 2010 MADRID

Secondary
and
Glassy Relaxations

Tuesday 7/Sept
Room A

11:45 - 12:15	**R. Richert**
12:15 - 12:30	L. Delbreih
12:30 - 12:45	M. Shanin-Thayyil
12:45 - 13:00	K. Grzybowska
13:00 - 13:15	P. Frübing

The heterogeneous nature of physical aging

R. Richert,
Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287, U.S.A.
Email address: ranko@asu.edu

Dielectric relaxation experiments at sufficiently high electric fields display non-linear features based upon the absorption of energy from the external field,[1] analogous to microwave heating.[2] As a result, the independently relaxing modes of a system with heterogeneous dynamics as in Fig. 1 are shifted to higher frequencies. The amount of change is a matter of the energy absorbed, the configurational heat capacity, and the overall activation energy, and can be modelled quantitatively.[3] In a time resolved variant of these experiments, the time dependence of how configurational (or fictive or structural) temperatures T_{cfg} adjust towards steady state or equilibrium can be studied in detail and obeys $dT_{\mathrm{cfg}}/dt = -(T_{\mathrm{cfg}}-T)/\tau$. The same 'thermal relaxation' is expected in the process of physical aging, where the real temperature T is lowered rapidly and the experiment monitors how the configurational temperatures T_{cfg} follow behind.

For the majority of modes, e.g. τ_1 through τ_4 in Fig.1, we find that the thermal relaxation scales with the frequency of the field, as expected for heterogenous dynamics. This implies that physical aging should also proceed in a heterogeneous fashion, in contrast to the results of many experiments. We solve this apparent contraction between heterogeneous relaxation and homogeneous aging by finding that the thermal relaxation of very fast modes, e.g. τ_5 in Fig. 1, are slaved to macroscopic softening. As a consequence, aging of the few fastest percent of modes is not representative of the majority and appears homogeneous regarding physical aging.

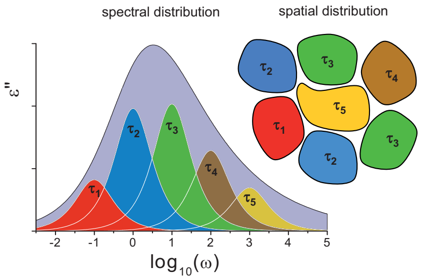


Fig.1. Sketch of the spectral and spatial distribution of relaxation times in a system with heterogeneous dynamics. The dispersion is represented by five distinct time constants, τ_1 through τ_5 in the order of decreasing relaxation time constant. The spatial figure is meant to indicate that a relatively fast mode is likely to be confined by much slower ones.

References

[1] R. Richert, S. Weinstein, Phys. Rev. Lett. 97, 095703 (2006).
[2] W. Huang, R. Richert, J. Phys. Chem. B 112, 9909 (2008).
[3] L.-M. Wang, R. Richert, Phys. Rev. Lett. 99, 185701 (2007).
[3] W. Huang, R. Richert, J. Chem. Phys. 130, 194509 (2009).
[4] R. Richert, Phys. Rev. Lett. 104, 085702 (2010).

Temperature dependence of the characteristic length scale for glassy dynamics: Combination of dielectric and specific heat spectroscopy

L. Delbreilh[1*], **A. Saiter**[1], **H. Couderc**[1], **K. Arabeche**[1], **E. Dantras**[2], **A. Schönhals**[3], **J.-M. Saiter**[1].
[1]Institute of Material Research, FED4114, Equipe LECAP, Université de Rouen, Site du Madrillet, 76801 Saint Etienne du Rouvray Cedex, France
[2] Laboratoire de physique des polymeres - Institut Carnot - CIRIMAT - UMR CNRS5085 – 118 route de Narbonne - 31062 Toulouse Cedex 09, France
[3]BAM Federal Institute for Materials Research and Testing, Unter den Eichen 87, 12205 Berlin, Germany
*Email address: laurent.delbreilh@univ-rouen.fr

Literature shows a great interest of scientists in determining the temperature dependence of glass-former cooperativity[1] either by using the Adam and Gibbs Theory[2,3], or by calculating a correlation number from the four point correlation function χ_4[4,5]. Broadband Dielectric Spectroscopy and Temperature Modulated Differential Scanning Calorimetry allow to study the CRR size (Donth's approach) temperature dependence in the temperature range of ergodicity loss for glass-forming liquids, starting from the onset of cooperativity in the crossover region down to the glass transition temperature. Furthermore, the correlation between these two techniques allows to explore a large frequency range (from 1 mHz to 10 MHz). The goal of this work is to follow the cooperativity evolution along the Arrhenius plot for a set of fully amorphous glass-forming polymers.

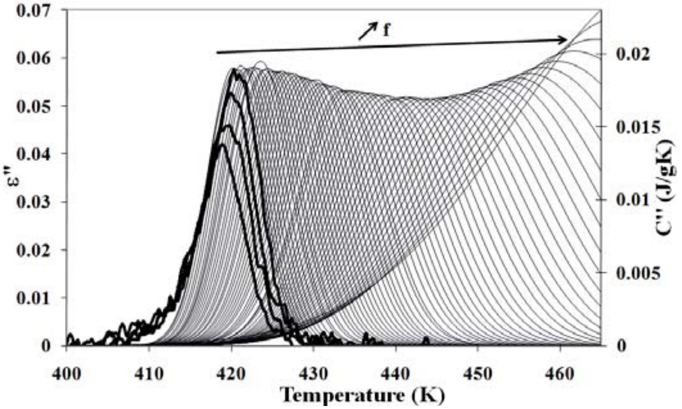


Fig.1. Superposition of the loss peaks obtained by TMDSC (thick line) and BDS (thin line) for poly(bisphenol A carbonate).

References
1 K.Schröter, J Therm Anal Calorim 98 591-599 (2009)
2 S. Capaccioli, G. Ruocco, F. Zamponi, J. Phys. Chem. B 112 10652 (2008)
3 D. Cangialosi, A. Alegria, J. Colmenero, Phys. Rev. E 76 011514 (2007)
4 L. Berthier, G. Biroli, J.-P. Bouchaud, L. Cipelletti, D. El Masri, D. L'Hôte, F. Ladieu, M. Pierno, Science 310 1797 (2005)
5. C. Dalle-Ferrier, C. Thibierge, C. Alba-Simionesco, L. Berthier, G. Biroli, J.-P. Bouchaud, F. Ladieu, D. L'Hôte, G. Tarjus, Phys. Rev. E 76 041510 (2007)
6 E. Donth, E. Hempel, C. Schick, J. Physics : Condens. Matter 12 L281 (2000)

Universality of Johari-Goldstein Relaxation – Crucial Evidences from Flexible Dipolar Molecules

M. Shahin Thayyil [1,2,*], **S. Capaccioli**[2], **D. Prevosto**[2], **S. Ancherbak**[2],
M. Lucchesi[2], **P. A. Rolla**[2], **K. L. Ngai**[3]
[1]Department of Physics, University of Calicut, Kerala, India
[2]CNR-INFM, polyLab & Dipartimento di Fisica, Università di Pisa, I-56127, Pisa, Italy
[3] Naval Research Laboratory, Washington DC 20375-5320 USA.
*Email address: shahin@df.unipi.it

The Johari-Goldstein (JG) β-relaxation, i.e. truly intermolecular secondary relaxation, is supposedly a universal feature in glassy dynamics by showing its presence in common as well as exotic glassformers and having strong connections to the structural α-relaxation [1-2]. However, against the hypothesis of its universality, some widely studied flexible small molecular glassformers like low molecular weight phthalates [3] and benzophenone [4], which, in addition to a fast secondary γ-relaxation due to dipoles coupled to intra-molecular degrees of freedom, give no indication that JG relaxation is present despite investigations using a variety of experimental techniques. Interestingly, for most of these systems in their neat phase the α-relaxation loss peaks have narrow widths with quite high values of stretching parameter β_{KWW} (β_{KWW} = 0.65-0.64 in phthalates and 0.7 in BZP), when fitted to the KWW function. Theoretical considerations suggest that the JG β-relaxation is present but not resolved in these glassformers because it is sandwiched between the more intense α- and a faster but non-JG secondary γ-relaxation [5].

We investigate such suggestion on several glass formers and report the data on small molecular phthalates *viz.* dimethylphthalate (DMP), diethylphthalate (DEP), dibutylphthalate (DBP), diisobutylphthalate (DiBP), dioctylphthalate (DOP) and benzophenone (BZP) by dissolving small quantities of the probes in apolar glassformers of much higher glass transition temperature, like oligostyrenes or *o*-terphenyl (OTP). We were able to move the α-relaxation further away from the γ-relaxation, and find the JG β-relaxation for the first time [6]. We verified that this newly resolved secondary relaxation is the JG process by performing experiment at elevated pressures showing its pressure dependence and pressure-temperature superposition [7]. Getting confidence and modifying the pressure apparatus to have very high cooling rates, we could resolve JG in neat DMP as a clear resolved process for the first time. The JG of BZP is resolved in BZP rich mixture of 90% mole-fraction with apolar OTP (since BZP is quickly crystallizing). These results evidences that JG relaxation is universal.

References

[1] G. P. Johari, M. Goldstein, J. Chem. Phys. **1970**, 53**,** 2372.
[2] K. L. Ngai, M. Paluch, J. Chem. Phys. **2004,** 120, 857.
[3] M. Sekula, S. Pawlus, S. Hensel-Bielowka, J. Ziolo, M. Paluch, C. M. Roland, J. Phys. Chem. B **2004**, 108, 4997.
[4] L. C. Pardo, P. Lunkenheimer, A. Loidl, Phys. Rev. E **2007**, 76, 030502(R).
[5] K. L. Ngai, J. Phys.: Condens. Matter **2003,** 15, S1107.
[6] S. Capaccioli, M. Shahin Thayyil, K. L. Ngai,. J. Phys. Chem. B, **2008**, 112, 16035.
[7] K. Kessairi, S. Capaccioli, D. Prevosto, M. Lucchesi, S. Sharifi, P. A. Rolla, J. Phys. Chem. B, **2008**, 112, 4470.

Molecular dynamics and physical stability of amorphous anti-inflammatory drug – celecoxib

K. Grzybowska[1*], **Z. Wojnarowska**[1], **M. Paluch**[1], **A. Grzybowski**[1],
K. Adrjanowicz[1], **P. Wlodarczyk**[1], **and K. L. Ngai**[2]
[1]Institute of Physics, University of Silesia, ul. Uniwersytecka 4, 40-007 Katowice, Poland
[2]Naval Research Laboratory, Washington, DC 20375-53 USA
*Email address: kgrzybow@us.edu.pl

Many crystalline drugs, including celecoxib (CEL, a non-steroidal anti-inflammatory agent), are poorly water soluble, and therefore they are characterized by low bioavailability. Preparation of the compounds in amorphous forms is a promising method for improving solubility of poorly water-soluble drugs. It has been shown that the aqueous solubility of amorphous CEL is significantly higher than that of its crystalline counterpart.[1] Unfortunately, amorphous systems are usually characterized by relatively poor physical stability and may undergo re-crystallization over the time course of processing, storage and use of the product. We found that CEL crystallizes above the glass transition temperature T_g as well as during storage in normal conditions at T=20°C (more than 30°C below its T_g). A key question that arises with such materials is "how does their molecular mobility influence their stability?". Performing measurements of molecular dynamics of CEL by using broadband dielectric spectroscopy we are able to determine time scales of molecular motions in the glassy and liquid states. We have found that CEL reveals as many as three secondary relaxations (see Fig. 1), which suggest a high local molecular mobility in the glassy state. We identified one of them as the Johari-Goldstein process that is considered to control the rates of crystal growth below T_g.[2] Moreover, we have established that CEL is characterized by a big value of isobaric fragility m_p=95, which is suggested to correlate with the tendency of material to crystallization.[3] We intend to verify how role these factors play in keeping the physical stability of amorphous CEL.

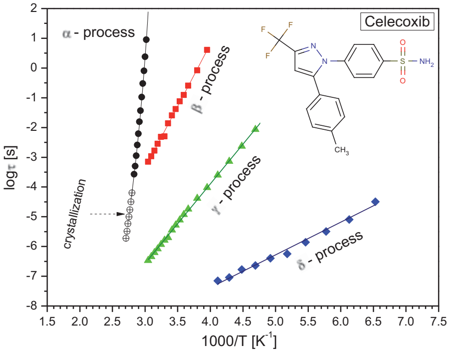


Fig.1. Relaxations map of celecoxib.

References
[1] P. Gupta, G. Chawla, and A. K. Bansal, Molecular Pharmaceutics, 1 (6), 406 (2004)
[2] T. Hikima, M. Hanaya, M. Oguni, J. Mol. Structure, 479, 245 (1999)
[3] H. Tanaka, J.Non-Cryst. Solids, 351, 678 (2005)

Relaxation processes and structural transitions in stretched films of poly(vinylidene fluoride) and its copolymer with hexafluoropropylene

Peter Frübing[1*], Feipeng Wang[1], Reimund Gerhard[1], and Michael Wegener[2]
[1] Department of Physics and Astronomy, University of Potsdam, Karl-Liebknecht-Straße 24-25, 14476 Potsdam, Germany
[2] Fraunhofer Institute for Applied Polymer Research, Geiselbergstraße 69, 14476 Potsdam, Germany
*Email address: fruebing@uni-potsdam.de

Uniaxially stretched films of poly(vinylidene fluoride) (PVDF) and its copolymer with hexafluoropropylene (P(VDF-HFP)) show ferroelectric properties. Moreover, P(VDF-HFP) exhibits relatively strong electromechanical activity because of its low elastic modulus [1]. However, the ferroelectric polarisation is thermally not stable, which limits the temperature range for applications.

Dielectric relaxation spectroscopy (DRS) is combined with dynamic mechanical analysis (DMA) in order to study the relaxation processes and structural transitions in PVDF and P(VDF-HFP) which are expected to induce the thermal decay of the ferroelectric polarisation. Emphasis is put on the effect of uniaxial stretching. Up to now, relaxation processes in P(VDF-HFP) were studied in detail only on non-stretched films [2]. These investigations are supplemented by calorimetric and X-ray diffraction measurements in order to link the mechanical and dielectric losses to thermal transitions and changes of crystallinity and crystallite size which are induced by stretching.

It is shown by Vogel-Fulcher-Tammann analysis that mechanical and dielectric relaxations connected with the glass transition are closely related. In contrast, the relation between mechanical and dielectric processes above the glass transition is more complicate and strongly determined by stretching. Stretching transforms the equilibrium spherulitic and non-ferroelectric α-phase crystallites into small-sized linear β-phase crystallites with spontaneous polarisation. Hence, it removes the so-called dielectric α_c relaxation which is attributed to motions of CF_2 dipoles in α-phase crystalline lamellae. On the other hand, stretching does not significantly change the elastic modulus above glass transition. Hence, it does not render the polymer structure more rigid. A continuous softening process above the glass transition is observed particularly in the copolymer which is associated with strong mechanical losses.

Furthermore, a structural transition above room temperature is found associated with frequency-independent dielectric and mechanical loss peaks. It is not induced by stretching. In the dielectric spectra it is superimposed by the α_c relaxation, thus it becomes visible only on stretched films. It is probably caused by the transformation or degradation of a certain crystalline structure.

Finally, these findings are used in order to explain the temperature dependence of the piezoelectric activity of P(VDF-HFP) as the result of an interplay between build-up and decay of electric polarisation and decrease of elastic modulus.

References

[1] A. C. Jayasuriya, A. Schirokauer, and J. I. Scheinbeim, *Journal of Polymer Science, Part B: Polymer Physics*, Vol. 39, 2793-2799 (2001)

[2] V. V. Kochervinskii, I. A. Malyshkina, G. V. Markin, N. D. Gavrilova, N. P. Bessonova, *Journal of Applied Polymer Science*, Vol. 105, 1101-1117 (2007)

Heterogeneous Materials (I)

Tuesday 7/Sept
Room B

11:45 - 12:15	**C: Lacabanne**
12:15 - 12:30	F. Aliev
12:30 - 12:45	A. Lyaschenko
12:45 - 13:00	B. Ishai
13:00 - 13:15	T- Blochowicz

Dielectric relaxations and Electrical behaviour in polyamide matrix nanocomposites:

PA 11 / NTC and PA 11 / $BaTiO_3$

J.- F. Capsal, D. Carponcin, E. Dantras, C. Lacabanne
Laboratoire de Physique des Polymères Institut Carnot CIRIMAT, Université Paul Sabatier, Toulouse, France,
*Email address: lacabane@cict.fr

The dispersion of ferroelectric [1] or conductive [2] nanofillers into a thermoplastic polymer allows us to realize nanocomposites with new electroactive properties. Polyamide 11 (PA 11) has been chosen as matrix. Barium titanate (BT) nanoparticles and CNTs have been chosen as fillers.

PA 11/$BaTiO_3$ 0-3 nanocomposites with a volume fraction of BT ranging from 0.024 to 0.4 and diameters ranging from 50 to 700 nm were elaborated [3]. Attractive piezoelectric and pyroelectric properties were obtained for composites with 20 volume % of BT (700 nm diameter). The combination of dynamic dielectric spectroscopy and thermo stimulated current analysis allows us to point out the influence of the filler on the physical structure of the polymeric matrix. A specific attention has been paid to the influence of the volume fraction (ϕ) of 700 nm nanoparticles. The molecular mobility in the liquid state is not influenced by the volume fraction of nanofillers. In the vitreous state, the evolution of low frequency relaxation has been attributed to the decrease of the size of Cooperative Rearranging Region (CRR). It reflects the increase of intra/inter molecular interactions in the amorphous phase of the polymeric matrix.

Initially, carbon nanotubes (CNTs) have been introduced in amorphous thermosets like polyepoxy [4]. It is of course more difficult to disperse them in a semi crystalline polymer like polyamide. Two routes have been compared: a solvent way and a melt mixing process. For the later, twin screw extruder parameters have been optimized to ensure CNTs dispersion in polyamide 11. A good dispersion is required for preserving a large apparent aspect ratio in order to reach percolation for lower CNTs content. A comparative study of the dynamic electrical conductivity of nanocomposites has been performed. The variation of the DC conduction at the percolation threshold has been used as a marker of the level of dispersion. The use of a semi crystralline matrix instead of an amorphous one, results in an increase of the percolation threshold. This finding is coherent with literature data. The higher CNTs content required for insuring the conduction path might be due to the presence of crystallites.

References

[1] J-F. Capsal, E. Dantras, J. Dandurand, C. Lacabanne, Journal of Non Crystalline Solids, 353, 4437-4442, 2007
[2] S Barrau, P Demont, A. Peigney, C. Laurent, C. Lacabanne, Macromolecules, 36, 14, 5187-5194, 2003
[3] J-F Capsal, PhD Thesis, Toulouse/F (2008)
[4] S Barrau, PhD Thesis, Toulouse/F (2002)

Dynamic and thermodynamic properties of dry and hydrated novel networks from ring-opening metathesis polymerization

F. Aliev[1*], **V. Dolidze[1]**, **Ke Zhang[2]**, **Gregory N. Tew[2]**
[1]University of Puerto Rico. Department of Physics, PO BOX 23343, 00931 San Juan, USA
[2]University of Massachusetts, Amherst, 120 Governors Dr., Amherst, MA 01003, USA
*Email address: fmaliev@uprrp.edu

Broadband dielectric spectroscopy (BDS) and Brillouin light scattering (BLS) methods were applied to investigation of the dynamic behavior of dry and hydrated novel ROMP-based (ring-opening metathesis polymerization) polymer network. We observed two relaxation processes (Fig. 1) with high values of low frequency dielectric permittivity typical for contribution from electrode polarization. We assigned the second process to segmental dynamics. The temperature dependencies of dielectric strength and of relaxation time of this process showed the presence of an order/disorder (crystallization/melting) first order phase transition at approximately T_m=47.5 ^{o}C for the dry sample. The contribution of the second process to total polarization was not completely frozen below T_m, but showed a visible, step-like slowing down of the process. In the hydrated sample we did not observe the phase transition. The dynamics of the processes investigated by BDS and BLS were drastically modified by hydration of the sample. The presence of water made a large contribution to the dielectric permittivity of the sample. It could not be attributed to molecular (dipole) properties of water, but the observed increase of low frequency dielectric permittivity of the hydrated sample was attributed to interfacial polarization at the polymer/water interface. At temperatures T>47 ^{o}C the relaxation rates of the second process of the hydrated sample were about twice as high as that of dry sample, due to increased segmental mobility in the hydrated sample. BLS experiments showed that the elasticity of the hydrated sample changed substantially with respect to the elasticity of the dry sample at the same temperature: the modulus of compression of the dry sample was 4-5 times greater than that of the hydrated sample. Complementary differential scanning calorimetry experiments provided additional information on the phase transition in dry sample and its absence in the hydrated state.

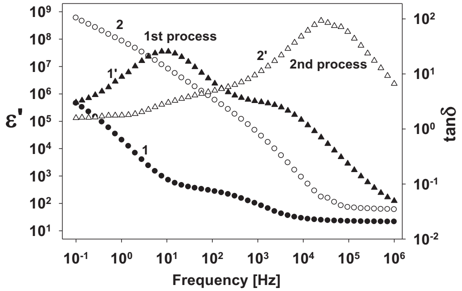


Fig. 1. Dielectric spectra of dry (1, 1′) and hydrated (2, 2′) novel ROMP-based network at T = 328.15K; 1 and 2 – ε′, 1′ and 2′ - tan δ.

Dielectric spectroscopy of aqueous electrolyte solutions in all orientation frequency range.

A. Lyashchenko[1]*, A.Lileev[1], T.Novskova[2]
[1]Kurnakov Institute of General and Inorganic Chemistry RAS 119991 Leninsky pr. 31
Moscow, Russia
[2]Institute of Radio Engineering and Electronics RAS 141120 Vvedenky sq. 1, Fryazino
Moscow district, Russia
*Email address:aklyas@mail.ru.

We have considered experimental and theoretical aspects of this problem. The mechanism of elementary dynamics of water molecules in hydration shells of ions is considered on the basis of confined rotator1/… confined rotator N theoretical scheme for different (N) fraction of solution water, experimental dielectric (in the range 7-120 GHz) and absorption (up to 800 cm^{-1}) data. The spectra of complex dielectric permittivity and absorption in far IR, submillimeter and microwave regions are described using the theoretical model. The specification of millimeter area is established. The high frequency boundary of Debye relaxation zone is determined. The difference of ions with positive and “negative” hydration (Samoilov’ s approach) or ions “without hydration” (Bernal and Fouler’s approach) is determined at the level of elementary orientation processes.

The measurements of high frequency dielectric permittivity and losses were carried out at the frequency range 7-120 or 7-25 GHz and temperatures 283-313 or 288-308 K for 46 binary water-electrolyte systems. They include the aqueous solutions of fluorides, chlorides, nitrates, sulfates, formates, acetates, propionates of alkali metals, ammonium salts and the solutions of tetralkylammonium (TAA) and tetraallylammonium salts. The low frequency specific conductivity of these solutions was measured for determination of the ionic losses. The concentration and temperature dependences of losses were analyzed. The relation between the dipole and ionic losses was determined at various concentrations and temperatures up to 150 GHz. Complex dielectric permittivity of the investigated solutions is described by the Debye or Cole-Cole equations. Thus only one relaxation process with the most probable relaxation time takes place in this spectral dielectric window. It is connected with bulk water and hydration shells of ions. The static dielectric permittivity, activation enthalpy and dielectric relaxation time are calculated for the above mentioned solutions.

We present systematic dielectric data for aqueous electrolytes with the hydrophilic and hydrophobic hydration of cations and anions. The temperature effect is also examined. Based on this study, new criteria of the difference between the hydrophilic and hydrophobic hydration of ions are suggested.

General relations between dielectric parameters and structural effects in aqueous salt solutions are considered. The increase in the order of complementary structural organization for water in the bulk and hydration shells of ions gives rise to the molecular-kinetic stabilization of water and to the structure-making effect. Structure breaking effect realizes in the opposite case. This explains the difference between dielectric relaxation characteristics for a wide variety of electrolyte solutions.

This work is supported by the grants of Presidium RAS and RFBR N 08-03-00095

EXPOSING THE DIELECTRIC BEHAVIOR OF 'EXOTIC' GELS

P. Ben Ishai [1*], D. Libster [2], A. Aserin [2], N. Garti [2] and Yu. Feldman [1]
[1] Dept. of Appl. Physics, The Hebrew University of Jerusalem, Givat Ram, Jerusalem 91904, Israel.
[2] Casali Inst. of Appl. Chemistry, The Hebrew University of Jerusalem, Givat Ram, Jerusalem 91904, Israel.
*Email address: paulb@vms.huji.ac.il

In the search for tailorable drug delivery systems "exotic" gels offer inviting possibilities. One avenue is structures, such as reverse hexagonal mesophases [1,2] (H_{II}) that can be tuned to drug release under specific biological conditions. We present a dielectric study of ternary glycerol monooleate (GMO)/tricaprylin (TAG)/ phosphatidylcholine (PC) /water hexagonal systems that form long "pipes" encasing water [3]. The results, presented in fig. 1, reveal an intriguing percolation of the heavy TAG molecule, intercalated between the GMO tails [3]. Adding an even heavier macromolecule, such as the drug Cyclosporin A (CSA) [4,5], disrupts the percolation of TAG. The power and stretch parameters of the correlation functions of this process reveal a critical temperature, $T_0=307$ *°K*, at which the breakdown of interfacial water can "release" the drug [3]. Additionally the study reveals further complex molecular behavior in and around the interfaces of the mesoscopic structures of the gel. Once again the critical temperature is revealed in the behavior of the Cole-Cole parameter *α* of these processes. The implications towards drug delivery are explored.

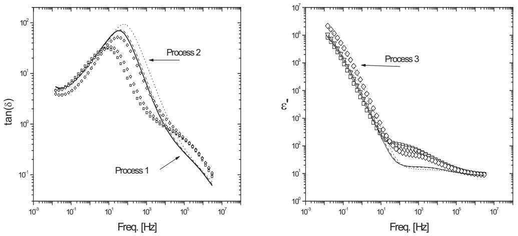


Fig. 1 - Tan (δ) and the real component of the dielectric permittivity, ε', of HEX_{II} mesophase with and without the drug CSA entrapped. 3 temperature slices are shown without CSA (□293 K, □ 301 K, and □ 319 K) and with CSA (solid line 293 K, dashed line 301 K and dotted line 319 K). Three temperature activated processes are noted and labeled respectively, Processes 1, 2 and 3 in each.

References

[1] Amar-Yuli I., Aserin A., and Garti N., J. Phys. Chem. B 112, 10171 (2008).
[2] Amar-Yuli I., Wachtel E., Ben Shoshan E., Danino D., Aserin A., and Garti N., Langmuir 23, 3637 (2007).
[3] Ben Ishai P., Libster D., Aserin A., Garti N., and Feldman Yu., J. Phys. Chem. B 113, 12639 (2009).
[4] Libster D., Aserin A., Wachtel E., Shoham G., and Garti N., J. Colloid Interf. Sci. 308, 514 (2007).
[5] Libster D., Ben Ishai P., Aserin A., Shoham G., and Garti N., Int. J. Pharm. 367, 115 (2009).

Intrinsic Confinement Effects in the Blend Dynamics of Binary Glass-Forming Systems

T. Blochowicz[1], S. Schramm[1], E. Gouirand[1], P. Gutfreund[2], B. Stühn[1] ,B. Frick[2]
[1]TU-Darmstadt, 64289 Darmstadt, Germany
[2]Institut Laue-Langevin, 38043 Grenoble, France
*Email address: thomas.blochowicz@physik.tu-darmstadt.de

By combining broadband dielectric spectroscopy (BDS), differential scanning calorimetry (DSC), and quasielastic neutron scattering (QENS) we investigate the dynamics in a series of low molecular weight binary glass forming liquids (Methyl-THF in Oligo-Styrene or Oligo(Methyl Methacrylate), Picoline in Oligo-MMA). It turns out that, although the systems are fully miscible in the whole temperature range, in many mixtures two glass transition steps can be clearly distinguished in DSC measurements due to the high T_g contrast of the components. By means of BDS the corresponding relaxation processes are identified and it turns out that the distribution of relaxation times of the small molecules in the mixture is extremly broad and contrary to expectation the small molecule M-THF takes part in both glass transitions. Moreover, the relaxation connected with the lower glass transition shows properties typical of dynamics in confinement like an Arrhenius-type temperature dependence and a broad distribution of relaxation times. In particular, when the system crosses the upper glass transition, the matrix transforms from a "slow" to an actual "hard" confinement for the remaining mobile small molecules. This is reflected in a fragile-to-strong crossover in the relaxation times of the small molecules, which becomes visible when results of QENS and BDS are combined. Moreover, a detailed study of the dielectric strength indicates that below the upper T_g the number of mobile small molecules continuously decreases as the second glass transition is approached, which may be due to an increasing number of small molecules that are immobilized close to the frozen matrix.

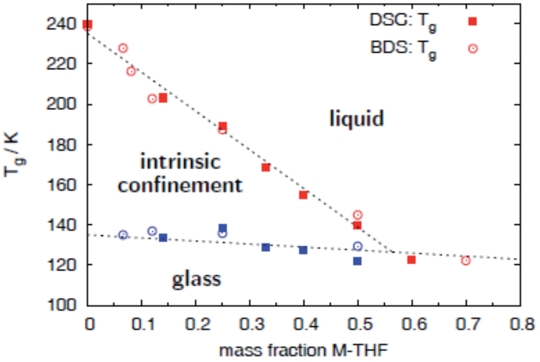


Fig. 1: Two glass transitions as observed in a mixture of M-THF and tri-styrene by DSC and broadband dielectric spectroscopy and the region where intrinsic confinement effects are observed.


6TH INTERNATIONAL CONFERENCE ON
BROADBAND DIELECTRIC
SPECTROSCOPY AND ITS APPLICATIONS

www.dielectric2010.com
07-10 MADRID
SEPTEMBER 2010

Ionic Liquids
-
Charge Transport
(I)

Tuesday 7/Sept
Room A

15:15 - 15:45	**B. Roling**
15:45 - 16:00	C. León
16:00 - 16:15	R. J. Sengwa
16:15 - 16:30	M. Drüschler
16:30 - 16:45	A. Mogus Milankovic

Characterisation of Nonlinear Ion Transport in Solid and Liquid Electrolytes

Bernhard Roling, Halgard Staesche, Jan Kirchberg

Department of Chemistry, University of Marburg,
Hans-Meerwein-Strasse, 35032 Marburg, Germany
Email address: roling@staff.uni-marburg.de

Modern electrochemical cells for energy storage and conversion, such as lithium batteries, supercapacitors, and dye solar cells, require solid or liquid electrolyte materials with high ionic conductivity and broad electrochemical window. Liquid electrolyte materials with promising properties are, for instance, mixtures of ionic liquids and molecular solvents. Solid electrolytes are often used in the form of thin films, e.g. thin glass films for micro-lithium batteries. In thin films, a voltage drop in the range of some Volts generates high electric fields, which in turn lead to a nonlinear (i.e. field-dependent) ionic conductivity of the films.

Here, we study the nonlinear ion conductivity of solid and liquid electrolytes by means of nonlinear impedance spectroscopy. Ac electric fields with large amplitudes > 50 kV/cm are applied, and higher harmonics in the current response of the samples are analysed [1-3]. Thereby, we are able to obtain spectra of the higher-order conductivity $\sigma_3(\omega)$ over broad frequency ranges, see blue squares in Fig. 1. At low frequencies, where long-range ion transport is probed, $\sigma_3(\omega)$ is found to be positive. At higher frequencies, where local (subdiffusive) ion hopping is probed, $\sigma_3(\omega)$ exhibits negative values. We show that there are significant differences between different electrolytes regarding the nonlinearity of the dispersive conductivity, and we discuss the origin of these differences.

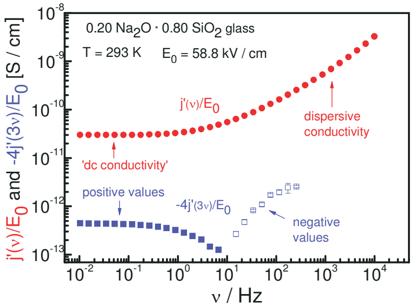


Fig. 1: $\sigma_1(\omega)$ spectrum (red) and $\sigma_3(\omega)$ spectrum (blue) of a Na$^+$ ion conducting glass

References

[1] H. Staesche, S. Murugavel, B. Roling, *Z. Phys. Chem.* **223** (2009) 1229.

[2] B. Roling, S. Murugavel, A. Heuer, L. Lühning, R. Friedrich, S. Röthel, *Phys. Chem. Chem. Phys.* **10** (2008) 4211.

[3] S. Murugavel, B. Roling, *J. Non-Cryst. Solids* **351** (2005) 2819.

ac conductivity and nearly constant loss in oxide-ion conductors $Gd_2(Zr_yTi_{1-y})_2O_7$

M.R. Díaz-Guillén [1], J.A. Díaz-Guillén [1], A.F. Fuentes [1], J. Santamaría [2], C. León [2*]

[1] Cinvestav Unidad Saltillo, Apartado Postal 663, 25000-Saltillo, Coahuila, Mexico.

[2] GFMC, Departamento de Física Aplicada III, Facultad de Física, Universidad
Complutense de Madrid, Campus Moncloa, 28040 Madrid, Spain
*Email address: carlos.leon@fis.ucm.es

At enough low temperatures, or high frequencies, ionic conductors show a universal behavior consisting of a linear frequency dependence of their ac conductivity, i.e. a nearly constant dielectric loss (NCL). Interestingly, a clear correlation has been recently reported[1,2] between the high values of the dc conductivity σ_{dc}, with technological importance, found in superionic conductors, and the high values of the NCL magnitude that they show. This finding has triggered the interest in understanding the origin of the NCL behavior, and while different theoretical models have been proposed to explain it[3,4], there is still some debate on this issue since experimental data of enough resolution, necessary to test these models, are scarce. Here we report on ac conductivity data, at temperatures between 150 and 500 K and in the frequency range 1 Hz – 3 MHz, of several oxide ion conductors with composition $Gd_2(Zr_yTi_{1-y})_2O_7$, where we are able to identify the crossover to the NCL behavior when lowering temperature or increasing frequency. This crossover is found to be thermally activated, and its activation energy E_{NCL} to be much lower than the activation energy E_{dc} for the dc conductivity. We also found that the values of E_{NCL} are almost independent of composition, and therefore of the concentration of mobile oxygen vacancies, unlike those of E_{dc}. Our results support the interpretation of the NCL in ionic conductors arising from the cage decay dynamics[5], and highlight the importance of interactions among mobile ions in determining the dc conductivity values at higher temperatures[6].

References

[1] K. L. Ngai, J. Chem. Phys. 110, 10576 (1999).
[2] C. León, K. L. Ngai, and A. Rivera, Phys. Rev. B 69, 134303 (2004).
[3] J. Habasaki, K. L. Ngai, and Y. Hiwatari, Phys. Rev. E 66, 021205 (2002).
[4] D. M. Laughman, R. D. Banhatti and K. Funke, Phys. Chem. Chem. Phys. 11, 3158 (2009).
[5] K. L. Ngai and C. León, Phys. Rev. B 66, 064308 (2002).
[6] M. R. Díaz-Guillén, K. J. Moreno, J. A. Díaz-Guillén, A. F. Fuentes, K. L. Ngai, J. García-Barriocanal, J. Santamaría and C. León, Phys. Rev. B 78, 104304 (2008).

Dielectric relaxation and ionic conduction behaviour of melt compounded PEO-blend salt-MMT nanocomposite electrolytes

R.J. Sengwa*, Sonu Sankhla, Shobhna Choudhary
Dielectric Research Laboratory, Department of Physics, J N V University.
Jodhpur – 342 005 India
*Email address: rjsengwa@rediffmail.com

In recent years there has been an increasing technological and academic interest to develop the novel polymer nanocomposite electrolytes (PNCEs) of improved thermal stability, mechanical strength, electrochemical, photochemical and electrical properties[1-6]. It has been revealed that an addition of a small amount of montmorillonite (MMT) clay in polymer-salt complex matrix play an important role in the development of desired physical and electrical properties of the PNCEs materials[1-4]. In the present manuscript, the PNCEs comprising poly(ethylene oxide) (PEO) and blend salt (lithium perchlorate-sodium perchlorate) complexes loaded with MMT upto 20 wt% were synthesized by melt compounding technique. Complex dielectric function, electric modulus, alternating current (ac) electrical conductivity and complex impedance of the synthesized PNCEs were investigated as a function of MMT concentration in the frequency range 20 Hz to 1 MHz. The frequency dependent ac conductivity spectra of the studied materials at higher frequencies follow the power law whereas deviation was found from dc conductivity plateau due to electrode polarization effect at lower frequencies (Fig. 1). In Fig. 2, spectra of the loss part of electric modulus of the PNCEs materials shows the peaks of ionic conduction relaxation. The relaxation times corresponding to electrode polarization and ionic conduction processes were determined. It is observed that ionic conductivity of the PNCEs are governed by the nanoscale dispersed exfoliated/intercalated MMT structures in the PEO matrix.

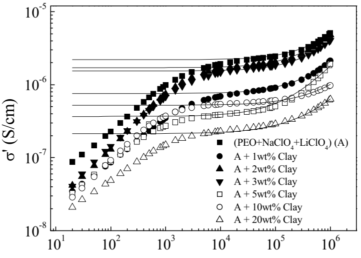


Fig. 1 AC conductivity spectra of the PNCEs

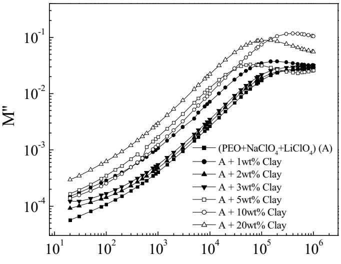


Fig. 2 Loss electric modulus spectra of the PNCEs

References

[1] W. Loyens, F.H.J. Maurer, P. Jannasch, Polymer 46, 7334 (2005).
[2] S. Kim, E.J. Hwang, Y. Jung, Colloids Surf. A 313–314:216 (2008).
[3] M. Wang, S. Dong, J. Power Sources 170, 425 (2007).
[4] D.K. Pradhan, R.N.P. Choudhary, B.K. Samantaray et al, Ionics 15, 345 (2009).
[5] R.J. Sengwa, S. Choudhary, S. Sankhla, Polym. Int. 58, 781 (2009).
[6] R.J. Sengwa, S. Sankhla, S. Choudhary, Colloids Polym. Sci. 287, 1013 (2009).

Temperature-dependent Measurements of Differential Capacitance at Pt / RTIL Interfaces

M. Drüschler*, B. Huber, B. Roling
Department of Chemistry, University of Marburg, Hans-Meerwein-Straße,
35032 Marburg, Germany
*Email address: drueschm[at]staff.uni-marburg.de

Room temperature ionic liquids (RTIL) show interesting properties leading to a wide range of applications[1]. However, electrochemical properties have not been investigated in detail yet. In particular, the electrochemical double layer at the interface between an RTIL and another homogeneous phase, e. g. a metal wire, has not been studied in a satisfying manner although the knowledge of its structure and properties is essential for a multiplicity of implementations. For instance, RTILs can be used as electrolytes in electrochemical double layer capacitors[2]. Since they show much broader electrochemical windows than aqueous and organic solvents, a significant improvement of energy storage seems to be possible. In a recent article[3] the frequency- and potential-dependent differential capacitance of imidazolium- and pyrrolidinium-based RTILs was measured at a polycrystalline platinum interface by means of broadband electrochemical impedance spectroscopy (EIS). A strong increase of the measured differential capacitance with decreasing frequency points to slow pseudo-capacitive processes. These processes are most likely related to ion adsorption. These slow processes cause hysteresis effects in the double layer capacitance which become apparent if the differential double layer capacitance is measured against the dc-potential of the working electrode since the values and the shape of the curves depend on the scan direction of the dc-potential. To investigate the temperature-dependence of the differential double layer capacitance as well as the temperature-dependence of the slow processes, a novel home-made measurement cell was used enabling further investigations under temperature-control.

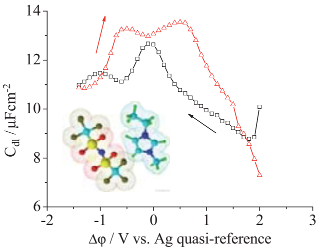


Fig.1. Differential double layer capacitance per unit area of [EMIm][N(Tf)$_2$] versus working electrode potential

References
[1] P. Hapiot, C. Lagrost, Chem. Rev. 108, 2238 (2008).
[2] P. Simon, Y. Gogotsi, Nature Materials 7, 845 (2008).
[3] M. Drüschler, B. Huber, S. Passerini, B. Roling, J. Phys. Chem. C 114, 3614 (2010).

Correlation between electrical properties and microstructure of crystallized ZnO-Fe_2O_3-P_2O_5 glass

A. Moguš-Milanković[1], K. Sklepić[1], Ž. Skoko[2], S.T. Reis[3]

[1]Ruđer Bošković Institute, Bijenička c.54, 10000 Zagreb, Croatia
[2]Physics Department, Faculty of Science, University of Zagreb, P.O. Box 331, Croatia
[3]Graduate Center for Materials Research, Missouri University of Science and Technology
Rolla, MO 65409-1170, USA
Email address: mogus@irb.hr

The effect of heat treatment of $10ZnO-30Fe_2O_3-60P_2O_5$ glass on the structural and dielectric properties was studied by impedance spectroscopy (IS), X-ray diffraction (XRD), differential thermal analysis (DTA) and scanning electron microscopy (SEM). The XRD and Raman spectroscopy have shown that the glass undergoes structural changes: from amorphous, to partially crystalline after nanocrystallization close to the first crystallization temperature,T_{C1}, 680^0C and massive crystallization after heat treatment at higher temperature, T_{C2}, 760^0C. SEM observations exhibited that the average size of grains after nanocrystallization near T_{C1} was estimated to be about 20-50 nm. The dielectric measurements show that the crystalline growth orientation of the $Fe_3(P_2O_7)_2$ grains embedded in the glass matrix is random. The frequency dependent conductivity and dielectric relaxation of as-quenched glass and crystallized glasses head treated up to 760^0C at various crystallization times were investigated.

The presence of crystalline $Fe_3(P_2O_7)_2$ grains formed after thermal treatment at T_{C1}, 680^0C, enhances the electrical conductivity as compared with the as-quenched glass. This conductivity enhancement is related to the conduction at the interfaces between the crystallites and glassy phase in which the concentration of Fe(II)-Fe(III) pairs responsible for electron hopping is higher than in side the glass matrix. Further thermal treatment at higher temperature, T_{C2}, 760^0C, leads to formation of ferric orthophosphate, $FePO_4$ along with pronounced growth of $Fe_3(P_2O_7)_2$ crystals. Electrical conductivity of this glass-ceramics is lower than before thermal treatment. The decrease in electrical conductivity is explained by a considerable weakening in the interactions between Fe sites in crystalline phases caused by poorly defined conduction pathways. This is a result of the presence of larger crystalline grains and disappearance of glassy matrix in fully crystallized sample.

6TH INTERNATIONAL CONFERENCE ON
BROADBAND DIELECTRIC
SPECTROSCOPY AND ITS APPLICATIONS

www.dielectric2010.com
07 - 10 MADRID
SEPTEMBER 2010

Biological Materials (I)

Tuesday 7/Sept
Room B

15:15 - 15:45	**J. Swenson**
15:45 - 16:00	S. Cappaccioli
16:00 - 16:15	Y. Katsumoto
16:15 - 16:30	Y. Hayashi
16:30 - 16:45	I. Ermolina

Slow relaxations in liquids and the role of solvent for the protein glass transition

J. Swenson, H. Jansson, R. Bergman
Department of Applied Physics, Chalmers University of Technology SE-412 96
Göteborg, Sweden
*Email address: jan.swenson@chalmers.se

In this presentation two topics will be discussed; an ultraslow dielectric Debye-like relaxation in liquids and how the surrounding solvent affects the calorimetric glass transition of proteins. In the case of the ultraslow Debye-like relaxation it is well known that such a process exists in monoalcohols [1], although its origin is still not clear. For monoalcohols this slow Debye-like relaxation is 2-3 orders of magnitude slower than the viscosity related α-relaxation, and it is also much more intense [1]. Here we show that a similar Debye-like process exists also in a wide range of other liquids (possibly all liquids), although its intensity is substantially weaker than in the monoalcohols, and also a few more orders of magnitude slower than the α-relaxation [2,3]. Whether this weak and ultraslow process in a wide range of liquids has the same physical origin as the well-known Debye-like relaxation in monoalcohols remains to be elucidated.

For the investigations of the protein glass transition, myoglobin in different water-glycerol solvent mixtures was studied by broadband dielectric spectroscopy and differential scanning calorimetry (DSC). In particular, the relation between the protein and solvent dynamics was analysed with the aim to better understand the calorimetric glass transition, T_g, of proteins and the role of hydration water for protein dynamics. The results show that several different protein relaxations are involved in the calorimetric glass transition, and that the broadness (ΔT_g) of the transition depends strongly on the total amount of solvent [4,5]. The reason for this is that the protein relaxation processes become more separated in time with decreasing solvent level. In the case of the glycerol containing samples the freezing-in of the viscosity related α-relaxation of the solvent gives a direct, and strong, contribution to the total calorimetric T_g. This is in contrast to myoglobin in pure water where the low temperature water process does not give any direct contribution to the calorimetric T_g, although the α-relaxation in the hydration water causes the protein dynamics that freeze-in at T_g [4,5]. Thus, in the case of pure water as solvent the onset of the calorimetric T_g occurs when the high temperature α-relaxation in the solvent vanish. Below this temperature the nature of the dynamics changes dramatically and only local motions remain. Finally, the dielectric data show clearly that the protein relaxation processes exhibit similar temperature dependences as the α-relaxation in the solvent, as suggested for solvent-slaved protein motions [6].

References

[1] L. M. Wang and R. Richert, J. Chem. Phys. 121, 11170 (2004).
[2] R. Bergman, H. Jansson, and J. Swenson, J. Chem. Phys. 132, 044504 (2010).
[3] H. Jansson, R. Berman, and J. Swenson, Phys. Rev. Lett. 104, 017802 (2010).
[4] H. Jansson and J. Swenson, Biochim. Biophys. Acta: Proteins and Proteomics 1804, 20 (2010).
[5] H. Jansson, R.Bergman and J. Swenson, submitted to J. Chem. Phys.
[6] P. W. Fenimore, H. Frauenfelder, B. H. McMahon, and R. D. Young, Proc. Nat. Acad. Sci., USA 101, 14408 (2004).

Slow and Fast Dynamics of Hydrated Proteins: the pivotal role of secondary β-relaxation of Water

S. Capaccioli[1,2*], M. Bertoldo[2], P.A. Rolla[1,2], N. Shinyashiki[3], K.L. Ngai[4],
[1] Dipartimento di Fisica, Università di Pisa, Largo Pontecorvo 3, 56127 Pisa, Italy
[2] Istituto per i Processi Chimico Fisici (IPCF), CNR, Pisa, Italy
[3] Department of Physics, Tokai University, Hiratsuka, Kanagawa 259-1292, Japan
[4] Naval Research Laboratory, Washington DC 20375-5320, USA
*Email address: Simone.Capaccioli@df.unipi.it

Function of proteins and their dynamic properties depend strongly on hydration level and temperature. The dynamics of proteins is coupled to that of the solvent surrounding the protein molecules over a wide range of timescales[1,2,3]. Slow dynamics of solvent and conformation fluctuations of proteins have been reported to undergo a structural arrest in the vicinity of some temperature T_g, usually around 200-230 K, according to a process often likened to glass transition. Additionally, there is a number of evidences that fast dynamics of hydrated proteins show, at some temperature $T_D>T_g$, a marked "dynamic crossover" related to the temperature behavior of the mean square displacement measured by Mössbauer effect and by neutron scattering (on the timescale ns-ps) both on protein motions and solvent dynamics. However, a complete understanding of the conformation fluctuations of hydrated proteins is still not available, and in the literature different views of the coupling with solvent and explanation of the dynamics have been offered[1,2,3,4].

In this study, we have analyzed the dynamic behavior of two bio-macromolecules, both mixed with ultra pure water at different concentrations: the protein Bovine Serum Albumin (BSA) and the polysaccharide glycogen. Dielectric measurements were performed in the broad frequency range 2 mHz-20 GHz and at temperatures between 80K and 300K. In addition, calorimetric data were analyzed. Our results, along with a critical review of the literature data on dynamics of hydrated proteins and a comparison to results related to dynamics of aqueous mixtures, allowed to clarify the mechanisms underlying the coupling between dynamics of solvent and bio-macromolecules. Two main dynamic processes were identified. The slowest process, with features of structural α-relaxation of ordinary glass-formers, is responsible for the glass transition observed by adiabatic calorimetry and is due to cooperative motion of water physically coupled to the bio-macromolecule. The fastest process can be identified as the secondary relaxation of water in the hydration shell: its relaxation times show a crossover at T_g from stronger temperature dependence at high temperatures to approximately Arrhenius dependence at lower temperatures, paralleling the behavior of secondary relaxation time of water in aqueous mixtures[5,6]. Moreover, we found that this last process controls also the "dynamic crossover" of fast dynamics occurring at some temperature T_D, i.e. it is responsible for the rise of the mean square displacement measured by neutron scattering or of the intensity of high frequency dielectric permittivity.

References

[1] D Ringe, G. A. Petsko, Bioph. Chem. 105, 667–680 (2003).
[2] P. Fenimore, H. Frauenfelder, B. McMahon, R.D. Young, PNAS 101,14408 (2005)
[3] W. Doster, Eur Biophys.J. 37, 591 (2008).
[4] S. Khodadadi, S. Pawlus, A.P. Sokolov, J. Phys. Chem. B 112: 14273 (2008).
[5] S.Capaccioli, K.L. Ngai, N. Shinyashiki, J.Phys.Chem.B, 111, 8197 (2007).
[6] K.L. Ngai, S.Capaccioli, N. Shinyashiki, J.Phys.Chem.B 112, 3826 (2008).

Dielectric spectroscopy on flowing single lymphocytes

Y. Katsumoto[1*], S. Omori[1], K. Sato[1], T. Umetsu[1], Y. Hayashi[1], H. Soma[1],
T. Hayakawa[1], M. Saito[1], S. Lee[1], A. Yasuda[1],
M. Nagasawa[2], T. Morio[2], S. Mizutani[2]
[1]Life Science Laboratory, Advanced Materials Laboratories, Sony Corporation, 113-8510 Tokyo, Japan
[2] Department of Pediatrics and Developmental Biology, Tokyo Medical and Dental University, 113-8510 Tokyo, Japan
*Email address: Youichi.Katsumoto@jp.sony.com

The electric properties of the cell constituents such as the membrane and cytoplasm can be assessed by dielectric spectroscopy, although they are inherently the average values of all the cells in a suspension. If single cell dielectric spectroscopy is established, it allows discriminating different cells without staining them for future clinical applications such as cell therapy and regenerative medicine.

We have developed a prototype of dielectric spectro-cytometer for single cell dielectric spectroscopy, which rapidly measures and analyzes dielectric spectrum of single cells passing one by one through a fluidic channel. Two important components of the instrument are the sensing structure made of layered films and the high-speed impedance analyzer. The film produced by industrial fabrication processes includes the fluidic channel and embedded electrodes in it. It is carefully designed in such a way that the change of complex impedance induced by single cells passing through the detection region is detectable by the analyzer and that the parasitic capacitance originating from electrode polarization does not affect measurement of complex permittivity purely attributable to the cell in a solvent. The analyzer enables simultaneous measurement of complex impedances over multiple frequency points in the range of 30 MHz with sampling rate of 2.5×10^3 per second.

Our system is different from other flow-cytometric systems based on electric detection principles previously proposed [1] or realized [2] in that it accurately measures complex impedances over frequencies around the relaxation frequency while suppressing effects of electrode polarization, and the number of frequencies for simultaneous measurement is larger.

Simple demonstrations of the prototype were performed for several kinds of lymphocyte. For example, the wild-type and mutant lines of Jurkat cells were subject to stimulation of CD95 antibody and subsequent measurements repeated for three hours after the stimulation. For the wild-type line, remarkable change of the complex permittivity was observed in correspondence to the generation of apoptotic bodies. In addition, it was suggested that the electric properties of the cell constituents start to change even before the morphological change of the cells occurs.

References

[1] H. Morgan, T. Sun, D. Holmes, S. Gawad, N.G. Green. J. Phys. D: Appl. Phys. 40(1),61(2007).
[2] G. Schade-Kampmann, A. Huwiler, M. Hebeisen, T. Hessler, M. Di Berardino. Cell Prolif. 41(5),830(2008).

Venous thrombosis risk assessment by dielectric spectroscopy

Y. Hayashi[1*], **Y. Katsumoto**[1], **M-A. Brun**[1], **S. Omori**[1], **M. Kaibara**[2], **I. Uchimura**[3]
[1]Life Science Laboratory, Advanced Materials Laboratories, Sony Corporation, 113-8510 Tokyo, Japan
[2] Institute of Physical and Chemical Research (RIKEN), 351-0198 Saitama, Japan
[3]Department of Endocrinology and Metabolism, Tokyo Medical and Dental University, 113-8510 Tokyo, Japan
*Email address: Yoshihito.Hayashi@jp.sony.com

We studied the coagulation of blood obtained from diabetic patients and healthy donors by dielectric spectroscopy (DS) and rheological methods. The results allow us to propose a novel test method for risk assessment of venous thrombosis. Venous thrombus formed in a deep leg vein moves through veins, and finally occlude a lung artery after passing through the heart. This pulmonary thromboembolism (PTE) is often lethal, and the third cause of death in cardiovascular diseases in the US. PTE is known to occur in a period of sitting or flight for many hours; yet its occurrence after surgical operations is much higher. A number of risk factors such as diabetes, cancer, pregnancy or ageing are associated with a high incidence of PTE. However, there has been no popularized method for assessing accurately the coagulability of blood. In this work, we established a simplified coagulation model system consisting of fibrinogen solution and washed erythrocytes. This model system makes it possible to control the coagulation rate by changing the amount of thrombin added to the suspension. Figure 1a shows the normalized dielectric spectra during the coagulation of blood sample. It is clear that the peak position of the DS data at 730 kHz is in good agreement with the onset time of coagulation obtained by a rheological method (Fig. 1b). Our theoretical estimation indicates that the observed DS response is due to the aggregation of erythrocytes and the increase of mesoscopic inhomogeneity with the progress of coagulation. The main mechanism of the DS response for the coagulation of human whole blood and the model system are the same, although our experimental results for the whole blood suggested additional and non negligible effects including enzymatic reactions of clotting factors and local aggregation of erythrocytes such as rouleaux formation. For blood of diabetic patients, we found that the coagulation time obtained from the peak position of the normalized dielectric permittivity inversely correlates with HbA1c level that is an indicator of the averaged glucose level in blood. If the DS data are compared in details over wide ranges of frequency and time, they would differ from one patient to another. These differences may reflect the medical condition of individuals or the influence of medication. Therefore, the present work strongly suggests the high potential of DS for the risk assessment of thrombosis and subsequent medication.

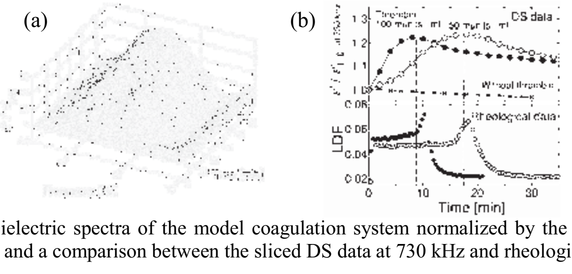


Fig.1. Dielectric spectra of the model coagulation system normalized by the spectrum at time zero (a), and a comparison between the sliced DS data at 730 kHz and rheological data (b).

Investigating temperature-induced phase transition in aqueous solutions of poly(vinyl methyl ether) by dielectric, terahertz and microscopic techniques

I. Ermolina[1*] **and V. Khutoryanskiy**[2]
[1]School of Pharmacy, De Montfort University. The Gateway, Leicester LE19BH, UK
[2]Reading School of Pharmacy, University of Reading, Whiteknights, Reading RG66AD, UK
*Email address: iermolina@dmu.ac.uk

Water-soluble synthetic polymers attract significant interest due to various potential applications as pharmaceutical excipients, adhesives, and thickening reagents. In aqueous solutions amphiphilic polymers often display lower critical solution temperature (LCST), which implies that the polymer is soluble in water at lower temperatures and undergoes phase separation upon heating [1, 2]. Amphiphilic poly(vinyl ethers) often exhibit LCST behaviour, i.e. temperature-responsive properties, promising for biomedical and biotechnological applications. Poly(vinyl methyl ether) (PVME) has a LCST at physiological temperature range around 35 °C, making it a potential candidate for developing temperature-responsive drug delivery systems.

In the present work we have studied the phase behaviour in aqueous solutions of PVME by different physical techniques such as time domain dielectric spectroscopy (TDS), broadband dielectric spectroscopy (BDS), terahertz spectroscopy and hot stage microscopy.

Three dielectric relaxation processes were found in 5 wt % aqueous solution of PVME in TDS experiment (frequency range from 500 KHz to 3 GHz and temperature range from 10^{o}C to 60^{o}C). All of them demonstrated a transition in the relaxation time and dielectric strength near the transition temperature of 35 °C. The total dielectric strength increased almost in 10 times, whereas the conductivity dropped down significantly. Independent measurements of the conductivity by conductivity-meter have shown that its behaviour against temperature is non-linear and reversibility at decrease of temperature is time dependent. In BDS experiment (frequency range from 0.1-10^{6} Hz and temperature range from -120^{o}C to 80oC) the dielectric behaviour is dramatically changed near transition temperature. Also 2 relaxation processes in sub-zero temperature range were observed.

Hot-stage optical microscopy allowed visualising the phase transition in polymer solutions and recording the transition temperature. Terahertz spectroscopy was used to study PVME solutions in spectral range from 0.06 THz to 3 THz (2 cm^{-1} – 100 cm^{-1}). In this range the absorbance spectra and refractive index of polymer solution were studied. At temperature above 35 °C the non-linear behaviour of absorbance was observed, whereas the refractive index demonstrated hysteresis behaviour.

The transition in PVME solutions might probably be associated with the competition between hydrogen-bonding and hydrophobic effects. The hydrophilic ether groups stabilize PVME macromolecules in aqueous solution by forming hydrogen bonds with water molecules and hydrophobic methyl groups destabilize the solution by altering normal water structure. The hydrophobic effects intensify monotonously upon heating, whereas water-macromolecule hydrogen bonding is partially disrupting, which finally breaks the balance and induces the phase separation. The molecular mobility becomes slower in compact globules, but amplitude of relaxation increases due to bigger scale of mobile units.

References

[1] Zhunuspayev D.E., Mun G.A., Khutoryanskiy V.V. *Langmuir,* DOI: 10.1021/la904403k, ASAP article (2010)

[2] Khutoryanskaya O.V., Mayeva Z.A., Mun G.A., Khutoryanskiy V.V. *Biomacromolecules*, 9, 3353-3361 (2008).

Ionic Liquids
-
Charge Transport (II)

Tuesday 7/Sept
Room A

17:15 - 17:45	**J. Ulanski**
17:45 - 18:00	C. Filipic
18:00 - 18:15	L. I. Trakhtengerg
18:15 - 18:30	G. F. Novikov
18:30 - 18:45	J. R. Sangoro

Charge carrier transport in organic *p-n* junctions as seen by impedance spectroscopy

Jaroslaw Jung, Krzysztof Kisiel, Jacek Ulanski*
Department of Molecular Physics, Faculty of Chemistry, Technical University of Lodz,
Zeromskiego street 116, 90-924 Lodz, Poland
*Email address: jacek.ulanski@p.lodz.pl

Impedance spectroscopy is one of the standard techniques for investigations of inorganic electronic devices. In general it helps to characterize charge carriers generation and transport mechanisms and to determine an influence of contact materials and junction geometry on the device performance. Recently the impedance spectroscopy was applied also in organic electronics with an aim to gain better understanding of functioning of the devices and in particular the organic *p-n* junctions [1, 2]. However most of the studies reported so far were performed in rather limited ranges of frequency and temperature.

This work presents results of the impedance spectroscopy studies for several model systems: organic semiconductors (*p*-type, like polythiophene derivative and *n*-type, like perylene derivative) with different electrodes and also *p-n* junctions obtained by original technique consisting in *in situ* crystallization of low-molecular-weight component in polymer matrix [3]. The measurements were performed in a broad frequency and temperature ranges. Dependence of the alternative current on frequency and phase shift between the voltage and the current were analysed in order to verify the models of charge carrier transport and to determine the nature of the *p-n* junction.

Acknowledgements

This work was supported by NoE PolyNet 7 FP UE ICT 214006 and FlexNet 7 FP UE ICT 247745

References

[1] K.P. Chandra, K. Prasad, R.N. Gupta, Physica B, 388 (2007) 118–123
[2] A. Bekkali, I. Thurzo, T. Kampen, D. Zhan, Applied Surface Science, 234 (2004) 149-154
[3] M. Wiatrowski et al.,. Thin Solid Films, 518 (2010) 2266-2270

Polarons in Magnetoelectric $K_3Fe_5F_{15}$ and $K_3Fe_2Cr_3F_{15}$

C. Filipič, V. Bobnar, G. Tavčar, B. Žemva, and A. Levstik
Jožef Stefan Institute, Jamova 39, 1000 Ljubljana,
Slovenia
*Email address: cene.filipic@ijs.si

The ac electrical conductivity of magnetoelectric $K_3Fe_5F_{15}$ and $K_3Fe_2Cr_3F_{15}$ was investigated as a function of the frequency and temperature. In both substances at higher temperatures the charge transport is governed by a thermally activated process, while at lower temperatures the real part of the complex ac electric conductivity was found to follow the universal dielectric response $\sigma' \propto \nu^s$, being typical for hopping or tunneling of localized charge carriers. A detailed analysis of the temperature dependence of the UDR parameter s in terms of the theoretical model for tunneling of small polarons revealed that, below 80 K, this mechanism governs the charge transport in $K_3Fe_5F_{15}$. In $K_3Fe_2Cr_3F_{15}$ below 200 K the hopping or tunneling of localized charge carriers is caused by tunneling of small polarons. The substitution of three iron atoms with three chromium atoms in $K_3Fe_2Cr_3F_{15}$ does not change the mechanism of charge transport at low temperature.

Non-phenomenological description of complex dielectric permittivity of metal oxide nanocrystals films

L.I. Trakhtenberg[1,2*], **M.A. Kozhushner**[1], **V.F. Gromov**[2], **G.N. Gerasimov**[2],
A. Greenbaum (Gutina)[3]
[1]Semenov Institute of Chemical Physics of RAS, Kosygina Street 4, 119991 Moscow, Russia
[2]State Scientific Centre RF ‘Karpov Institute of Physical Chemistry’,
Vorontsovo Pole 10, 105064 Moscow, Russia
[3]The Hebrew University of Jerusalem. Department of Applied Physics,
Edmond J.Safra Campus, 91904 Jerusalem, Israel
*Email address: trakh@cc.nifhi.ac.ru

Two component composite semiconductor films, consisting of metal oxide nanocrystals with different electron affinity A: SnO_2 with A about 4.8 eV and In_2O_3 with A about 3.7 eV have been investigated. Conductometry and Dielectric spectroscopy methods have been applied with the purpose to insight into the mechanism of the conductometric sensor effect of interaction of the film nanocrystals with an analyzed substance from environment. The sensitivity of these composite sensors has been checked on hydrogen atmosphere. Dielectric properties of the materials were investigated using Broad Band Dielectric Spectrometer (NOVOCONTROL BDS 80) in wide frequency (0.1 Hz ÷1 MHz) and temperature (-100 ^{0}C ÷ 300 ^{0}C) ranges. The dielectric behavior of such composite materials confirmed the existence of different electron hopping mechanisms in the studied composite films. For description of dielectric response of the metal oxide nanocrystals films a non-phenomenological model has been proposed based on hopping of electrons between traps around the metal nanoparticles[1].

References

[1] L.I. Trakhtenberg, M.A. Kozhushner, V.F. Gromov, V.L. Bodneva, T.V. Antropova, G.N. Gerasimov, E. Axelrod, A. Greenbaum (Gutina), Yu. Feldman, J. Non-Cryst. Solids 356, 642 (2010).

Broadband photodielectric spectroscopy: history, progress and near prospects

G.F. Novikov
Institute of Problems of Chemical Physics, RAS.
Semenov's pr., 1, Chernogolovka, Moscow region, Russia, 142432
Email address: ngf@icp.ac.ru

There are a large number of materials known which demonstrate a variation of the complex permittivity ε^* by light excitation or ionizing radiation. Variations can be both reversible and irreversible. For example the irreversible modifications are observed during photopolymerization, photocrosslinking and other photochemical reactions. Usually in the case of reversible effects the variation of the imaginary part of the permittivity $\Delta\varepsilon^{//}$ is called the photoconductivity, and the variation in the real part of the permittivity $\Delta\varepsilon^{/}$ is called the photodielectric effect (PDE). Quite a lot of materials shows PDE, e.g. organic and inorganic compounds, crystalline and amorphous matters, materials based on short molecular chains and long oligomeric or polymeric molecules. In the above listed group of the materials the semiconductors possess maximal «sensitivity» to light influence.

Despite the fact that PDE was discovered almost century ago[1], the nature of the effect is still poorly understood. Directly after detection it has not been given sufficient attention to this effect. New interest came into view only in the end of 1940th (see Fig. 1, region "I"). The second maximum happened in 1980th years (see region "II") was caused by beginning of microwave investigations.

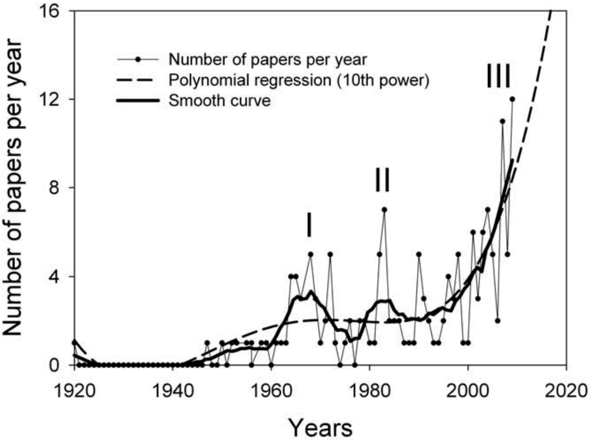


Fig.1. Growth of number of papers on PDE per year.

However most sharply expressed maximum falls at present time (Fig. 1, region "III"). The beginning of this maximum well correlates with development of instrument base of BDS. That has resulted in method Broadband Photodielectric Spectroscopy (BPDS). Its history, progress and near prospects are discussed in this presentation.

---

[1] Gudden B. and Pohl U. // Z. Phys. 1920. 1. 365.

Characteristic hopping lengths and molecular volumes of imidazolium-based ionic liquids

J. R. Sangoro*, C. Iacob, and F. Kremer
Institute of Experimental Physics I, Linnéstr. 5, 04103, Leipzig, Germany
*Email address: sangoro@physik.uni-leipzig.de

Translational diffusion in bis(trifluoromethylsulfonyl)imide-based glass-forming ionic liquids (ILs) is investigated in a wide frequency and temperature range by means of Broadband Dielectric Spectroscopy (BDS), and Pulsed Field Gradient Nuclear Magnetic Resonance (PFG NMR) [1-3] as shown in Fig. 1. It is experimentally shown that in the time-scale characterizing the cross-over from sub-diffusive to diffusive ion dynamics, the hopping lengths are of the order of molecular diameters determined from quantum-chemical calculations [3]. This provides a direct means – via Einstein-Smoluchowski relation – to determine diffusion coefficient by BDS over more than 8 decades unambiguously and in quantitative agreement with PFG NMR measurements. Unprecedented possibilities in the study of charge transport and dynamic glass transition are thus opened.

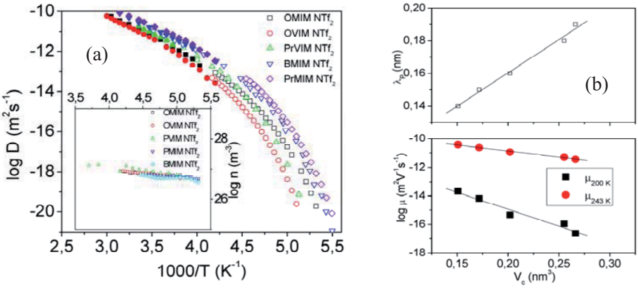


Fig. 1: (a) Diffusion coefficients determined from broadband dielectric spectra (open symbols) upon applying the Einstein-Smoluchowski equation for a series of ionic liquids based on bis(trifluoromethylsulfonyl)imide anion as well as the diffusion coefficient measured by PFG NMR (filled symbols) versus inverse temperature. Inset: the effective number density of charge carriers as a function of inverse temperature. (b) The experimentally obtained hopping lengths (upon combining PFG NMR and BDS) versus the sum of molecular volumes of anions and cations obtained from quantum chemical calculations for the different ionic liquids based on the same bis(trifluoromethylsulfonyl)imide anion. The calculations are carried out in the temperature ranges spanned by both techniques. The mobility at two selected temperatures are also compared to the computed volumes.

References

[1] *Broadband Dielectric Spectroscopy*, edited by F. Kremer and A. Schönhals, Springer (2003).
[2] J. R. Sangoro, A. Serghei, S. Naumov, P. Galvosas, J. Kärger, C. Wespe, F. Bordusa, and F. Kremer, Phys. Rev. E 77, 051202 (2008); J. R. Sangoro et al, J. Chem. Phys. 128, 214509 (2008) ; J. R. Sangoro, C. Iacob, A. Serghei,C. Friedrich, F. Kremer, *Phys. Chem. Chem. Phys.* 11, 913 (2009).
[3] J. R. Sangoro et al, (2010) Submitted.

Biological Materials (II)

Tuesday 7/Sept
Room B

17:15 - 17:45	**Y. Feldman**
17:45 - 18:00	V. Samouillan
18:00 - 18:15	I. Stroe
18:15 - 18:30	R.B. Talware

Dielectric properties of bound water in biological systems; The Beauty of Nature

Yuri Feldman , **Alexander Puzenko and Paul Ben Ishai**

Department of Applied Physics,
The Hebrew University of Jerusalem, 91904,
Israel
*Email address: yurif@vms.huji.ac.il

The interaction of water with biological structures is the mediator of many biological reactions. In many dielectric relaxation processes involving water in biological systems, the mechanisms are governed by Cole-Cole (CC) behavior. It is typical for various aqueous systems [1], including aqueous solutions of physiologically active non-ionic molecules (such as nucleotides), amino acids and sugars [2]. The phenomenological CC law can be represented by a frequency dependent dielectric permittivity $\varepsilon^*(\omega) = \varepsilon_\infty + \Delta\varepsilon/[1 + (i\omega\tau)^\alpha]$, where ε_∞ is the dielectric permittivity at the high frequency limit, $\Delta\varepsilon$ is the dielectric strength, τ is a characteristic time scale and the exponent α is referred to as a measure of symmetrical broadening in the dielectric losses relaxation peak ($0<\alpha<1$). It has been found experimentally that α is strictly dependent on temperature, structure, composition, pressure and other controlled physical parameters [2]. According to the Ryabov model [3] the $\alpha(\tau)$ dependence reflects the rate of dipole interaction between the matrix (polymer, or other soluble molecule) and solvent dipoles (Figure 1). These findings are very similar to the recently obtained results of hydration water studied in rice kernels (Figure 2) [4]. A main challenge in complex systems including biological is to uncover a physical model underlying the CC behaviour.

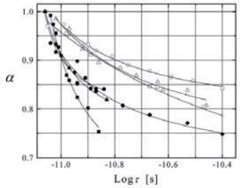


Figure 1 - CC exponent α versus relaxation time τ for different polymer samples [3]. The curves correspond to equation (10). The full symbols correspond to the hydrophilic polymers and the open symbols correspond to the hydrophobic samples.

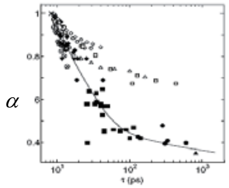


Figure 2 – CC exponent α versus relaxation time τ for rice kernels, rice flour, and boiled rice with various moisture contents [4].

The paper will review the nature of the CC model and the relationship between the stretch parameter, α, of the CC formula and the relaxation time, τ, of the process. It will be shown that this links structural and dynamic elements of the relaxation mechanism.

---

[1]. Y. Hayashi, N. Shinyashiki and S. Yagihara, *J. Non-Cryst. Solids* **305**, pp. 328–32, 2002.
[2]. Y. Feldman, A. Puzenko and Ya. Ryabov, *Adv. Chem. Phys.* **133 A**, pp. 1-126, 2006.
[3]. Ya.E. Ryabov, N. Shinyashki, S. Yagihara and Yu. Feldman, *J. Chem. Phys.* **116**(19), pp.8611-8615, 2002.
[4]. S. Yagihara, M. Oyama, A. Inoue, M. Asano, S. Sudo and N. Shinyashiki, *Meas. Sci. Technol*. **18**, pp. 983–990, 2007.

Scanning of the hydrogen bond network of hydrated elastin by dielectric spectroscopy

D. Tintar, V. Samouillan, J. Dandurand, I. Bocchichio and C. Lacabanne
[1]Polymer Physic, CIRIMAT UMR5085, Institut Carnot, Université de Toulouse, France
[2]Department of Chemistry, University of Basilicata, Potenza, Italy.
*Email address: vsamou@cict.fr

The biological function of many proteins is strongly correlated to the existence of a hydration shell, but the complete understanding of the underlying coupling of protein and water motions is still lacking. So it is of peculiar interest to study the temperature dependence of proteins and water dynamics, in particular trough the protein dynamic transition at about 200K, which was found to be related to a freezing of biological functions[1]. We used dielectric spectroscopy, a well-suited experimental method[2,3] to characterize the system elastin-water and elastin-based polypeptides/water in the low temperature range. Elastin is a main protein of connective tissues such as lung, arteries and skin, and the mechanism of elasticity of this hydrophobic and insoluble protein is still subject to debate. The global protein and some of its peculiar sequences were studied between 123 and 313 K in the $10^{-2}/10^{6}$ Hz range, at different hydrations levels. The influence of environment was also taken into account, changing pure deionised water by a trifluoroethanol-water mixture, known to induce folded structures in proteins. The relaxation maps of the different systems were established and the temperature dependence of the two modes β_1 and β_2 was found to be Arrhenius-like, with a direct proportionality between β_1 and β_2, for elastin hydrated at 50% (cf. figure 1.). The elastin dynamics are “slaved” by water dynamics[4]. The first analysis of the temperature dependence of associated relaxation times gives an insight into the mutual localized dynamics of solvents and peptides, trough the dynamics of the associated hydrogen bonds network of these systems.

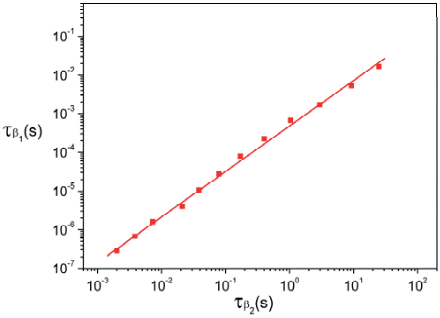


Fig.1. Relaxation time $\tau\beta_1$ plotted versus relaxation time$\tau\beta_2$ for elastin containing 50% of water in weight

References

[1] S.A. Lusceac, M. Vogel, C.R. Herbers, cond-mat.soft arXiv:0904.4424v1 (2009)
[2] S. Cerveny, A. Alegria, J. Colmenero, Phys. Rev. E. 77, 031803 (2008)
[3] S. Khodadadi, S. Pawlus, A.P. Sokolov, J. Phys. Chem. B 112, 14273 (2008)
[4] P.W. Fennimore, H. Frauenfelder, B.H. McMahon, R.D. Young, Proc. Natl. Acad. Sci. 101, 14408 (2004)

Detection of Amyloid Precursors by Dielectric Relaxation Spectroscopy

I. Stroe[1*], D. Barry[1], F. Prifti[1]
[1]Worcester Polytechnic Institute, Department of Physics, 100 Institute Road, Worcester MA, 01609,USA
*Email address: izabela@wpi.edu

Recent clinical and experimental evidence suggest that the occurrence of amyloid deposits in Alzheimer's disease (AD) could actually be a defense mechanism employed to avoid serious tissue degradation while the major toxic effects to cells are mediated by preamyloid oligomers[1,2]. Therefore, detection of preamyloid oligomers is crucial for treating, preventing, and inhibiting the progression of these devastating diseases. Recent work shows that amyloidogenic peptides associate to form oligomers through long-range hydrophobic attractions[3]. When peptides aggregate in larger composites, their hydrophobic patches are buried inside the newly formed amyloidogenic assembly. This gradually changes the interaction with the surrounding water molecules. Dielectric relaxation spectroscopy is a very sensitive technique to detect such changes. By using this method we can assess the dielectric relaxation (DR) signal of the interface water and differentiate between various amyloidogenic molecular structures. We measured the dielectric permittivity of amyloidogenic and non-amyloidogenic peptides as a function of frequency, concentration and incubation time. We compared our DR results with data obtained from transmission electron microscopy and immunochemistry assays[4] to test the molecular structures associated with the measured dielectric signal. Our preliminary work shows that structural transitions from monomers to oligomers and to protofibrils shift the DR signal toward the DR signal of bulk-like water. This is in agreement with recent theoretical and computational results.

References

[1] S. Baglioni,F. Cassamenti, M. Bucciantini, L.M. Luheshi, N. Taddei, H. Benveniste, G. Einstein, K.R. Kim, C. Hulette, G.A. Johnson. Proc. Natl. Acad. Sci. 96, 14079 (1999).
[2] C. Haas, D. J. Selkoe. Nat. Rev. Mol. Cell Biol. 8, 101 (2007).
[3] F. Despa, A. Fernandez, R.L. Scott, R.S. Berry. J. Biol. Phys 34, 577 (2008).
[4] F. Despa, J. H. Walton, S. E. Anderson, S.I. Despa, J. R. Groza and R. S. Berry. Amyloid 2010.

Dielectric Relaxation study of Biomolecules using Time Domain Reflectometry (TDR) technique

R. B. Talware*, **P. G. Hudge, and A. C. Kumbharkhane**+
School of Physical Sciences, Swami Ramanand Teerth Marathwada University,
Nanded – 431 606, India
*Email address: ravindratalware@yahoo.co.in
+Email address: akumbharkhane@yahoo.co.in

Dielectric dispersion in the systems of amino acids, peptides and proteins in aqueous media has received considerable attention[1]. The study of dielectric relaxation of amino acid in water mixture may reveal details about their interaction with water. Mostly all of the amino acids in cells are dissolved in aqueous region of the cell. The complex permittivity of biomolecules in water mixture for various temperatures and concentrations have been measured as a function of frequency between 10 MHz to 30 GHz using time domain reflectometry (TDR)[2] technique. Dielectric parameters i.e. static dielectric constant and relaxation time were obtained from the complex permittivity spectra using nonlinear square fit method. From the values of relaxation time, thermodynamic parameters were determined.

References

[1] M. P. Lokhande, S. Muzumdar, S. C. Mehrotra, Indian Journal of Biochemistry & Biophysics, 34, 385-390 (1997).
[2] A.C. Kumbharkhane, S. M. Puranik, S. C. Mehrotra, J. Chem. Soc., 87(10), 1569 (1991).

6TH INTERNATIONAL CONFERENCE ON
BROADBAND DIELECTRIC
SPECTROSCOPY AND ITS APPLICATIONS

www.dielectric2010.com
07 - 10 MADRID
SEPTEMBER 2010

Nanoconfined systems (I)

Wednesday 8/Sept
Room A

9:00 - 9:30	**F. Kremer**
9:30 - 9:45	S. Napolitano
9:45 - 10:00	K. H. Nguyen
10:00 - 10:15	K. Verkhovskaya
10:15 - 10:30	C. Rotella
10:30 -11:00	**K. Fukao**

Dielectric relaxations at nanometric length-scales

F. Kremer, E.Mapesa, M.Tress and A. Serghei*
University of Leipzig, Germany, Amherst

Broadband Dielectric Spectroscopy (BDS) as one of the maior tools in studying molecular dynamics benefits from the extraordinary advantage that its sensitivity increases with decreasing thickness of a sample capacitor and hence with a decreasing amount of sample material. By use of refined preparation techniques and with novel nanostructured electrodes it is possible to avoid the (conventional) evaporation of a metal counterelectrode onto the polymerlayer. This enables one to analyse the molecular dynamics of polymerlayers being *thinner than 5 nm* and poviding usually no full coverage of the underlying surface. Even measurements of the dynamics of *quasi-isolated* polymer coils are possible. This is demonstrated for a variety of polymers in a wide spectral range (10^{-2}Hz – 10^{6}Hz) and at temperatures between 150 K to 350 K. Furthermore ellipsometric and AC-calorimetric studies are encluded. The results are analysed and discussed within the framework of the physical understanding of the dynamic glass transition.

Adsorption and deviations from bulk behavior, from dead to self-accelerated layers

S. Napolitano *, **M. Wübbenhorst**

Laboratory for Acoustics and Thermal Physics, Department of Physics and Astronomy,
Katholieke Universiteit Leuven, Celestijnenlaan 200D, B-3001 Leuven, Belgium

*Email address: simone.napolitano@fys.kuleuven.be

A large number of experimental works highlighted how properties of ultrathin polymer films depend on the annealing conditions used during their preparations. We show clear evidences that the changes ultrathin films undergo during annealing are strongly correlated to the amount of chains irreversibly adsorbed at the interface. A careful analysis of the time evolution of the dielectric function during annealing step above T_g revelead three different regimes: at short times the thickness of the adsorbed layer is constant and the interface mimics the effects of a free surface; when the vacant sites start to be filled by new chains the films undergo a series of metastable states characterized by the largest changes in the deviations from bulk behavior; finally the system approach a new equilibrium whose properties are fixed by the new interfacial configurations.

Finally, we add more evidence on the unusual confinement effects of poly(tert-butylstyrene)[1]. Differently from polystyrene, below 50 nm, both the glass transition temperature and the thermal expansion coefficients decreased. Such a mixed behavior implies an enhancement of the molecular mobility, without the presence of any free surface, but dead layers. On the basis of a careful analysis of averaged quantities, measured by capacitive dilatometry, we deduced a profile of thermal expansivity that explains our experimental data and previous observations in polymer nanocomposites. The effect of density-conformation coupling in proximity of a non-attractive interface allows the coexistence of an immobilized fraction in contact with the metal and an excess of thermal expansivity, arising from the long range effects of packing frustration penetrating inside the bulk-like core of the film.

[1] S. Napolitano, A. Pilleri, P.Rolla, M. Wübbenhorst, ACS Nano 4(2), 841-848 (2010).

Relaxation dynamics of ultrathin polymer films investigated on the nanoscale by local dielectric spectroscopy

K. H. Nguyen[1]*, **D. Prevosto**[2], **M. Labardi**[2], **S. Capaccioli** [1,2], **M. Lucchesi**[1,2], **P.A. Rolla**[1,2]
[1] Dipartimento di Fisica, Università di Pisa, Largo Pontecorvo 3, 56127 Pisa, Italy
[2] Istituto per i Processi Chimico-Fisici, CNR, Largo Pontecorvo 3, 56127 Pisa, Italy
*Email address: nguyen@df.unipi.it

The dielectric relaxation of ultrathin polymer films has been investigated effectively by several techniques and most of them were used to measure relaxation properties on macroscopic regions of the sample. A possible approach to obtain highly local measurements of dielectric properties of ultrathin films is the local dielectric spectroscopy[1]. This technique has been implemented by means of an atomic force microscope (AFM)-based method named frequency-modulated electrostatic force microscopy[2]. In essence, an excitation voltage, $V(t) = V_{AC} \cos(\omega t)$, is applied to the conductive tip of an AFM, inducing a variation of the tip resonant frequency, which is proportional to the gradient of the electrostatic force between the tip and the sample. This variation at the second harmonic, 2ω, is measured in amplitude and phase by using dual-phase lock-in technique locked at the excitation voltage. In particular, the phase angle, δ_v, is related to the dielectric relaxation properties of the sample.

This method has been applied to study the change in dynamics of ultrathin poly(vinyl acetate) films as the film thickness is decreased. Dielectric loss spectra were obtained as a function of frequency at different temperatures in controlled atmosphere (relative humidity less than 5%) (Fig. 1). The influence of the polymer molecular weight on the dielectric relaxation of the films was also investigated.

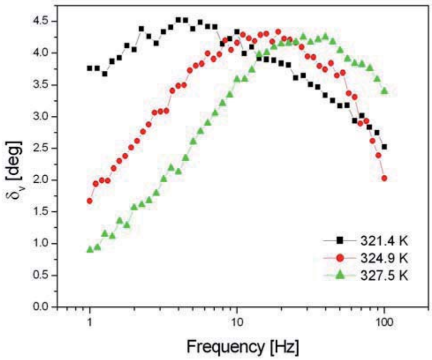


Fig. 1 Frequency dependence of the phase angle δ_v at different temperatures for a 55 nm ultrathin film of poly(vinyl acetate).

References

[1] P.S. Crider, M.R. Majewski, J. Zhang, H. Oukris, N.E. Israeloff, Appl. Phys. Lett. 91, 013102 (2007).
[2] J. Colchero, A. Gil, A.M. Baró, Phys. Rev. B 64, 245403 (2001).

DIELECTRIC RELAXATION SPECTRA IN ULTRATHIN FERROELECTRIC POLYMER FILMS AND NANOCRYSTALS

K.Verkhovskaya[1], A.Plakseev[1], A.Lotonov[2] and N. Gavrilova[2]

[1] Shubnikov Institute of Crystallography, Russian Academy of Sciences, Leninskii pr. 59, Mosco
119333, Russia
[2] Lomonosov Moscow State University, Moscow, Russia
e-mail: kira@crys.ras.ru

In 1995 the first ultrathin ferroelectric Langmuir-Blodgett (LB) films were prepared from copolymer vinylidenefluoride with trifluoroethylene P(VDF/TrFE) [1]. The first nanocrystals of copolymer P(VDF/TrFE) were prepared in [2].

In the present work dynamic dielectric measurements were carried out for LB films (1-2 monolayes) of copolymer P(VDF/TrFE) 70/30 over the frequency range 10^{-1}-$2\cdot10^{7}$ Hz for tempera interval 25-130°C. The observed dielectric relaxation follows the Debye-type frequency depend of ε* for ultrathin LB films. The mean relaxation time τ was obtained from the ε'' peak frequenc ($\tau = 1/2\pi f_m$, $f_m = 5\cdot10^5$ Hz, $\tau = 3\cdot10^{-7}$ s). Since the dipoles are rigidly attached perpendicular to polymer chain, the dipole motion is caused by the rotation of chain molecules. The new observa for ultrathin LB film 2nm thick is the appearance of second relaxation maximum ε'' at the freque $f = 5\cdot10^3$ Hz in paraelectric phase at $T = 110^0$C (Fig.). These two maxima of ε'' exist during coolin the region of temperature hysteresis, where the coexistance of ferroelectric and paraelectric phases takes place. The one maximum appears again in ferroelectric phase. We assumed, that the medium polarization of Maxwell-Wagner type exists at phase transition due to injection of charge carriers f electrodes and accumulation of carriers on the boundaries in inhomogeneous medium, connected the coexistence of two phases.

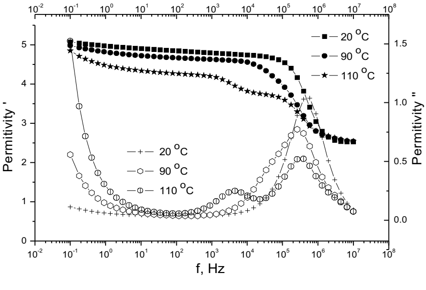


Fig. Frequency dependences of ε′ and ε″ for a P(VDF-TrFE) (70/30) film with thickness 2 nm for differe temperatures upon heating.

The phase transition in nanocrystals has not been studied previously. This transition was observed by the dielectric dispersion method.The character of frequency dependences of ε' and ε' nanocrystals exhibits changes at 100^0C. The another relaxation maximum of ε'' appears at $f = 3\cdot10^3$ Thus for nanocrystals the temperature of phase transition is equal to 100^0C.

Acknowledgment. This work was supported by Russian Foundation for Basic Research (Grant 09 -02-00096)

References

1. S. Palto, L. Blinov, K. Verkhovskaya, et al. Ferroelectrics Letters, 19, 65 (1995).
2. M. Bai and S. Ducharme, Appl. Phys. Lett., 85, 16 (2004).

Dielectric relaxation spectroscopy signature of polymer adsorption at a solid surface

Cinzia Rotella, **Simone Napolitano**, **Michael Wübbenhorst**
Katholieke Universiteit Leuven, Laboratory of Acoustics and Thermal Physics, Department of Physics and Astronomy, Leuven, Belgium
cinzia.rotella@fys.kuleuven.be

upported thin polymer layers are important for many applications such as microelectronics, anocomposites or biomedical devices. In particular, the interaction between the polymer layer and th olid surface is critical and alters the effective properties of the layer, as evidenced by the variations of th lass transition temperature (T_g). What is still unclear is how adsorbed chain segments modify th ynamics of the whole system.

ere, we investigate polymers adsorbed at surfaces by dielectric relaxation spectroscopy (DRS), which i powerful technique to study glass transition dynamics and local relaxation processes in ultrathin olymer films. We used ultrathin films of neat polystyrene (PS) as well as PS labelled with the highl olar dye molecule "*disperse red 1*" at a concentration in the order of 1 – 2 %. For both kinds c olymers, we prepared 25 nm thin films that were capped between aluminium electrodes. Subsequentl e performed isothermal time-resolved dielectric measurements, for at least 20 h and well above T_g (12 C – 145 °C). In the case of the labelled polymer, we observe during annealing a tremendous decrease c e dielectric strength $\Delta\varepsilon_\alpha$ accompanied by a systematic increase of the structural relaxation time $_\alpha$ (Fig.1). Analogous experiments on neat PS of same molecular weight did not reveal such an effect o quivalent timescales. In relation with the different attraction strengths of both polymers with the surfac e propose the following scenario. The reduction of $\Delta\varepsilon_\alpha$ originates from a specific interaction betwee e labelled PS and the Al substrate, taking place through an immobilization mechanism of the dye oieties at the metal surface. The polar groups of the labelled PS could physisorb onto the aluminiu urface and form an interface containing strongly adsorbed moieties. The adsorption must proceed vi ansport of the dye molecules trough the film, which occurs by sub-chain diffusion. In addition, th crease of the structural relaxation time indicates a slow down of the overall molecular mobility veraged over the thickness. Extensive studies performed with various multilayer systems support the vidence of the adsorption process.

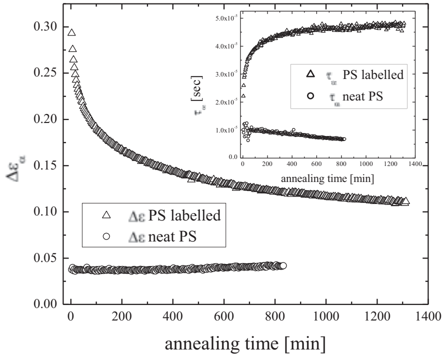


Fig.1. Temporal dependence of the dielectric strength $\Delta\varepsilon_\alpha$ and relaxation time τ_α (inset) for 25 nm thick films of neat PS and PS labelled. Data were obtained fitting dielectric spectra recorded during annealing at 140 °C.

Glass transition dynamics of single and stacked thin films of polymers

K. Fukao*, **Y. Oda, T. Terasawa, K. Nakamura, D. Tahara**
Department of Physics, Ritsumeikan University, Kusatsu 525-8577, Japan
*Email address: fukao.koji@gmail.com

Recent investigations revealed that T_g of thin polymer films decreases with decreasing film thickness in many cases[1]. As the physical origins for the depression of the T_g, there are some candidates such as surface or interfacial effects[2], and confinement effects in thin film geometry. It has been reported recently that stacked thin polymer films exhibit the glass transition behavior typical both of the ultra thin polymer film and of the bulk system depending on the annealing conditions[3]. This might give us the possibility of controlling the interfacial interaction between ultra thin polymer layers on the T_g. In this study, we have investigated the glass transition behavior of single thin films and stacked thin films of poly(2-chlorostyrene)(P2CS) by dielectric relaxation spectroscopy in order to investigate the effect of the interfacial interaction between polymer layers on the glass transition behavior.

Fig.1 shows the thickness dependence of T_g of single thin films of P2CS together with T_g of the stacked thin films. The thickness of the stacked films in Fig.1 is that of each layer in stacked films. In Fig.1 T_g of the stacked films annealed at 120C is about 10K lower than that of the corresponding single thin film and it increases during annealing process. In the case of PS thin films, it has been reported that the magnitude of the depression of T_g of the freely standing films is by about 50 K larger than that of the supported thin films[4]. If the magnitude of the depression of T_g of the freely-standing thin films of P2CS can obey the same law for PS, it is concluded that the T_g of the stacked thin films of P2CS is located between the supported single thin films and the freely standing films. This result is consistent with the results observed for PS stacked thin films[3]. Furthermore, we can expect that T_g of the stacked thin films should approach the bulk T_g with further annealing. In order to check the expectation, we have monitored the time evolution of the dielectric spectra during the isothermal annealing at a given temperature T_a. The initial state of the sample was stacked films of 10 thin layers that have experienced the thermal history of only one cycle of heating and cooling between 0°C and 152°C at a rate of 1K/min. The results observed during the isothermal annealing will be presented in the presentation.

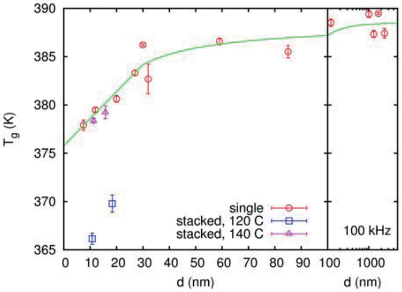


Fig.1: thickness dependence of Tg for single thin films and stacked thin films of P2CS, The stacked films are annealed at 120C or 140C for 2 hours.

References

[1] J.Keddie, R.A.L.Jones, R.A.Cory, Europhys. Lett. **27**, 59-64 (1994).
[2] T.Kajiyama et al., Macromolecules, **27**, 7932 (1994).
[3] P. K.Yung et al., J. Polym. Sci.,Part B: Polym. Phys. **44,** (2006) 3518-3527.
[4] J.A.Forrest, K.Dalnoki-Veress, J.R.Stevens, J.R.Dutcher, Phys. Rev. Lett. **77**, (1996) 2002-2005.

Hydrogen Bonded - Aqueous Materials (I)

Wednesday 8/Sept
Room B

9:00 - 9:30	**C. M. Roland**
9:30 - 9:45	R. Nozaki
9:45 - 10:00	R. Casalini
10:00 - 10:15	J. Bartos
10:15 - 10:30	K. Kaminski
10:30 - 10:45	R. Pelster
10:45 - 11:00	Z. Chen

Dynamic heterogeneity and relaxation properties of supercooled liquids

C.M. Roland[1*], D. Fragiadakis[1], R. Casalini[1], K.L. Ngai[1], and S. Capaccioli[2]
[1]Naval Research Lab, Washington, DC 20375-5342, USA
[2]Universita di Pisa, Largo B. Pontecorvo 3, 56127, Pisa, Italy
*Email address: roland@nrl.navy.mil

Molecules in a dense liquid exert reciprocal influences, and these correlated, many-body interactions are a distinguishing feature of the supercooled dynamics. We determined the number of dynamically correlated molecules, N_c, as a function of temperature and pressure from derivatives of the linear dielectric response function[1,2] and (for polymers) from intersection of the normal mode and segmental relaxation times.[3,4] The various methods of obtaining N_c are compared. We find that N_c depends only on the magnitude of the relaxation time, τ_α, independently of T and P, a result consistent with the invariance of the shape of the relaxation dispersion at constant τ_α; that is, both the distribution of relaxation times (reflected in the Kohlrausch-William-Watts β) and the spatial extent of the fluctuations transpiring over a time scale $\approx \tau_\alpha$ are determined entirely by the magnitude of τ_α.[5,6] Furthermore, since N_c and β both reflect dynamic heterogeneity, these two quantities are expected to be approximately (inversely) correlated; however, this expectation is not borne out by the data. As shown in Figure 1, any correlation is weak or non-existent (R = -0.32), notwithstanding the connection of β to many relaxation properties and the fact that various phenomena (e.g., rotation-translation decoupling and confinement effects on τ_α) have been ascribed to dynamic heterogeneity. Evidently the mapping of correlation volumes to correlation times is quite chemical structure dependent.

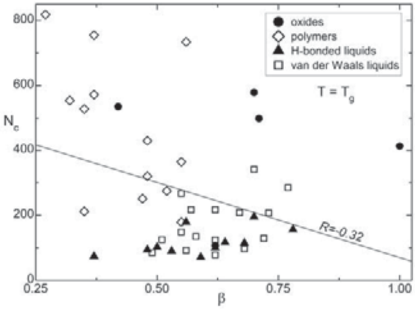


Fig.1. Number of dynamically correlated molecules *versus* the KWW exponent for the α-dispersion in the dielectric loss. Data from ref. [2].

References

[1] L. Berthier, G. Biroli, J.P. Bouchard, L. Cipelletti, D. El Masri, D. L'Hote, F. Ladieu, M. Pierno. Science 310, 1797 (2005).
[2] S. Capaccioli, G. Ruocco, F. Zamponi. J. Phys. Chem. B 112, 10652 (2009).
[3] A. Schönhals, E. Schlosser. Physica Scripta, T49A, 233 (1993).
[4] C. Gainaru, W. Hiller, R. Böhmer. Macromolecules 43, 19078 (2010).
[5] D. Fragiadakis, R. Casalini, C.M. Roland. J. Phys. Chem. B 113, 13134 (2009).
[6] D. Coslovich, C.M. Roland. J. Chem. Phys. 130, 014508 (2009).

Dielectric spectroscopy of alcohols up to 2.5THz

Y. Yomogida, R. Nozaki[*]
Department of Physics, Faculty of Science, Hokkaido University, Sapporo 060-0810, Japan
*Email address: nozaki@dielectrics.sci.hokudai.ac.jp

Dielectric response of hydrogen-bonding liquids is quite different from that of usual ones like simple polar liquids or their dilute solutions in non-polar solvents. According to many investigations so far, water and some alcohols with one or two hydroxyl groups (OH) show a Debye-type dielectric relaxation with relatively large relaxation strength, so called the primary process, and the secondary process with small strength in the high-frequency side of the primary process. This feature is very common for many materials even with different chemical structure such as 1-alcohols, 2-alcohols and diols. However, origins of the processes are still under discussion because of some complicated situations. One of the example is that 1-alcohols and corresponding diols have almost the same dielectric relaxation time at room temperature, however, the values of viscosity for them are much different[1]. On the other hand, polyhydric alcohols like glycerol and sorbitol easily undergo supercooled liquid. It is well known that most of the supercooled polar liquids show the structural alpha relaxation process and the secondary beta process. Since the alpha process is continuously connected to the "primary" relaxation observed in the high temperature liquid state, it has long been considered that the alpha process is essentially the same as the primary process. However, there are many different characteristics between the two processes. Recently, we have reported that the supercooled sugar alcohols show an ultra-slow process below the alpha relaxation frequency[2]. Although relation between the ultra-slow and the primary processes is of great interest from the point of understanding the primary process, we still don' t have enough information to consider that in detail. Why do we have these problems to understand dielectric relaxation processes observed in the hydrogen-bonding liquids? One of the reasons is considered to be that these processes have too much "universality" among different materials. Recently, we have demonstrated that THz dielectric response of alcohols, which has not been well investigated so far, is very sensitive if compared to the response blow microwave frequency range[3-5]. 1-alcohols and its isomers, and corresponding diols show a common feature in dielectric behavior in the frequency range of 0.2-2.5THz: (i) the high-frequency side of dielectric relaxation processes, (ii) the broad vibration mode around 1-1.5THz, (iii) the low-frequency tail of an intermolecular stretching mode located above 2.5THz. Behavior of the broad vibration mode observed in alcohols is very sensitive to the molecular structure even appearance of the relaxations below 20GHz is not. Since this broad vibration mode is considered to be strongly connected to the local molecular dynamics only with several molecules, which is coupled with the elementally relaxation process, careful comparison of the mode among many alcohols gives us useful information to understand all the dielectric relaxation processes of hydrogen-bonding liquids.

References

[1] Y. Yomogida and R. Nozaki, AIP conference Proceedings, CP982, 350 (2008).
[2] Y. Yomogida et al., Phys. Rev. E, 73, 041510-1 (2006).
[3] Y. Yomogida et al., Physica B (2010) in press.
[4] Y. Yomogida et al., J. Mol. Struct., accepted.
[5] Y. Yomogida et al., J. Mol. Liqs., accepted.

Insights On The Origin Of The Debye Process In Monoalcohols From Dielectric Spectroscopy Under Extreme Pressure Conditions

D. Fragiadakis, C.M. Roland and R. Casalini

Chemistry Division, Naval Research Laboratory, Washington DC

The dielectric spectra of most simple liquids are characterized by two relaxation processes: (i) the α-process, an intense, broad non-Debye relaxation with a non-Arrhenius temperature dependence and (ii) a β–process, evidently mainly below the glass transition and having a nearly Arrhenius temperature behavior. However, the dielectric spectra of monoalcohols show three processes, two that resemble those of normal liquids, and a third very intense Debye peak at lower frequencies, which is non-Arrhenius. Interestingly, this third process is not observed with other techniques, such as light scattering and mechanical spectroscopy. There is disagreement in the literature concerning the nature of this third relaxation. We investigated 2-ethyl-1-hexanol under high pressures (up to ~1.4GPa) over a broad range of temperatures. The Debye process, which is the slowest, is strongly affected by pressure. At higher pressures the relaxation times and intensities of the two non-Arrhenius relaxation become nearly equal. In light of these results, we propose a modified interpretation of the relaxation processes and their underlying structures in monoalcohols.

On the mutual relationships between atomistic and molecular probe dynamics and broad-band dielectric spectroscopy

J Bartoš[1*], H.Švajdlenková[1], O.Šauša[2], J.Krištiak[2], P.Lunkenheimer[3], A.Loidl[3]
[1]Polymer Institute of the Slovak Academy of Sciences, Dúbravská cesta 9,
842 36 Bratislava, Slovak Republic
[2]Institute of Physics of the Slovak Academy of Sciences, Dúbravská cesta 9,
842 28 Bratislava, Slovak Republic
[3]Experimental Physics V, Center for Electronic Correlations and Magnetism,
University of Augsburg, 861 35 Augsburg, Germany
*Email address: upolbrts@savba.sk

We present a combined study of the local free volume and rotational dynamics in prototypical strong and fragile glass-formers *glycerol (GL)* and *propylene carbonate* (*Pc*) by means of the two probe techniques in relation to broadband dielectric spectroscopy (BDS). The atomistic probe method is based on the annihilation behavior of the ortho-positronium (o-Ps) probe as measured by positron annihilation lifetime spectroscopy (PALS). The molecular probe one consists in using the smallest spin probe of nitroxide type:*2,2,6,6-tetramethyl-1-piperidinyloxy* (*TEMPO)* investigated by electron spin resonance spectroscopy (ESR). First, the o-Ps lifetime, τ_3, and the extracted free volume parameter,V_h, are compared with the reorientation dynamics of the *TEMPO* probe as quantified by the spectral parameter of mobility, $2A_{zz}$, and the correlation time, τ_c. Next, both the PALS and ESR responses are closely correlated with the dipolar relaxation dynamics of *GL* and *Pc* as obtained from the detailed BDS studies[1].

In the case of strong *glycerol*, three distinct regions of the *TEMPO* rotation dynamics can be found: the two ones within the slow motional regime with an acceleration crossover at the characteristic ESR temperature, T_{X1}, which coincides with the characteristic PALS temperature, T_{b1}. Both these crossovers are related to an influence of the secondary β process in the supercooled liquid state *above* T_g. Next, the slow to fast regime transition occurs at the characteristic ESR temperature, $T_c \sim T_{50G}$, which is again close to the characteristic PALS temperature, T_{b2}, being related to the primary α process in *GL*. In the fast motional regime, a close coupling between the spin probe reorientation process with the primary α relaxation in the liquid *GL* occurs.

In contrast, for fragile *Pc*, two different regions of reorientation dynamics of the *TEMPO* were found. The slow to fast regime transition at the characteristic temperature, $T_c \sim T_{50G}$, being close to the characteristic PALS temperature, T_{b2}, is connected with the primary α process in *Pc*. In the fast motional regime, the spin probe reorientation process is closely coupled to the structural relaxation of the *propylene carbonate* liquid.

Finally, for both small molecule glass-formers it was revealed that the slow to fast regime transition at the spectral temperature, T_{50G}, is connected with the o-Ps lifetime, $\tau_3(T_{50G}) = 2.2\pm0.1$ ns which is in agreement with the empirical finding of $\tau_3(T_{50G}) = 2.14\pm0.08$ ns discovered previously for the same spin probe in a series of amorphous polymers[2]. It means that the slow to fast crossover is independent of the topological (small molecule vs. polymer) and chemical (interparticle-bonding) structure of the glass formers and is connected with the local free volume fluctuation of about 117±9Å^3.

References

[1] P. Lunkenheimer, U. Schneider, R. Brand, A. Loidl: Contemp. Phys. 41, 15 (2000).
[2] J. Bartoš, Z. Hloušková: Polymer 34(21), 4570 (1993).

Dynamic of the clusters in monosaccharides followed by dielectric spectroscopy

<u>K. Kaminski</u>[1]*, K. Adrjanowicz, Z Wojnarowska, P. Wlodarczyk, K. Grzybowska, R. Wrzalik, M. Paluch

[1] *Institute of Physics, University of Silesia., ul. Uniwersytecka 4, 40-007 Katowice, Poland*

*Email address: kaminski@us.edu.pl

Dielectric and FTIR measurements were performed on six carbon monosaccharides in thier supercooled liquid phase. Surprisingly except structural relaxation we found much slower relaxation mode. Analysis of the dielectric data indicated that this new mode reveals characteristic features of the cluster relaxation, i.e. exponential relaxation function of this process, equilibration time much longer than the relaxation time. Therefore we attributed this process to the Long Range Correlations of Density Fluctuations (LRCDF). We also show that above T=370 K dielectric strength of the cluster relaxation in D- glucose start to decrease very quickly. On the other hand FTIR measurements indicated that at T=366 K reorganization of liquid structure occurs. Combined dielectric and FTIR data indicated that above T=366 K clusters become less stable and probably being destroyed in this particular saccharide. Moreover we determined splitting temperature T_s=387 K from dielectric data which corresponds very well to the temperature T=385 K at which change of dynamics of hydroxyl group (hydrogen bonds) can be seen. One can anticipate that change of dynamics of the D-glucose (at T_s) is related to the temperature at which LRCDF vanishes. It should be added that in the best our knowledge it is first dielectric study on dynamics of the clusters in carbohydrates. Finally our study completes whole relaxation map of the monosaccharides.

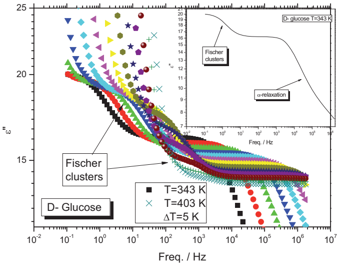


Fig 1

Crystallization and induced glass transition of n-alcohols confined in silicon-nanochannels

R. Pelster*, **R. Berwanger, Ch. Schumacher**
FR 7.2 Experimentalphysik, Universität des Saarlandes, D-66123 Saarbrücken, Germany
*Email address: rolf.pelster@mx.uni-saarland.de

We have investigated the molecular dynamics of n-alcohols (C_4H_9OH - $C_{11}H_{23}OH$) confined in mesoporous silicon and silicon oxide. For this purpose, silicon wavers were electrochemically etched resulting in the formation of approximately parallel nano-channels. The procedure allows us to vary the pore dimensions in a well-defined way. The mesoporous samples can be easily filled with alcohols. Using dielectric and infrared spectroscopy we show, that the temperature of the liquid-solid phase transition and the structure of the solid phase depend on both the chain length and the radius of the pores (r= 3.5 nm – 7 nm):

Long-chain alcohols exhibit a crystalline structure at low temperatures[1]. The confinement induces a lowering of the freezing temperature T_{fr}. The shorter the chain length or the smaller the pore radius, the lower $T_{fr.}$ Below the phase transition only the dynamics of amorphous wall layers are observable.

Short-chain alcohols behave differently. While bulk alcohols still freeze upon slow cooling, we observe a glass transition for the confined phase. The glass transition temperature is close to that reported for quenched bulk alcohols.

We thus conclude that nano-confinement suppresses the crystallization process and induces a glass transition.

References

[1] R. Berwanger, A. Henschel, P. Huber, K. Knorr, R. Pelster, Phys. Rev. B, 79, 125442 (2009).

Phase transition of 5CB/DDAB/Water microemulsion as a function of temperature and time: detected by dielectric spectroscopy

Z. Chen*, R. Nozaki
Dielectrics Laboratory, Department of Physics, Faculty of Science, Hokkaido University, 060-0810 Sapporo, Japan
*Email address: czdrs2006@hotmail.com

In a recent report[1], 5CB/DDAB/Water inverse microemulsion exhibits intriguing phase transition, during which a new superstructure called "Transparent Nematic (TN) phase" shows up. However, it is argued[2,3] that this phase transition is a simple phase demixing due to paranematic fluctuation, which contradicts the notion of TN phase. Since dielectric spectroscopy is sensitive to dipolar motions on different length scales, dielectric study on the phase transition can provide information on this controversy.

In this study, we performed the dielectric measurement on 5CB/DDAB/Water microemulsion as functions of temperature and time. The temperature dependence of its dielectric behavior is shown in Fig.1 (a), which is turned out to be the result of phase transition with temperature. In addition to relaxations of bulk-like 5CB, a new relaxation was observed in lower frequency range. The relaxation intensity of this new relaxation is enormously increased in the vicinity of phase transition temperature, and its relaxation time shows nonmonotonic temperature dependence. On the other hand, since the isotropic-nematic phase transition is companied by phase demixing and diffusion of water droplets, we believe the phase transition is also time dependent. At fixed temperature close to transition temperature, the dielectric behavior of the system varies obviously with time, as shown in Fig.1 (b). The result indicates a complete exclusion of isotropic phase from nematic phase. Interestingly, even when isotropic phase has been totally excluded, the new relaxation is still present in the nearly "pure" nematic phase, which hints a superstructure composed by water droplets and 5CB.

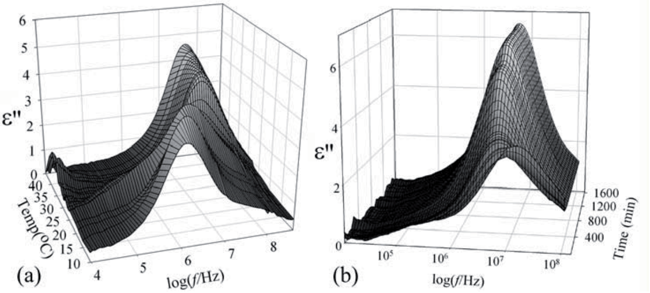


Fig.1. 3D plots of dielectric loss spectra at different temperature (a) and time (b).

References

[1] J. Yamamoto and H. Tanaka, Nature (London) 321, 409 (2001).
[2] T. Bellini, M. Caggioni, *et al.*, Phys. Rev. Lett. 085704, 91 (2003).
[3] M. Caggioni, A. Giacometti, *et al.*, J. Chem. Phys. 214721, 122 (2005)

Hydrogen Bonded
-
Aqueous Materials
(II)

Wednesday 8/Sept
Room A

15:30 - 16:00	**M. Wubbenhorst**
16:00 - 16:15	M. Dionisio
16:15 - 16:30	E. Dantras
16:30 - 16:45	S. Ancherbak
16:45 - 17:00	M. C. Lanca
17:00 - 17:15	A. V. Adejanov

Dynamics in H-bonding glass forming liquids: From ultrathin films to ultrastable glasses

M.Wübbenhorst[1], S. Capponi[1], S. Napolitano[1], S. Rozanski[1], G. Couderc[2], Norwid-Rasmus Behrnd[2], Jürg Hulliger[2]

[1]Department of Physics and Astronomy, Katholieke Universiteit Leuven,
Celestijnenlaan 200D, Leuven, 3001, Belgium.

[2]Department of Chemistry and Biochemistry, University of Berne, Freiestr. 3, 3012
Berne, Switzerland.

*Email address: wubbenhorst@fys.kuleuven.be

Confinement effects on the glass transition have been widely studied in the past decade using various nanometer geometries and experimental techniques. This paper focuses on the dynamics of ultrathin films of glycerol and other members from the homologue series (threitol, xylitol and sorbitol) as studied by dielectric spectroscopy (DRS). Ultrathin films are produced by molecular beam deposition onto a glass substrate patterned with an interdigitated comb electrode (IDE), a configuration that allows the real-time study of the relaxation dynamics of the liquid films upon continuous variation of the film thickness by deposition or desorption.

Thin films of glycerol and threitol revealed a remarkable broadening of the relaxation time distribution of the structural relaxation (α-process) below 20nm, indicating enhanced mobility at the free surface coexisting with a slow molecules at the liquid/solid interface. For films below 3nm, slight up- or down shifts in the mean relaxation time were found, the actual trend particularly depending on the surface roughness.

For Xylitol, a qualitatively different picture was found: the relaxation dynamics in a thickness range from 1 – 50 nm revealed gradual changes of the relaxation pattern from bulk behaviour towards a full suppression of the α-process for the thinnest films. Below 5nm, a single Arrhenius-type relaxation could be observed, characterised by a remarkable dielectric strength and an increasing activation energy upon decreasing thickness.

Finally, the relaxation properties of various “ultrastable” glasses will be discussed in the context of dynamic heterogeneities and local order fluctuations in dense glasses.

Physico-Chemical and Dynamical Characterization of a Cellulose Acetate Membrane

M.Sousa[1], A. R. Brás[1], F. C. Ferreira[2], M. N. de Pinho[3], N. T. Correia[1], M. Dionísio[1]*

[1]REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa, 2829-516 Caparica, Portugal.
[2]Universidade Técnica de Lisboa, Instituto Superior Técnico, IBB/DQEB, 1049-001 Lisboa, Portugal
[3]Universidade Técnica de Lisboa, Instituto Superior Técnico, ICEMS/DQEB, 1049-001 Lisboa, Portugal

*Email address: madalena.dionisio@dq.fct.unl.pt

A comprehensive characterization of a cellulose acetate (CA) asymmetric membrane, with pore radius at the nanometer scale in the surface of the dense layer, is provided and compared with CA in the powder state. Several techniques (DSC, TGA, FTIR, SEM and DRS) have been used to gather information on the CA molecular organization, from which dielectric relaxation spectroscopy (DRS) plays a special relevance providing dynamical information. The role of the water is particularly highlighted.

DSC revealed that both materials have a low crystallinity degree. The CA membrane displayed a sharper melting endotherm, higher thermal stabilization (as seen by TGA) and a more resolved FTIR spectrum compared to CA powder, indicating a more ordered chain arrangement. Two sub-glass relaxation processes between 173 and 298 K in both membrane and powder were identified by DRS. The process detected at higher frequencies and lower temperatures (emerging even below 173 K) is significantly influenced by the water content, undergoing a plasticizing effect. Its mobility is enhanced in the polymer powder due to a looser structure of the material offering more internal sites to be accessible for water uptake: the water concent in CA powder is 2.7 % w/w against 1.6% w/w in the membrane. The pre-exponentail factor and activation energy are compatible with a local motion. It is concluded that both exocyclic groups and main chain oxygen atoms should be involved in this process in a coupled motion with water molecules.

The relaxation process that emerges later (198 K) is compatible with localized motions being similar for both CA powder and membrane; in opposition to the first process, it undergoes a slight anti-plasticizing effect with hydration. For both materials the two processes merge into a broad relaxation upon dehydration. In the membrane, this relaxation undergoes an intensity enhancement for temperatures higher than 353 K, clearly differentiating from the CA powder behavior, whose dielectric response instead reaches a plateau. This effect can be associated with a skin densification and partial collapse of the membrane porous network, as observed by SEM.

Acknowledgments: Financial support to Fundação para a Ciência e Tecnologia (FCT, Portugal) through the project PTDC/CTM/64288/2006 is acknowledged. A. R. Brás acknowledges FCT for a PhD grant SFRH/BD/23829/2005.

Dielectric analysis of water/polymer interactions: from synthetic to natural polymers

E. Dantras[1], F. Roig[1], N. Caussé[1], M. Chevalier[2], C. Tonon[2], P. Guigue[3], C. Puig[2], C. Durin[3], C. Lacabanne[1]

[1] Laboratoire de Physique des Polymères Institut Carnot CIRIMAT,
Université Paul Sabatier, Toulouse,
[2] Astrium, 31 avenue des Cosmonautes, Toulouse
[3] Centre National d'Etudes Spatiales, Toulouse
*Email address: dantras@cict.fr

Influence of water interactions on physical structure of polymers remains a wide issue for many domains of applications. This study tries to shed some light on this phenomenon and illustrates it thanks to two examples: polyepoxy and cellulose.

During spacecraft integration - in clean room - materials are used under humid and thermally controlled conditions. This approach is based on a simulated ageing of an epoxy-amine adhesive used in aluminium assemblies. We will focus on ground ageing (also called humid ageing). A peculiar attention has been devoted to the influence on the physical structure of accelerated testing conditions or real-time ageing. As the most common form of biomass, wood concentrates suddenly a high interest. The influence of hydration on cellulose molecular mobility has been investigated at different molecular scales.

In both examples, dielectric measurements were performed in a very broad temperature and frequency range. Thermo Stimulated Current (TSC) analyses combined with Dynamic Dielectric Spectroscopy (DDS) have been applied to the investigation of molecular mobility influenced by water interactions. Such investigations based on the analysis of relaxation times associated with molecular mobility involved in polymers and polymer/water complexes exhibit the major role of interactions.

In polyepoxy, a splitting of the relaxation mode associated with the glass transition is observed: The lower temperature component has been attributed to a plasticization of molecular mobility in the glassy state. The splitting is due to the heterogeneity of the amorphous phase of polyepoxy. In the rubbery state, the increase of localized molecular mobility has been assigned to the mobility of hydroxyether / water reorientations.

In cellulose, the α relaxation mode is significantly shifted towards lower temperatures. Such a relaxation is assigned to the delocalised cooperative mobility liberated at the glass transition. It is plasticized by water. The study of activated parameters deduced from Fractional Polarization procedure, shows a decrease of the activation enthalpy range upon hydration. This evolution has been assigned to an increase of hydrogen bonds density leading to a more extended cooperative motion.

Dynamics of aqueous mixtures at low T and high P

S. Ancherbak[1*], **S. Capaccioli**[1], **D. Prevosto**[1], **K. Grzybowska**[2], **M. Paluch**[2]
[1] CNR-IPCF & Physics Dept., Pisa University, Largo B. Pontecorvo 3, 56127 Pisa, Italy
[2] Institute of Physics, Silesian Univ., Ul. Uniwersytecka 4, 40-007 Katowice, Poland
*Email address: ancherbak@df.unipi.it

An easy way to study water in an amorphous state at very low temperature is to mix it with hydrophilic liquids[1]. We have performed broadband dielectric spectroscopy experiments on water mixed with saccharides (glucose, trehalose) and propylene glycol (PG) oligomers (n repeating units: n=1, 3, 7). We covered a dynamic interval from 0.1 μs to 1 ks, under a very wide temperature (T=100-350 K) and pressure (P=0.1 MPa-1.8 GPa) range. Glucose and trehalose were mixed in the range 15-30% of water weight fraction. As for the PG oligomers, we selected mixtures with two concentrations (4 and ~30 % wt. fraction of water) previously studied at ambient pressure[2]. All the systems with high concentration of water have shown a similar dynamic scenario, with two relaxation processes: a slower α-process, related to cooperative large scale motions of solute and water molecules, and a faster secondary ν-process, due to the local motions of water[1]. The relaxation time of ν-process shows a marked crossover (T_c), always occurring just below T_g, from a Vogel-Fulcher temperature behaviour to an Arrhenius one on cooling (see Fig.1). The same scenario is common to all the systems and also to all the different isobaric scans. High pressure experiments on water mixtures reveal a very general phenomenology: both glass transition and crossover temperatures, T_g and T_c, increase with pressure and a similar trend, at least below 1 GPa, is common to the activation energy of ν relaxation in the glassy state. The crossover time of ν-process, $\tau_\nu(T_c)$, becomes shorter with increasing pressure. As far as we know, this is the first systematic study on slow dynamics of aqueous systems under high pressure.

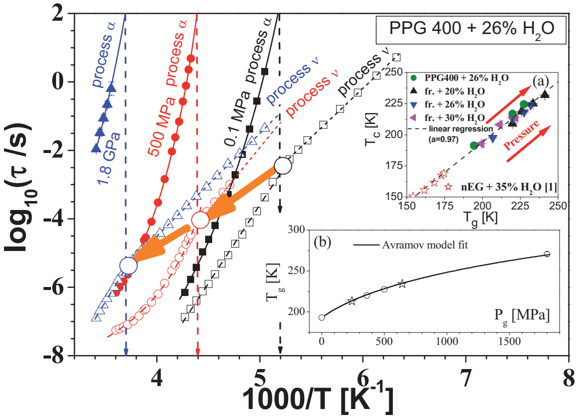


Fig.1. Selected isobaric scans for PPG400(n=7)+26% water mixture. Insets: a) correlation between T_c and T_g, b) T_g vs. P_g.

References

[1] S. Capaccioli, K. L. Ngai, N. Shinyashiki, J. Phys. Chem. B, 111, 8197 (2007).
[2] K. Grzybowska A. Grzybowski, S. Pawlus, S. Hensel-Bielowka, M. Paluch, J. Chem. Phys. 123, 204506 (2005).

Controlling the electrical and dielectric properties of a cork derivative and their relation to humidity

M. C. Lança[*1], **I. Cunha**[1], **J. P. Marques**[1], **E. R. Neagu**[1], **C. Dias**[1], **L.Gil**[2], **J. N. Marat-Mendes**[1]
[1]Cenimat/I3N, Departamento de Ciência dos Materiais, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal
[2] Laboratório Nacional de Energia e Geologia (LNEG), Est. do Paço do Lumiar, 22, 1649-038 Lisboa, Portugal
*Email address: carmo@dcm.fct.unl.pt

A composite of recycled cork and TetraPak® was developed at LNEG and possible applications are still under study. The study and understanding of the electrical and dielectrical properties may lead to applications in the area of sensors. The structure of cork (a cellular material with closed cells in the microscale filled with gas) may suggest that it possible to make the composite piezoelectric. Previous studies[1] have shown that the relavant properties are strongly dependent on the humidity. So the latest efforts have been devoted to better control the amount of humidity and understand its influence[2]. The material is produced by grinding and hot pressing of the two components. In order to reduce amount of water in the final product a wax was added to the material and also the powders are dried previous to pressing. After pressing the samples are stored under controlled humidity and temperature.

In this work a composite of cork(48% wt.)/TetraPak®(48% wt.)/Commercial paraffin(4% wt.) was produced. After pressing the samples were kept also at 70 °C until measurements were made.

The composite samples were analyzed using isothermal charging and discharging currents (ICC and IDC) measurements, thermally stimulated discharging currents (TSDC) and dielectric relaxation spectroscopy (DRS). For the isothermal measurements the value of the applied electric field was 2 to 10 kV/m and the ICC/IDC temperature was kept constant. The DRS measurements were performed in the frequency range of 10^{-1} Hz to 2 Mhz and the temperature range of –50°C to 120°C. Several runs were made in order to evaluate the influence of thermal cycling in the dielectric properties (and also water content).

The influence of water content was investigated in order to understand space charge storage. The effect of the processes of water absorption and desorption was studied.

The results were compared with previous ones published for the cork/TetraPak® composite, natural cork and cork agglomerates. Special attention was given to the differences arising from different conditions during samples preparation and conditioning.

References

[1] J.N Marat-Mendes., E.R Neagu: Ferroelectrics 294, 123(2003).
[2] M. Carmo Lança, W.Wirges, E.R. Neagu, R. Gerhard-Multhaupt, J. Marat-Mendes, J. Non-Crystalline Solids 353, 4501(2007).

Dielectric and electric properties of nanodiamonds water suspensions

A.V. Adeljanov[1*], **O.A. Gorobchenko[1]**, **E.M. Mamotyuk[2]**, **O.T. Nikolov[1]**,
V.N. Ivaschenko[3], **S.V. Gatash[1]**
[1]V.N.Karazin Kharkov National University, Svobody Sq. 4, 61077 Kharkov, Ukraine
[2]S.P. Grigor'ev Kharkov Institute of Oncology and Medical Radiology, Pushkinskaya Street 82, 61000 Kharkov, Ukraine
[3]Scientific Production Enterprise "SINTA" Ltd., Gvardeyskoy Armiy Street 143, Kulinychi, 62404 Kharkov, Ukraine
*Email address: adel_vil@mail.ru

At the present time, the nanodiamonds (NDs) find application in various technologies. The use of NDs in biology and medicine offers the greatest promise [1]. It was revealed that NDs could be the new class of medical nanomaterials for delivering anti-cancer chemicals to cells [2]. NDs could also be employed against tuberculosis or viruses. The instability of NDs water suspensions is a serious obstacle to their use in medicine. The investigation of the water state in the NDs suspensions is of obvious interest in connection with the problem of the stability of NDs suspensions and revealing the mechanisms of the NDs influence on biological objects.

In the present work the NDs water suspensions produced by Scientific Production Enterprise "SINTA" Ltd (Kharkov, Ukraine) were studied. The concentrations of NDs in the suspensions were 0,1 wt % - 3,5 wt %. The real (ε') and imaginary (ε'') parts of the complex permittivity ($\varepsilon^*=\varepsilon'-j\varepsilon''$) of the suspensions were measured by the microwave dielectric method described [3]. A resonator type ultra high frequency (UHF) dielectrometer at the frequency of 9.2 GHz has been used. The low-frequency conductivity was measured by the alternating current bridge at 1 kHz. The static dielectric permittivity and the frequency of water molecules dielectric relaxation were found from the Debye equations.

It was found that the real part of the complex permittivity decreases and the imaginary part increases with the increase of the NDs concentration. It was also found the reduction in the static dielectric permittivity and in the frequency of water molecules dielectric relaxation with the increase of the concentration of NDs. These observations can result from decreasing of the amount of bulk water in the system and from the ordering of its structure. The values of ε_s were compared with the theoretically obtained values of the effective permittivity of NDs suspensions. The hydration of NDs was taken into account. The two types of the structured water in the suspensions of NDs were found.

References

[1] Nanodiamonds: Applications in Biology and Nanoscale Medicine. / Dean Ho (Ed.) Springer, 288 (2010).
[2] Houjin Huang, Erik Pierstorff, Eiji Osawa, Dean Ho. Nano Letters 7(11), 3305 (2007).
[3] E.V. Hackl, S.V. Gatash, O.T. Nikolov. J. Biochem. Biophys. Meth. 63(2), 137 (2005).

6TH INTERNATIONAL CONFERENCE ON
BROADBAND DIELECTRIC
SPECTROSCOPY AND ITS APPLICATIONS

www.dielectric2010.com
07 - 10 MADRID
SEPTEMBER 2010

Heterogeneous Materials (II)

Wednesday 8/Sept
Room B

15:30 - 16:00	**A. Schönhals**
16:00 - 16:15	O.I.H. Dimitry
16:15 - 16:30	V. Boucher
16:30 - 16:45	A. Kyritsis
16:45 - 17:00	J. L. Wojkiewicz
17:00 - 17:15	J. M. Kenny

Structure-Property Relationships of Polymeric Nanocomposites with Layered Nanofillers
Interplay between Matrix and Interfacial Effects

A. Schoenhals
BAM Federal Institute for Materials Research and Testing, Unter den Eichen 87, 12205
Berlin, Germany
Email address:Andreas.Schoenhals@BAM.de

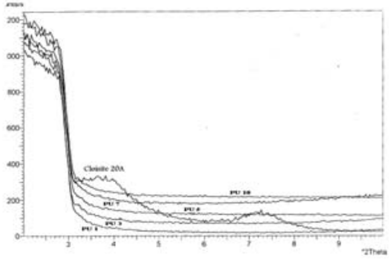
Different types polymerbased nanocomposites with a broad variety of nanofillers are prepared where the concentration of the nanofiller is varied. TEM images show both an intercalated and exfoliated morphology in dependence on the nanofiller and the matrix. All systems are studied in detail by dielectric spectroscopy (DS) but also complementary methods like gas transport measurements, calorimetry, and FTIR spectroscopy are employed. Besides the dispersion, the interfacial region between the nanoparticles and the polymer matrix is crucial for the properties of the nanocomposites. Therefore attention is paid to investigate this interfacial area by DS because the polar groups of both the surfactant and compatibilizer are located close to the layers. For some systems it is found that the molecular mobility in the interfacial area is essentially higher than in the matrix. In addition a Maxwell/Wagner/Sillars polarization is found due to the blocking of charges at the layers. The time constant of this MWS-process can be correlated with characteristic length scales in the nanocomposites and provides information about the dispersion of the nanofiller.

Studies of some polyurethane/organically modified montmorillonite nanocomposites

O. I.H. Dimitry[1*], A.I.Abdeen[1] E. A. Ismail[1], and A.L.G.Saad[2]

[1]Petrochemicals Dept., Egyptian Petroleum Research Institute, 11727 Cairo,Egypt
[2]Microwave Physics Dept. National Research Centre, Dokki, 12311 Cairo, Egypt
*Email address: onsy_dimitry@hotmail.com

Nanostructured polymers have received much attention in the field of material sciences because of their unique properties and their applications in nanomaterials and nanodevices. In this study, an organophillic montmorillonite[1] (O-MMT), Cloisite 20A, which is a type of Cloisite Na^+ modified with a quaternary ammonium salt, was used as nanoclay. Polyether based-polyurethane (PU) / O-MMT nanocomposites containing 1, 3, 5, 7 and 10 wt% of Cloisite 20A were prepared via solution blending. Permittivity (ϵ') and dielectric loss (ϵ'') for the prepared composites have been investigated in the frequency range 100 Hz to 100 kHz at 30 to 100°C.Dielectic measurements show that PU nanocomposites have low ϵ'' and minor ϵ''_{dc}, that is, possess small electrical conductivity. Electrical conductivity (σ) measurements show that σ increases with increasing temperature from 30 to 100°C in PU and its nanocomposites due to the increased mobilities of ionic bodies that occur as a result of excitation by heating, and show a considerable increase in the σ of PU with increasing filler content up to 5 wt%, especially at higher temperatures. At still higher concentrations of filler, σ decreases to some extent due to the formation of some nanoparticle agglomerates resulting from more intense interfacial interactions between nanoparticles, which may cause some steric hindrance that partially contributes to decreasing the electrical charge mobility. Tensile strength, elongation(%) and Young's modulus of PU/Cloisite 20A nanocomposites are increased with increasing the content of organoclay from 0 to 5 wt% and then decrease with further increase in Cloisite 20A content. XRD Pattern of Cloisite 20A shows a characteristic diffraction peak at $2\Theta = 4.05°$ which is completely disappeared for all PU/Cloisite 20A nanocomposites indicating that most of the O-MMT platelets is successfully exfoliated and well dispersed in the PU matrix[2].XRD results have been confirmed by SEM analysis.



XRD patterns of Cloisite 20A and PU / (1, 3, 5, 7 and 10 wt%)
Cloisite 20A nanocomposites

References

[1] SS. Ray, M. Okamoto, Prog Polym Sci. 28,1539 (2003).

[2] M.Tortora, G. Gorrasi, V.Vittoria, G.Gall, S.Ritrovati,E.Chiellini Polymer,43, 6147(2002).

HM 7

Application of dielectric spectroscopy to the study of physical aging in PMMA/silica nanocomposites

V. Boucher[1*], D. Cangialosi[2], A. Alegrìa[2,3], J. Colmenero[1,2,3], I. Pastoriza-Santos[4], L. M. Liz-Marzan[4],
[1] International Physics Center, Paseo Manuel de Lardizabal 4, 20018 San Sebastián, Spain
[2]Facultad de Química, Centro de Física de Materiales Centro Mixto (CSIC-UPV/EHU), Apartado 1072, 20080 San Sebastián, Spain
[3]Departamento de Física de Materiales, Universidad del País Vasco (UPV/EHU), Apartado 1072, 20080 San Sebastián, Spain
[4]Universidad de Vigo, Departamento de Química Física Unidad Asociada CSIC, 36310 Vigo, Spain
*Email address: sckboucv@ehu.es

Polymer nanocomposites have recently attracted much interest, due to their improved properties in comparison to the bulk. However, the time evolution of their properties towards those of the equilibrium liquid below the glass transition temperature (Tg), the so-called physical aging, still has to be clarified[1]. Indeed, this process results in many deleterious effects ranging from embrittlement to reduction in permeability.

As far as dielectric properties are concerned, during the course of physical aging the dielectric permittivity can show two opposing trends:[2] (i) it increases due to the increased number of polarizable entities per unit volume; or (ii) in the case of orientation polarization due to relaxed molecular dipoles, the permittivity decreases due to a reduced amplitude of angular fluctuations, which usually establish the secondary relaxation processes in the glassy state. This latter effect was shown in the past to be dominant during physical aging of several amorphous polymers[2,3,4,5] whereas the former effect has been found during PS physical aging.[6]

In the present study, focalized on poly(methyl methacrylate) PMMA/silica nanocomposites, the latter trend was found: during aging, the β relaxation, which dominates the dielectric response overall below Tg, decreases in amplitude as a consequence of the densification of the system. The physical aging in PMMA with and without silica nanoparticles was so monitored by measuring isothermally the change in the dielectric strength ($\Delta\varepsilon$) of PMMA secondary relaxation process with time.

Despite similar dynamics, the studied nanocomposite samples were found to display an accelerated physical aging in comparison to bulk PMMA. The physical aging rate was also shown to be related to the surface/volume ratio of silica in the polymer. This apparent correlation led to the hypothesis of a physical aging process driven by the diffusion of free volume holes towards polymer interfaces, as already proposed in the past,[2] and evidenced here by the fitting of BDS results to this diffusion model.

References

[1] R.D. Priestley, Soft Matter, 2009, 5, 919.
[2] D. Cangialosi, M. Wübbenhorst, J. Groenewold, E. Mendes, H. Schut, A. van Veen, S. J. Picken, Phys. Rev. B, 2004, 70, 224213.
[3] E. A. McGonigle, J. H. Daly, S. D. Jenkins, J. J. Liggat, R. A. Pethrick, Macromolecules, 2000, 33, 480-489.
[4] D. Cangialosi, M. Wubbenhorst, J. Groenewold, E. Mendes, S. J. Picken, J. Non-Cryst.Solids, 2005, 351, 2605-2610.
[5] R. Casalini, C. M. Roland, Phys. Rev. Lett., 2009, 102, 035701.
[6] K.Fukao, H.Koizumi, Phys. Rev. E, 2008, 77, 021503.

Thermal transitions of solvent and polymer dynamics in binary poly(ethyl acrylate) /p-xylene mixtures

A. Kyritsis[1*], A. Stathopoulos[1], F. Romero Colomer[2], A. Sanchez Alcazar[2], J.L. Gómez Ribelles[2], N. Shinyashiki[3]
[1] Department of Physics, National Technical University of Athens, Zografou Campus, 15780 Athens, Greece
[2] Centro de Biomateriales e Ingeniería Tisular, Universidad Politecnica de Valencia, P.O. Box 22012, E-46071 Valencia, Spain
[3]Department of Physics, Tokai University, Hiratsuka, Kanagawa 259-1292, Japan
*Email address: akyrits@central.ntua.gr

The present work deals with the investigation of polymer dynamics and solvent phase transitions in poly(ethyl acrylate, PEA)/p-xylene binary mixtures. PEA chains are either linear chains or in the form of networks with varied cross linking densities. P-xylene is a crystallisable non polar solvent and the maximum amount of p-xylene in the mixtures, c_{pxmax}, has been found to depend on the viscosity of the PEA network (c_{pxmax} varied from 0.86 to 0.35, the later corresponding to the network with the highest crosslinking density). Differential Scanning Calorimetry (DSC), Thermally Stimulated Depolarization Currents (TSDC) and Dielectric Relaxation Spectroscopy (DRS) were the experimental methods of investigation. Our results allow the construction of the so-called phase diagram for the binary mixtures[1,2]. With respect to PEA dynamics we focus on the segmental dynamics in both homogeneous mixtures (at low solvent contents) and systems with partial p-xylene crystallization (at high solvent contents), in terms of chain mobility, shape and strength of the relaxation process. Regarding the p-xylene component we are able to study the crystallization process of phase separated p-xylene (both during heating and cooling).

The effects of polymer chains on the phase transitions of the p-xylene and vice versa the influence of p-xylene molecules (molecularly distributed or phase separated) on the segmental mobility of the PEA network were systematically studied. Our results reveal that below a critical solvent concentration, c_{pxcrit}, the decrease of the T_g of the mixture as a function of the p-xylene content is well described by the Fox equation, indicating the homogeneous character of the mixing of the two components (plasticization action of p-xylene). In this c_{px} region the results suggest that the dynamics of the segmental process is not affected by the p-xylene molecules, plasticization action, thus, is expressed mainly through the decrease of the average relaxation time and the increase of the dielectric strength of α process. On the other hand, for $c_{px} > c_{pxcrit}$, the PEA/p-xylene mixtures exhibit a constant glass transition temperature corresponding to the gel phase of PEA with the non-freezable p-xylene fraction[3]. This unfreezable p-xylene content has been found to depend on the form of PEA chains (linear chains or networks with varied cross linking density) implying that the existence of non-freezable solvent is mainly due to a diffusion controlled phenomenon. Furthermore, p-xylene crystallites formed within PEA/p-xylene mixtures, for $c_{px} > c_{pxcrit}$, have been found to affect dramatically the segmental mobility of linear PEA chains.

References

[1] J. Rault Lucas A., Neffati R., Monleón Pradas M., Macromolecules 30, 7866 (1997).
[2] M. Salmerón Sánchez, Monleón Pradas M., Gómez Ribelles J.L., J. Polym. Sci., Part B: Polym. Phys. 41(14), 1713 (2003).
[3] S. Yagihara, Asano M., Kosuge M., Tsubotani S., Imoto D., Shinyashiki N., J. Non-Cryst. Solids 351, 2629 (2005).

Dielectric properties of polyaniline hybrid nanocomposites

<u>JLWojkiewicz</u>[1], N.El Kamchi[1], C.Saravanan[1], N.Redon[1], T.Lasri[2]
[1]I[1] *Université Lille Nord de France, Ecole des Mines de Douai, Dpt Chimie Environnement,*
59500 Douai, France
[2]*Institut d'Electronique, de Microélectronique et de Nanotechnologies, Groupe MITEC, UMR 8520,*
59652 Villeneuve d'Ascq, France
*Email address: wojkiewicz@ensm-douai.fr

Dielectric response of Polyaniline (PANI)- Polyurethane (PU) – Carbon Coated Cobalt (CCCo) hybrid nanocomposites were investigated at low frequency (20Hz-1MHz) and at microwave frequency(8-12 GHz). First, the effect of CCCo concentration in the composites with the polyaniline in the insulating form (PANI EB) was studied. Then polyaniline was doped with camphor sulfonic acid to show the drastic effect of the doping process on the dielectric behavior of the composites.
The first type of composites was made with PANI EB blended with PU in solution and by adding CCCo nanoparticles. After drying free standing films with appropriate dimensions were used for dielectric measurements. The conductivity increases with the rate of cobalt in the composites showing a percolation threshold at a mass fraction of 40% of CCCo in PANI-PU. In accord to the percolating behavior of the composites, the real and the imaginary part of the permittivity increase with the mass fraction of cobalt in the materials.
The second type of composite was obtained with the same components but with the conducting form of polyaniline (PANI ES). This conducting form was obtained by oxidation of PANI EB with camphor sulfonic acid (CSA) as described in literature [1] This process leads to a charge delocalisation by the creation of polarons and bipolarons along the polymer chain. The resulting conductivity depends on the rate of oxidation and of the rate of PANI ES in the composites. The materials are obtained as previously in the form of free standing films. As the conductivity of the composite increases with the doping of polyaniline, the dielectric constant is multiplied approximately by a factor of one hundred **[Fig 1]** and it is shown that the composites have magnetic properties. By a good choice of the doping, it has been shown that PANI can have intrinsic magnetic properties [2].

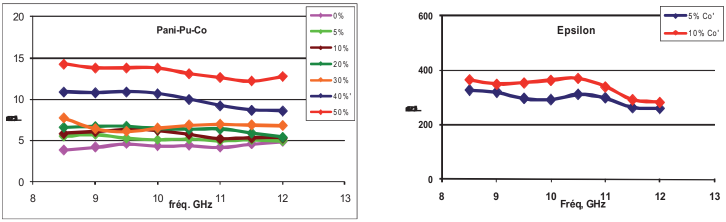


***Fig 1** : Real part of permittivity of PANI EB-PU CCo (on the left) and of PANI ES-PU-CCo (on the right)*

References

[1] Cao Y., Smith P., Heeger A.J., *« Counter-ion induced processibility of conducting polyaniline »* Synthetic Metals, 55-57 (1993) pp 3514-3519

[2]Silvia E. Jacobo , Juan C. Aphesteguy , R. Lopez Anton , N.N. Schegoleva ,G.V. Kurlyandskaya , *"Influence of the preparation procedure on the properties of polyaniline based magnetic composites*" European Polymer Journal, 43,2007, pp 1333-1346

Dielectric and Chemorheological Behavior of Carbon Nanotube Epoxy Nanocomposites

F. Scarponi[1], M. Leonardi[1], D. Fioretto[1], L. Valentini[2], J.M. Kenny[3*]
[1]Department of Physics, University of Perugia, 06100 perugia, Italy
[2]Materials Science and Technology Centre, Universituy of Perugia, 05100 Terni, Italy
[3]Institute for Polymer Science and Technology, ICTP-CSIC, 28006 Madrid, Spain
*Email address: kenny@ictp.csic.es

The dielectric behavior of epoxy polymers has been extensively analyzed in the last two decades of the XXth century and was the basis for several approaches to the development of monitoring strategies of the processing of advanced epoxy matrix composites. Although there is very complex contribution of different physical and chemical factors to the dielectric behavior of epoxy systems, the correlation of the permittivity with the changes in the viscosity of the matrix has been the main fundament of such strategies. The gradual development of the epoxy polymer network through polymerization and crosslinking reactions among the epoxy and hardener molecules provides the changes in the molecular dynamics responsible of the gradual increase in the viscosity correlated by the changes in the molecular polarizability. However, it has been also found that conductivity plays an important role in the dielectric behavior of these thermosetting systems.

It is evident that this complex behavior would be strongly affected by the presence of highly conductive nanofillers and this is the main objective of this research. So, the frequency dependent dielectric permittivity of a commercial epoxy mixture (Dow Chemicals DER 330) reacting isothermally with an aromatic amine hardener (MDEA) has been measured in the range 10 - 10^6 Hz. Dielectric spectra were taken at regular intervals during reaction, in the pure reactive system and in composites obtained by adding commercial carboxy-funcionalized double-walled carbon nanotubes (C-DWCNTs, Nanocyl 2100). The C-DWCNTs were stirred in the MDEA at the melting temperature of the amine (i. e. 100°C for 45 min.). The C-DWCNTs grafted with MDEA, MDEA/C-DWCNTs, were added to obtain a percentage of 0.1wt% and 1wt% respect to the DGEBA monomer maintaining a stoichiometric molar ratio (1:2.33) with MDEA. Calorimetric and rheological tests reveal how the presence of MDEA modified C-DWNTs speed up the maximum degree of cure and the gel time of the epoxy system. The dielectric response in the pure system appears to be dominated by ionic conductivity and by structural relaxation with characteristic time strongly increasing with curing time. In the nanotube loaded samples the presence of the filler originates a new and strong relaxation, which overcomes and hides the structural contribution. The characteristic parameters of the dielectric relaxation in the loaded samples are compatible with hopping dominated conduction mechanisms. An increase of DC conductivity in the final part of the reaction is also observed, which can be ascribed to dielectrophoretic migration of carbon nanotubes.

6TH INTERNATIONAL CONFERENCE ON
BROADBAND DIELECTRIC
SPECTROSCOPY AND ITS APPLICATIONS

www.dielectric2010.com
07-10 MADRID
SEPTEMBER 2010

Nanoconfined Systems (II)

Thursday 9/Sept
Room A

9:00 - 9:30	**E. Laredo**
9:30 - 9:45	I. Royaud
9:45 - 10:00	A. Serghei
10:00 - 10:15	A. Sanz
10:15 - 10:30	N. T. Correia
10:30 - 10:45	A. Naberezhov
10:45 - 11:15	**A. Alegría**

Bionanocomposites based on poly(ε-caprolactone), poly(lactide) and their blend

E. Laredo
Departamento de Física, Universidad Simón Bolívar, Caracas, Venezuela
Email address: elaredo@usb.ve

Bionanocomposites based on poly(ε-caprolactone), an aliphatic biodegradable semi-crystalline polyester, polylactide, an amorphous biopolymer, and their blend (PCL/PLA 70/30), filled with MWCNT were studied by AC conductivity ($10^{-3}\leq f \leq 3\text{x}10^{6}$ Hz) at both isothermal conditions and variable nanofiller % weight concentrations, p. Figure 1 is a compendium of the measured real part of the conductivity for the pure materials, the nanocomposites with MWCNT concentrations at the percolation threshold and for $p > p_c$. The higher percolation threshold in the case of the immiscible blend as compared to PCL confirms selective localization of the CNT in the PCL matrix and at the interfaces of the PLA inclusions[1] showing the depletion of CNT contributing to the formation of the conductive path. PLA which is 100 % amorphous is the least conductive before percolation but reaches comparable conductivities for $p > p_c$. Its high percolation threshold cannot be attributed to bundle formation as the dispersion of the functionalized MWCNT was observed by Transmission Electron Microscopy. The critical exponents of the scaling law for PCL and PCL/PLA were determined and point to a 3D cluster with t slightly larger than 2. Also the tunneling junction conduction through narrow potential energy barriers was found to be temperature independent in the case of PCL and PCL/PLA based composites. The universality of ac conduction in polymer/CNT composites was verified and the validity of time-temperature-concentration superposition was found for PCL and the blend, while for PLA only the normalized conductivity vs. frequency could be scaled into a single master curve with p variation. The molecular dynamics of PCL in the PCL/PLA/MWCNT nanocomposites is unchanged as compared to the neat homopolymer.[2]

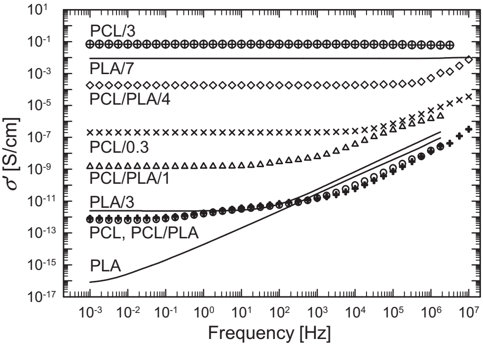


Fig.1. AC Conductivity of bionanocomposites: PCL/p, PCL/PLA/p (70/30/p), PLA/p; p indicates the weight % concentration of the MWCNT.

References

[1] D. Wu, Y. Zhang, M. Zhang and W. Yu, Biomacromolecules 10, 417 (2009).
[2] E. Laredo, M. Grimau, A. Bello, D. Wu, Y. Zhang and D. Lin (submitted to Biomacromolecules).

Molecular mobility at the interfaces of nanostructured systems

E. Nikaj[1], I. Royaud[1*], G. Seytre[1], L. David[1], E. Espuche[1], A. Jonquières[2], M. Billy[2], S. Etienne[3]

[1]Université de Lyon, Université Lyon 1, UMR CNRS 5223 IMP, Laboratoire des Matériaux Polymères et des Biomatériaux, Bât. ISTIL, 15, bd. Latarjet F-69622 Villeurbanne Cedex France

[2]Laboratoire de Chimie Physique Macromoléculaire, UMR CNRS 7568, Nancy Université, Ecole Nationale Supérieure des Industries Chimiques, 1 rue Grandville, BP20451, 54001 Nancy Cedex, France

[3]Institut Jean Lamour, UMR CNRS 7198, Ecole Nationale Supérieure des Mines, Nancy Université, Parc de Saurupt, 54042 Nancy, France/ EEIGM, 6 rue Bastien Lepage, 54010 Nancy, France

*Email address: isabelle.royaud@univ-lyon1.fr

The aim of this work was to study, by means of Broad band Dielectric Spectroscopy, the molecular dynamics in several polymer materials by modifying (i) the confinement geometry and (ii) the interactions between the confining environment ('confiner') and the polymer chains. Thus, the confinement effects were studied in a wide range of molecular motions in the following systems:

- Cellulose acetate grafted poly(methyl (diethylene glycol) methacrylate). In this case, the influence of the length and the number of the mobile grafted moieties on the molecular dynamics was studied. These two parameters impact the interactions between the rigid backbone chains and thus the overall molecular mobility of the copolymers.
- Semi-crystalline Poly(ethylene naphtalene - 2,6 - dicarboxylate) (PEN). The confinement effects induced by the presence of the crystalline lamellae on the mobility of the chains belonging to the amorphous intercrystalline region, was studied as a function of the morphology. In this system, the confining geometry and the interactions between the amorphous and crystalline phases were varied as the samples were crystallized at different annealing temperatures and during different crystallization times, inducing different semi-crystalline morphologies as evidenced by synchrotron SAXS.
- Polyamide 6 (PA6) and Montmorillonite (MMT) nanocomposites. The confinement effects induced by the MMT platelets on the PA6 matrix were studied as a function of the filler content and of the type of dispersion. In this case, only the confining geometry was changed as the MMT platelets were exfoliated or intercalated.

The prediction of confinement effects requires a decoupling of the size (geometry) and interactions effects in these different systems. As expected, cooperative motions are mostly affected by confinement effects. This occurs either in a highly constraining geometry or in the case of strong interactions between the confiner and the confined macromolecules.

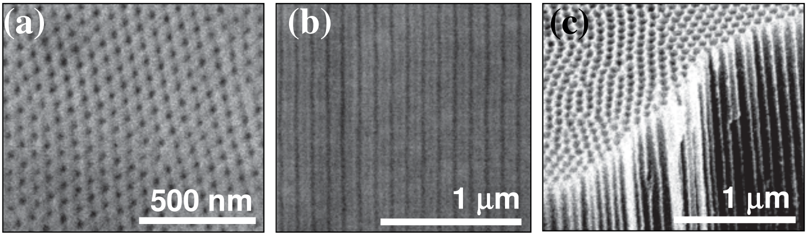
Nanofluidics by Broadband Dielectric Spectroscopy

A. Serghei, and T. P. Russell

Polymer Science and Engineering, University of Massachusetts Amherst,

Amherst MA 01003, USA

Ordered arrays of parallel cylindrical nanopores (with a narrow pore size distribution and diameters down to ~ 10 nm) are used as experimental platforms in the field of polymer nanofluidics (Fig. 1), in particular, to investigate the capillary flow of polymers in 2D geometrical nanoconfinement. Several aspects of the polymer dynamics – manifested on time scales covering more than 10 orders of magnitude – are investigated during the flow process: (i) molecular fluctuations corresponding to the segmental dynamics (dynamic glass transition); (ii) chain dynamics, as revealed in fluctuations of the end-to-end distance; (iii) velocity of the capillary flow in dependence on the diameter of the nanopores. The results are compared to the polymer dynamics in the bulk.



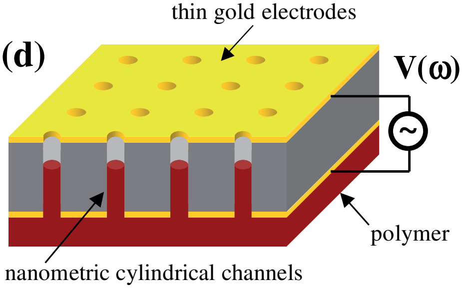


Fig. 1: (a,b,c) SEM images of ordered nano-porous media (top view in (a), cross-section view in (b) and edge-view in (c); (d) measurement cell for experiments in the field of nanofluidics. Thin electrodes of gold are deposited onto both sides of the porous membrane and connected to the BDS spectrometer.

A. Serghei, D. Chen, D.H. Lee, T.P. Russell, Soft Matter **6**, 1111 (2010).

Confined dynamics in semicrystalline polymers: A Dielectric Spectroscopy and Neutron Spin Echo Study

A. Sanz[1,*], A. Nogales[1], M. Soccio[2], N. Lotti[2] and T. A. Ezquerra[1]
[1]Instituto de Estructura de la Materia, CSIC, C/ Serrano 121, 28006, Madrid, Spain
[2]Dipartamento di Chimica Applicata e Scienze dei Materiali, Universita di Bologna, Via Terracini 28, 40131, Bologna, Italy
*Email address: asanz@iem.cfmac.csic.es

One simple way to confine disordered polymer chains at the nanometer scale is to induce crystallization. Due to entropic reasons, crystallization takes place only partially resulting in a heterogeneous morphology where the amorphous domains are confined by the crystalline lamellae[1]. In general, the amorphous chains become dynamically restricted by the crystals giving rise to a slowing down of the segmental modes associated to the α relaxation, as well as a broader distribution of the relaxation times. The α relaxation, only active above the glass transition temperature T_g, can be explored using broadband dielectric spectroscopy BDS. The complexity of the segmental relaxation in the amorphous regions confined between crystals give rise to features different from those found in pure amorphous systems[2]. Dielectric experiments show that the polarization autocorrelation function associated to the segmental relaxation evolves, upon crystallization, from a characteristic stretched exponent towards a more complex one[2]. Neutron Spin Echo (NSE) experiments allows one to measure the pair correlation function which in some aspects can be related to the polarization autocorrelation function[3]. Most of NSE studies related to polymer dynamics have been performed in amorphous systems. Therefore, no information about segmental dynamics in semicrystalline polymers as revealed by NSE has been made available in the past. By means of NSE, the pair correlation function of semicrystalline deuterated poly(ethylene terephthalate) d-PET has been obtained in a temperature range between 420 and 520 K at two values of the wave vector Q corresponding to characteristic interchain correlations, 0.94 and 1.38 Å^{-1}. BDS measurements on semicrystalline d-PET were also performed in a lower temperature range in order to explore the local and segmental dynamics. The dielectric α relaxation has been analyzed in the time-domain after inverse Laplace transformation of the HN function. By combing NSE with BDS data, we explored the relaxation map of semicrystalline d-PET and compared both time correlation functions in terms of temperature and length scale.

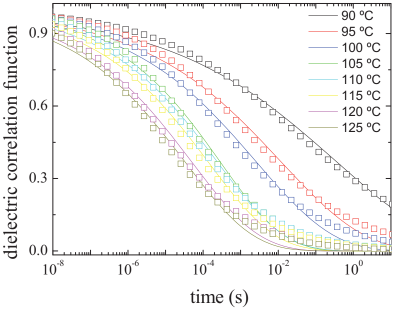


Fig.1. Normalized dipole correlation function and best fit to a stretched KWW at different temperatures.

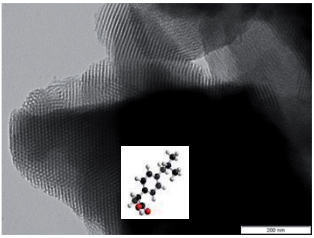
References

---

[1] A. Sanz et al. Macromolecules. 43, 671 (2010)
[2] T. A. Ezquerra et al. Physical Review B. 50, 6023 (1994)
[3] D. Richter et al. Neutron Spin Echo in Polymer Systems, Spinger, Berlin (2005)

Confinement effects in the molecular dynamics of ibuprofen studied by DRS

A. R. Brás[1], I. M. Fonseca[1], F. Affouard[2], A.Schönhals[3],
M. Dionísio[1], N. T. Correia[1]*
[1]Requimte, Departamento de Química, Faculdade de Ciências e Tecnologia,
Universidade Nova de Lisboa, 2829-516 Caparica, Portugal
[2]LaboUMET - UFR de Physique - BAT P5, UMR CNRS 8207, Universite Lille 1,
59655 Villeneuve d'Ascq France
[3]BAM- Federal Institute of Materials Research and Testing, Unter den Eichen 87, D-12205, Berlin, Germany
*Email address: n.correia@dq.fct.unl.pt



In this work, dielectric relaxation spectroscopy was applied to study the molecular mobility of racemic Ibuprofen confined to MCM-41 molecular sieves (100% Si chemical composition) with a hexagonal structure of cylindrical pores of 3.6 nm diameter.

A complex relaxation map including two secondary relaxations in the glassy state, γ and β, a main α process associated with the dynamic glass transition of the bulk-like molecules and a surface process is given for the first time. The β-relaxation speeds up, and its activation energy is lower than for the bulk, being also identified as the genuine Johari-Goldstein process. The temperature dependence of the relaxation time of the α process does not obey a VFTH law, oppositely to the bulk. Instead an apparent Arrhenius behavior is found, and thus an acceleration of the molecular dynamics of the bulk-like molecules is observed, which is interpreted as a confinement effect. Moreover, it is concluded that the molecular dynamics is determined by a counterbalance of the confinement and an adsorption effect. The latter is observed by the surface process which has an essentially lower molecular dynamics than the one found for the bulk relaxation processes. The temperature dependence of the surface process relaxation times follows a VFTH-equation, being attributed to the glass transition of the Ibuprofen molecules linked via weak hydrogen bonding to the inner pore surface.

Financial support was provided by Fundação Ciência Tecnologia (FCT) through the projects PTDC/CTM/64288/2006 and PTDC/CTM/098979/2008. A.R. Brás acknowledges FCT for SFRH/BD/23829/2005 grant.

Dielectric response and crystal structure of nanocomposites KNO_3 - porous glasses

A. Naberezhnov[1*], E. Koroleva[1], A. Sysoeva[1], S. Vakhrushev[1], E. Rysiakiewicz-Pasek[2], M. Tovar[3]

[1] A.F.Ioffe Physico-Technical Institute, 26 Polytechnicheskaya, S.-Petersburg 194021, Russia
[2] Institute of Physics, Wrocław University of Technology, W. Wyspiańskiego 27, 50-370 Wrocław, Poland
[3] Helmholtz Zentrum Berlin, Glinicker Straβe 100, D-14 109 Berlin, Germany
*Email address: alex.nabereznov@mail.ioffe.ru

It is known that properties of materials in a restricted geometry differ significantly from the properties of the bulk, especially if the characteristic size is comparable with correlation length of the order parameter critical fluctuations This contribution is devoted to the study of temperature evolution of structure and dielectric response of KNO_3 embedded into porous glasses with average pore diameters 320, 46 and 7 nm. The samples were prepared by immersing of the preliminary annealed matrices in the melted KNO_3. The principle aim of this work was the study the effect of restricted geometry on stability of ferroelectric phase observed in potassium nitrate on cooling. Dielectric properties have been studied in the temperature interval RT - 573 K (on heating and cooling) at frequencies 0.1 - 10^7 Hz. The temperature dependences of dielectric permittivity at 90 KHz are presented in Fig.1 Temperature evolution of structure was studied by neutron diffraction and small-angular neutron scattering (SANS). The characteristic sizes of KNO3 particles and corresponding temperature of α-β, β-γ and γ-α phase transitions were determined. It is shown that the decreasing of particle sizes leads to broadening of temperature interval where the ferroelectric γ-phase is stable. For all samples we have observed a sharp growth of dielectric permittivity in β-phase and frequency dispersion in our temperature interval. Dielectric permittivity for KNO3 within 7 nm glasses the temperature of low-temperature PT depends on frequency.

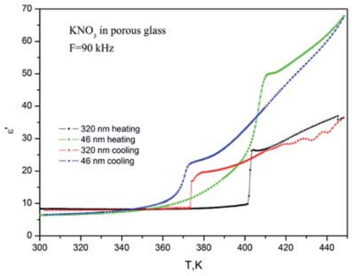


Fig.1. Temperature dependences of ε for KNO3 within 320 and 46 nm glasses at 90 KHz

This work was supported by the RFBR (Grant 09-02-00329) and Program of Presidium of RAS.

Dielectric relaxation in nano-structured diblock-copolymers: obtaining specific structural information

A. Alegría
[1]Centro de Física de Materiales (CSIC-UPV/EHU), M. de Lardizabal 5, 20018 San Sebastián, Spain.
[5]Departamento de Física de Materiales (UPV/EHU), Facultad de Química, Apdo 1072. 20080 San Sebastián, Spain.

*Email address: angel.alegria@ehu.es

Broad-band dielectric spectroscopy (BDS) is one of the most powerful methods to study the molecular dynamics under different sample environments, covering a huge frequency range (10^{-5}–10^{12}Hz). On the other hand, it is well established that the molecular dynamics of glass-forming systems in the range of the glass transition temperature is very sensitive to changes of control variables as temperature, pressure, concentration, etc. This is responsible of the strong changes in the dielectric relaxation behaviour in mixtures and crystallizing polymers as some two representative examples. For instance, this sensitivity has allowed accessing the spatial scale characteristic of the polymer glass transition from the study of the component segmental dynamics of polymer-based mixtures.[1]

In this talk, the results obtained during the last few years from BDS experiments on several nano-structured diblock-copolymers will be presented. On one hand, the results on the micellar structure of polyisoprene (PI) -polydimethylsiloxane (PDMS) diblock copolymers with varying core size will be considered. From the dielectric relaxation originated by the (minority) PI segmental dynamics the concentration profile at the micelle interface was extracted.[2] The resulting values agree well with those expected by the fluctuations of the interface induced by the presence of the high mobility PDMS chains in the surrounding. On the other hand, the PDMS nano-phase of strongly segregated diblock compolymers with polystyrene (PS) has been characterized. In this case, stiff PS limits the PDMS regions of high mobility, which produce an anchorage effect clearly detectable in the dielectric response.[3] Moreover, there are clear indications of a mobility gradient from the PS walls towards the PDMS core. Furthermore, on cooling the PDMS regions embedded in the PS matrix cannot reach the PDMS melt density, which give rise to a dramatic speed-up of the molecular motions in the PDMS nano-phase.[4]

References

[1] D. Cangialosi, A. Alegría, and J. Colmenero, Physical Review E **75** (2007) 011514.
[2] R. Lund, L. Willner, A. Alegría, J. Colmenero, and D. Richter, Macromolecules **41** (2008) 511.
[3] C. Lorthioir, A. Alegría, J. Colmenero, and B. Deloche, Macromolecules **37** (2004) 7808.
[4] L. del Valle, J. Colmenero, A. Alegría (to be published).

Polymers
-
Functional materials (I)

Thursday 9/Sept
Room B

9:00 - 9:30	**D. Prevosto**
9:30 - 9:45	V. Bovtun
9:45 - 10:00	V. A. Stephanovic
10:00 - 10:15	A. Levstik
10:15 - 10:30	N. Seleznev
10:30 - 10:45	H. Haspel
10:45 - 11:15	**E. A. Rossler**

Relaxation properties of polymer nanocomposites: a dielectric spectroscopy insight at the nanometric scale

D. Prevosto(1)*, **M. Labardi** (1), **Kim H. Nguyen** (2), **S. Capaccioli** (1,2), **M. Lucchesi**(1,2), **P. Rolla**(1,2)
[1] Istituto per i Processi Chimico-Fisici, CNR, Largo Pontecorvo 3, 56127 Pisa, Italy
[2] Dipartimento di Fisica "Enrico Fermi", Università di Pisa, Largo Pontecorvo 3, 56127 Pisa, Italy
*Email address: prevosto@df.unipi.it

The development of new organic materials by nanometer-scale mixing of two or more components, such as a polymer with carbon nanotubes or silica clays, is one of the most investigated routes in materials science for functional as well as structural applications. In such nanocomposites, the final macroscopic properties depend on the local properties of the polymer at the interface with the other component. In parallel, the investigation of the fundamentals of relaxation properties of inorganic disordered materials is increasingly focusing to phenomena occurring at the nanometric scale, to address open problems as the identification and characterization of dynamic heterogeneity regions in single-component glass formers, in asymmetric polymer blends, as well as dynamic properties at interfaces. All of these applicative and fundamental problems demand the possibility to investigate dielectric properties of nanometric regions of the material.

Some experimental techniques have intrinsic possibility to investigate physical properties, such as the dynamic properties, of nanometric regions of the sample. However, most of them reveal such properties as averaged over a large number of such regions, in other words they are not able to select single nanometric portions of the sample to evidence their different dynamics.

In the last years, dielectric relaxation properties of polymer films with a spatial resolution of few tens on nanometers was investigated by a new technique named local dielectric spectroscopy (DS) [1], that could also be applied to study static dielectric properties of polymers films [2,3]. Its great advantage is the capability of selecting and measuring the relaxation properties of single nanometric size portions of the sample. We applied such techniques to investigate dielectric relaxation in nanocomposite ultra thin films of poly(vinyl acetate)/montmorillonite clay [4]. Dielectric relaxation imaging on the nanometric scale was also performed at constant temperature demonstrating nanometer scale resolution of local DS on heterogeneous materials. Dielectric spectra measured across the boundary between pure poly(vinyl acetate) and montmorillonite show broadening of the structural peak and a slowing down of structural dynamics due to the presence of the clay. Moreover, spatially resolved dielectric measurements evidenced spatial heterogeneity of the polymer dynamics at the interface, ascribed to differences in the polymer-montmorillonite interactions. Such results directly verify, by local scale measurements, the changes of polymer mobility due to well dispersed and interacting montmorillonite layers, previously argued by macroscopic measurements on similar nanocomposite materials.

References

[1] P.S. Crider, M.R. Majewski, et al., Appl. Phys. Lett. 91, 013102 (2007).
[2] C. Riedel, R. Arinero, Ph. Tordjeman, M. Ramonda, G. Lévêque, G.A. Schwartz, D.G. de Oteyza, A. Alegria, J. Colmenero, J. Appl. Phys. 106, 024315 (2009).
[3] L. Fumagalli, G. Ferrari, M. Sampietro, G. Gomila, Appl. Phys Lett. 91, 243110 (2007).
[4] M. Labardi, D. Prevosto, et al., arXiv:cond-mat 0911.1655 and in press on Journal of Vacuum Science and Technology B.

Broadband dielectric spectroscopy of relaxor ferroelectrics with and without ferroelectric transition

V. Bovtun*, S. Kamba, D. Nuzhnyy and J. Petzelt
Institute of Physics ASCR, Na Slovance 2, 18221 Prague, Czech Republic
*Email address: bovtun@fzu.cz

Phonon and relaxation dynamics in the classic relaxor ferroelectric (RFE) $PbMg_{1/3}Nb_{2/3}O_3$ (PMN)[1,2,3] and RFE with a ferroelectric phase transition $PbMg_{1/3}Nb_{2/3}O_3$-$PbTiO_3$ (PMN-35%PT)[4,5] is discussed and compared on the basis of broadband dielectric spectroscopy studies (10^2 – 10^{14} Hz). Polar phonon response of PMN (crystals and thin films) and PMN-35%PT (ceramics) is quite similar: 1) three main transverse optical modes typical for the simple cubic perovskite structure were revealed; 2) the lowest polar mode (TO1) splits in two components (A_1 and E) below the Burns temperature T_B, even above T_C in PMN-35%PT, due to the local anisotropy of polar nanoclusters; 3) A_1(TO1) component partially softens toward T_B, on heating showing no anomaly at T_C in PMN-35%PT or near the permittivity maximum T_m in PMN; 4) THz E(TO1) component is overdamped and partially softens toward T_C = 440 K in PMN-35%PT or T* ~ 400 K in PMN; 5) relaxation central mode splits from the phonon response below T_B and shifts to the microwave range on further cooling. Phonon dielectric contribution does not account for the permittivity maximum and dielectric response is dominated by the complex relaxation below phonon frequencies in both materials, even above T_C in PMN-35%PT, due to the relaxor dynamics of polar nanoclusters. Two relaxation modes were revealed and attributed to the polar nanocluster breathing (R1) and flipping (R2). In PMN, R2 slows on cooling down according to the Vogel-Fulcher law and freezes out at T_{VF} ~ 200 K, while R1 follows the Arrhenius law, extremely broadens and is responsible for the frequency independent dielectric losses at low temperatures. The ferroelectric phase transition in PMN-35%PT transforms polar nanoclusters into ferroelectric domains and therefore influences their relaxation dynamics, mainly the flipping mode R2. As a result unlike in PMN, the R2 relaxation slows down to 1 MHz only. Moreover, the Vogel-Fulcher and Arrhenius freezing of R2 and R1, respectively, is combined with a critical slowing down near T_C.

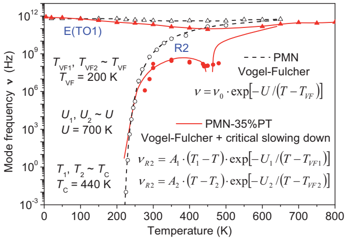


Fig.1. THz E(TO1) and relaxation flipping R2 modes.

References
[1] V.Bovtun, J.Petzelt et al., J. Eur. Ceram. Soc. **21**, 1307 (2001).
[2] V. Bovtun, S. Kamba, A. Pashkin. et al., Ferroelectrics **298**, 23 (2004).
[3] V. Bovtun, S. Veljko, S. Kamba et al., J. Eur. Ceram. Soc. **26**, 2867 (2006).
[4] J. Kroupa, V. Bovtun, D. Nuzhnyy et al., Phase Transitions **81**, 1059 (2008).
[5] V. Bovtun, S. Kamba, S. Veljko et al., Phys. Rev. B **79**, 104111 (2009).

Non - perovskite disordered ferroelectrics: relaxor vs mixed ferroelectric - dipole glass behavior

V.A.Stephanovich[1*] and E. V. Kirichenko[2]
[1]Institute of Physics, Opole University, Oleska Street 48, 45052 Opole, Poland
[2]Institute of Mathematics and Informatics, Opole University, Oleska Street 48, 45052 Opole, Poland
*Email address: stef@uni.opole.pl

We demonstrate that experimental data[1] on non-perovskite disordered ferroelectrics (NPDF) like tungsten bronze compound (TBC) $Ba_2Pr_xNd_{1-x}FeNb_4O_{15}$ can be well explained in our model predicting a crossover from ferroelectric (x=0) to orientational (dipole) glass (x=1), rather then relaxor, behavior. The main reason for “classic” relaxors (like $Pb(Mn_{1/3}Nb_{2/3})O_3$) not to become ferroelectrics is the nonstoichometry of the position of the central ion (in our case Mn-Nb) in their perovskite elementary cell. This nonstoichiometry actually "spoils" the phonon spectrum inherent in perovskite structure, destroying the ferroelectrically important soft mode[2]. Latter fact manifests itself in many observable quantities of relaxors, to name a few, the smearing of ferroelectric phase transition and the appearance of additional low-temperature peaks in dielectric spectra obeying Vogel - Fulcher law[3]. There are, however, differences between relaxors and disordered ferroelectrics like $KTaO_3$:Li (KTL). The major difference is that since above relaxors do not exhibit macroscopic ferroelectricity, they never have the ferroelectric hysteresis, while the substances like KTL exhibit it in their ferroelectric and mixed ferroglass phases. As TBC exhibits ferroelectric hysteresis[1], which disappears with growth of x, it rather shows a crossower between ferroelectric and dipole glass behavior similar to that in KTL family. To describe this crossover theoretically, we utilize a simple approach, based on replica-symmetric solution for disordered Ising model. We show that our simple approach is able to describe both the phase diagram and hysteresis loops in NPDF. We also predict that the absence of Curie-Weiss law in paraelectric phase of NPDF is related to the occurrence of Griffiths (para-glass) phase[4] in these substances.

References

[1] E. Castel, M. Josse, D. Michau and M. Maglione J.Phys. Cond. Mat. 21, 452201 (2009).
[2] P. M. Gehring, H. Hiraka, C. Stock, S.-H. Lee, W. Chen, Z.-G. Ye, S. B. Vakhrushev, and Z. Chowdhuri, Phys. Rev. B 79, 224109 (2009).
[3] D. Vieland, S.J. Jang, L.E. Cross and M. Wuttig, J. Appl. Phys. 68, 2916 (1990).
[4] V.A. Stephanovich European Phys. Journ. B, 18, 17 (2000).

Magnetoelectric Relaxor 0.8Pb($Fe_{1/2}Nb_{1/2}$)O_3-0.2Pb($Mg_{1/2}W_{1/2}$)O_3 and Burns temperature in ferroelectric relaxors

A. Levstik, C. Filipič, V. Bobnar, and Z. Kutnjak
Jožef Stefan Institute, Jamova 39, 1000 Ljubljana,
Slovenia
*Email address: adrijan.levstik@ijs.si

The site and charge disordered solid solution 0.8Pb($Fe_{1/2}Nb_{1/2}$)O_3-0.2Pb($Mg_{1/2}W_{1/2}$)O_3 (0.8PFN-0.2PMW) is a magnetoelectric relaxor which shows broad and frequency dependent maxima both in the electric as well as in the magnetic susceptibilities. The Vogel-Fulcher type electric relaxor freeze-out is accompanied by a significant magnetic anomaly demonstrating magnetoelectric coupling.

0.3Pb($Fe_{1/2}Nb_{1/2}$)O_3-0.7Pb($Mg_{1/2}W_{1/2}$)O_3 (0.3PFN-0.7PMW) solid solution is a magnetic and electric relaxor. In spite of its multiferroic properties the magnetoelectric coupling in this system is negligibly small.

It has been considered that polar nanoregions (PNR) in relaxors form at Burns temperature $T_d \approx 600$ K. High-temperature dielectric investigations of Pb($Mg_{1/3}Nb_{2/3}$)O_3 (PMN) and 0.7PMN-0.3PbTiO_3 reveal, however, that the dielectric dispersion around 600 K appears due to the surface-layer contributions. The intrinsic response, analyzed in terms of the universal scaling, imply much higher T_d or formation of PNRs in a broad temperature range, while high dielectric constants manifest that polar order exists already at the highest measured temperatures of 800 K. The obtained critical exponents indicate critical behavior associated with universality classes typically found in spin glasses.

Dielectric properties of dry rocks

Nikita Seleznev

Schlumberger-Doll Research, 1 Hampshire St., Cambridge, MA, 02139

The dielectric logging was originally developed for the purpose of distinguishing between fresh water and oil, which was difficult to do with resistivity logs alone. The methodology is based on the contrast in dielectric properties of water, rock matrix and hydrocarbons. The dielectric constant of water at ambient conditions is at least an order of magnitude higher than the dielectric constant of oil or the rock matrix, and, therefore, the measurements of the effective formation permittivity are sensitive to the formation water content. In combination with total formation porosity it is possible to directly determining the water saturation, thus avoiding difficulties associated with the determination of cementation and saturation exponents as is needed with the Archie equation and resistivity measurements. However, accurate interpretation of the dielectric measurements requires input of the rock matrix dielectric constant. It is, therefore, desirable to build a catalogue of the matrix dielectric constant for a wide variety of sedimentary formations encountered in oilfield logging. Furthermore, ability to determine the matrix dielectric constant from downhole measurements can simplify and improve dielectric log interpretation.

In the present paper we introduce methodology for accurate laboratory measurements of the complex permittivity of dry rocks and powders. We applied proposed technique to a collection of samples with variable lithology. On the same rock collection we obtained chemistry data and modeled nuclear logging responses. The correlations between dry rock matrix dielectric constant and logging parameters are examined.

This study will serve petroleum industry by introducing the methodology for accurate laboratory measurements of the matrix permittivity of porous rocks, expanding the database of the permittivity values for oilfield formations and presenting correlations between the rock matrix dielectric constant and other logging responses.

Dielectric spectroscopic studies on 1D titanate nanostructures

H. Haspel[1*], **A. Sápi**[1], **Á. Kukovecz**[1], **Z. Kónya**[1], **I. Kiricsi**[1]
[1]Department of Applied and Environmental Chemistry, University of Szeged, Rerrich Béla tér 1, 6720 Szeged, Hungary
*Email address: henya@t-online.hu

One-dimensional nanostructures such as nanotubes, nanowires and nanobelts have been actively studied recently in order to understand their novel physical properties and develop nanoscale electronic devices. Titanate nanotubes[1] and nanowires[2] are important representatives of one-dimensional oxide nanostructures. Although the physical properties of the native and modified[3] forms of these materials have been studied intensively by many authors, there are still open questions concerning their structure, conduction mechanism and the role of water molecules in these phenomena. Since these nanostructures are strongly heterogeneous ion conductors the use of dielectric spectroscopy seems to be the natural choice in pursuit of the answers.

Here we report on our dielectric spectroscopic studies on hydrothermally synthesized titanate nanotubes/nanowires. Recent impedance measurements performed at various frequencies, relative humidities and temperatures showed the dependence of the electrical conductivity on these parameters[4]. In order to separate the effect caused by each variable, we controlled/changed the water content (equilibration in 6-97 RH% atmosphere) and temperature (275-307 K) of the titanate samples independently and recorded the dielectric spectra in the 10^{-3}-10^{6} Hz frequency regime.

Since the spectra exhibited a strong Maxwell-Wagner-Sillars (MWS) peak and a conductivity tail as well as other features, very complex dielectric spectra had to be analyzed. In order to extract the most information from the measured spectra we used the permittivity and the electric modulus representations. Changing the heterogeneity of the sample with ball milling and the type of the charge carriers via ion exchange allowed us to fine-tune the MWS process and the conduction independently to get a better insight into mechanisms responsible for these relaxations. The parameters describing these processes were determined by non-linear fitting of model functions. Further conclusions could be drawn by analyzing the dependence of the parameters on the temperature, humidity, type of charge carriers and heterogeneity.

References

[1] Á. Kukovecz, M. Hodos, E. Horváth, G. Radnóczi, Z. Kónya, I. Kiricsi, J. Phys. Chem. B 109, 17781 (2005).
[2] E. Horváth, Á. Kukovecz, Z. Kónya, I. Kiricsi, Chem. Mater. 19, 927 (2007).
[3] M. Hodos, E. Horváth, H. Haspel, Á. Kukovecz, Z. Kónya, I. Kiricsi, Chem. Phys. Lett. 399, 512 (2004).
[4] Y.Zhang, W. Fu, H. Yang, M. Li, Y. Li, W. Zhao, P. Sun, M. Yuan, D. Ma, B. Liu, G. Zou, Sens. Actuators B: Chem. 135, 317 (2008).

Protracted crossover to full entanglement dynamics revealed by dielectric spectroscopy and field cycling ^{1}H NMR

A. Abou Elfadl, R. Kahlau, A. Herrmann, D. Kruk, V. N. Novikov, E.A. Rössler
Experimentalphysik II, Universität Bayreuth, 95440 Bayreuth, Germany
ernst.roessler@uni-bayreuth.de

We re-investigate dielectric spectra (DS) of polyisoprenes covering a wide range of molecular weights (M in g/mol) [1]. Normal mode (τ_n) and segmental relaxation (τ_α) are considered. The normal mode spectra are singled out by subtracting the spectra of the segmental relaxation. Regarding the Rouse regime we are able to construct a master curve which is reproduced by the Rouse theory with a weak stretching of the correlation function. In the entanglement regime ($M > M_e$) the normal mode spectrum changes its high-frequency flank until it saturates around $M_{rep} \cong 100000$. The power-law behavior of the ratio τ_n / τ_α changes from $M^{4.0}$ for $2M_e \cong 10000 < M < M_{rep}$ to $M^{3.0}$ for $M > M_{rep}$, the latter in agreement with the tube-reptation model (cf. Fig. 1). We take this as evidence for another characteristic molecular weight, namely, $M_{rep} \cong 20\ M_e$, beyond which the exponent of pure tube-reptation is reached.

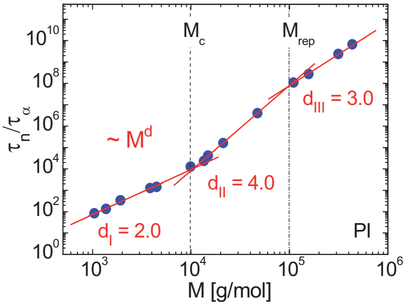


Fig. 1: Ratio τ_n / τ_α of normal mode and segmental correlation time for polyisoprene (PI) as a function of molecular weight M. Three dynamic regimes are revealed with different exponent d [1].

The protracted crossover to full entanglement dynamics is also confirmed by field cycling (FC) ^{1}H NMR which is applied to study the crossover from glassy through Rouse to reptation dynamics [2,3]. Dispersion data of the spin-lattice relaxation time $T_1(\omega)$ are transformed to the susceptibility representation $\chi''(\omega) = \omega/T_1(\omega)$, and using frequency-temperature superposition master curves $\chi''(\omega\tau_\alpha)$ are constructed. We are thus able to monitor the emergence of polymer specific relaxations and a direct comparison with DS is possible. Transforming the master curves into the time domain yields the segmental correlation function which we follow over six decades in amplitude. A comparison with predictions by the tube-reptation model as well as renormalized Rouse theory reveals discrepancies whereas good agreement is found with MC simulations. In agreement with the DS results the crossover to full entanglement dynamics is observable only at $M >> M_e$. Compiling time constants from DS and NMR a broad range ($10^{-11} – 10^2$ s) is covered and master curves are found as a function of $T – T_g$ [4].

[1] Abou Elfadl et al. Macromolecules (2010) in the press
[2] Kariyo et al. Macromolecules 41, 5313, (2008); dito 41, 5322 (2008)
[3] Herrmann et al. Macromolecules 42, 2063 (2009); dito 42, 5236 (2009)
[4] Hintermeyer et al. Macromolecules 41, 9335 (2008)

Polymer - Functional Materials (II)

Thursday 9/Sept
Room A

15:30 - 16:00	**G. Floudas**
16:00 - 16:15	S. Arrese Igor
16:15 - 16:30	M. Hernández
16:30 - 16:45	A. Bernes
16:45 - 17:00	R. Kisiel
17:00 - 17:15	S. Jurga
17:15 - 17:45	**J. Runt**

Effect of pressure on the dynamic heterogeneity of miscible polymer blends

G. Floudas
Dept. of Physics, University of Ioannina, 451 10 Ioannina, Greece and Biomedical Research Institute (BRI-FORTH)
*Email address: gfloudas@cc.uoi.gr

Miscible polymer blends despite being thermodynamically mixed, can exhibit distinct dynamic behavior, known as dynamic heterogeneity.[1] Different models have been proposed to account for the distinct component dynamics that emphasize either *intermolecular* concentration effects through the concentration fluctuation approach, or *intramolecular* effects through the chain connectivity or various combinations of both. Herein we review recent work on the effects of pressure on the dynamic heterogeneity on two miscible polymer blends with large dynamic asymmetry. The first system is the poly(methyl methacrylate) (PMMA)/poly(ethylene oxide) (PEO) blend.[2] The system facilitates a test of the predictions of the self-concentration model proposed by Lodge and McLeish[1], at elevated pressures. We find that pressure increases the glass temperature and slows-down the segmental dynamics but does not affect the length-scale or the self-concentration associated with the dynamic glass transition. The second system is the polystyrene (PS)/poly(methyl phenyl siloxane) (PMPS) blend.[3] In these blends there is interplay between spinodal decomposition and glass transition resulting in the enrichment of the high T_g component by the more mobile component. Model calculations using a lattice-based equation of state lead to prediction of the phase diagram, as well as the effect of pressure on the critical temperature. The weak pressure sensitivity of the critical temperature (dT_c/dP), compared to the two segmental relaxations, suggests that a transition to a thermodynamically miscible but dynamically heterogeneous state takes place for pressures above 300 MPa.

References

[1] C.M. Roland, K.L. Ngai, Macromolecules 24, 2261 (1991); A. Zetsche, E.W. Fischer, Acta Polymer. 45, 168 (1994); T.P. Lodge, T.C.B. McLeish Macromolecules 33, 5278 (2000); G.-C. Chung , J.A. Kornfield, S.D. Smith, Macromolecules 27, 964 (1994).
[2] K. Mpoukouvalas, G. Floudas, Macromolecules 41, 1552 (2008).
[3] A. Gitsas, G. Floudas, R.P. White, JEG Lipson, Macromolecules 42, 5709 (2009).

Effect of Blending on the Chain Dynamics of the "Low-T_g" component in non-entangled polymer blends

Silvia Arrese-Igor[1*], **Ángel Alegría**[1,2], **Juan Colmenero**[1,2,3]
[1]Centro de Física de Materiales CSIC-UPV/EHU.
[2]Dpto. de Física de Materiales UPV/EHU, Materials Physic Center (MPC)
[3]Donostia International Physics Center DIPC.
Apartado 1072, 20080, Donostia-San Sebastián, Spain.
*Email address: waaarirs@ehu.es

The effect of blending on the dynamics of polymers is a relevant topic from both a technological and a theoretical point of view. The separated segmental dynamics of each component in the blend and its phenomenology have been extensively studied in the last decade. In comparison, there are fewer works dealing with the effect of blending on the individual chain dynamics of different components in a blend. Here, we have characterized the effect of blending on the dynamics of Polyisoprene (PI) - the "fast" component- in Poly-*tert*-butylstyrene (PtBS) blends with very large dynamic asymmetry, and at molecular weights well below the entanglement limit, focusing on the normal mode (NM) process. The overall dielectric response of PI becomes slower as the high-T_g component PtBS increases. More interestingly, there is a gradual broadening of both low and high frequency tails of the NM-relaxation. The magnitude of the broadening depends on: i) the concentration; ii) the temperature; iii) the dynamic disparity, i.e. the difference between the component's pure T_g. The onset of the mentioned broadening correlates well with the moment when both the NM of the low-T_g component PI and the α-relaxation of the high-T_g component PtBS have similar characteristic times. The fact that the molecular weight of the components is well below the entanglement limit together with the correlation mentioned above, exclude more habitual interpretations based on topological size effects and point to other factors like dynamic heterogeneity in blends and its effects on the monomeric friction coefficient. Finally, contrary to the behaviour observed in the pure homopolymer, the comparison of the characteristic times for the α- and NM-relaxations shows that segmental dynamics of PI component exhibits a weaker T-dependence than its terminal dynamics. This effect is more pronounced the higher the PtBS content, and as a result, the separation between the maxima of both relaxations ranges from 3 decades in pure PI and PI>50% blends, to 5-6 decades for 20%PI blends.

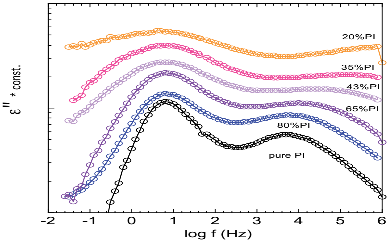


Figure 1: Relative dielectric permittivity of pure PI and PI in its blends with PtBS. For each concentration temperature was chosen so that the NM-relaxation time was 7Hz. All curves are plotted in the same logaritmic scale (2 decades) but have been shifted in the *y* axis for clarity

Effects of strain induced crystallization on the dielectric behavior of natural rubber

M. Hernández[1*], **R. Verdejo**[1], **M.A. López-Manchado**[1], **T.A. Ezquerra**[2]
[1]Instituto de Ciencia y Tecnología de Polímeros, CSIC, Madrid 28006, Spain.
[2]Instituto de Estructura de la Materia, CSIC, Madrid 28006, Spain.
*Email address: marherna@ictp.csic.es

Natural rubber is a well studied elastomer. It is one of the most important materials, which has been widely used in industry as well as in our daily life, e.g., pneumatic tires, tubes, films like surgical gloves, rubber bands, etc. As is typical of an elastomer, its mechanical and physical properties are dependent upon the degree and nature of crosslinking and may be significantly influenced by the surrounding physical environment[1]. Of particular interest is the ability of natural rubber to crystallize, specifically the strain-induced crystallization that takes place whilst the material is stretched. The good performance of natural rubber products has been thought to originate from this ability to crystallize immediately by extension compared to the synthetic counterpart (cis-1,4-polyisoprene rubber; IR). This phenomenon is of great importance because of its effect on the final mechanical properties; the enhancement of tensile modulus along with the superior stress at break and tear strength under fast deformation should be related to the formation of strain-induced crystals[2]. However, despite the knowledge developed thus far, there have been relatively few investigations on how the mechanical strain affects the chain dynamics of natural rubber[3]. These studies are important since an elongated polymer at equilibrium may be considered as a new anisotropic material whose distribution of dielectric relaxation times could be affected by the orientation of the chains[4].

In this communication, we report preliminary results on the influence of uniaxial extension on the dynamics of crosslinked natural rubber by means of broadband dielectric spectroscopy. Previous studies have shown that natural rubber presents two relaxation modes[5]. For temperatures above the glass transition temperature (T_g = -64 ºC), the segmental mode related to the segmental motion of the polymer chain is observed. At higher temperatures, a more intense process which can be assigned to the normal mode is clearly detected. However, when natural rubber is crosslinked, the normal mode becomes broader and decreases in amplitude upon vulcanization due to suppression of large-scale motions of the dipole oriented parallel to the polymer backbone. Thus, in this research, the effect of the orientation on the segmental mode was studied, as a function of the draw ratio. The relaxation times were also investigated. X-ray diffraction experiments were performed in order to study the morphological effects of orientation and to corroborate the strain induced crystallization.

References

[1] T. Suzuki, N. Osaka, H. Endo, M. Shibayama. Macromolecules 43, 1556 (2010).
[2] M. Tosaka. Macromolecules 42, 6166 (2009).
[3] S. Toki, I. Sics, S. Ran, L. Liu, B. S. Hsiao. Macromolecules 35, 6578 (2002).
[4] R. Díaz-Calleja, E. Riande, J. Guzmán. J. Polym. Sci., Part B: Polym. Phys. 28, 1551 (1990).
[5] M. Hernández, J. Carretero-González, R. Verdejo, T.A. Ezquerra, M.A. López-Manchado. Macromolecules 43, 643 (2010).

Storage effects in an adhesive system studied by dielectric relaxations

E. Carsalade[1,2], A. Bernès[1*], S. Perraud[2], C. Lacabanne[1]
[1]Laboratoire de Physique des Polymères - CIRIMAT. Université Paul Sabatier, 31062
Toulouse cedex 4, France
[2]Centre National d'Etudes Spatiales (CNES). 18 Avenue Edouard Belin, 31401
Toulouse cedex 9, France
*Email address: bernes@cict.fr

The stratospheric balloons are the only vehicles which can stay aloft in the stratosphere. Pressurized spherical balloons have been specially developed for onboard scientific experiments. Their specifications require good mechanical strength of an adhesive system in a broad temperature range from -90°C to +170°C. To improve this adhesive system, the correlations between the transitions and the dielectric relaxation processes of an oriented Poly(Ethylene Terephthalate) film (PET) pre-impregnated with a polyester thermoplastic adhesive have been investigated by differential scanning calorimetry (DSC) and dielectric spectroscopies. The polyester adhesive has been studied as reference sample. Two chemical sequences of different molecular mobility are present in the polyester adhesive: $-(CH_2)_4-$ and $-CH_2-CH(CH_3)-$.

This study evidences the adhesive chain segments is responsible of the physical structure evolution of PET film. Transitions and dielectric relaxation modes in the glass transition region appear characteristic of the interphase[1] between adhesive and PET, discussed in term of molecular mobility. Similar relaxations are observed by broadband dielectric spectroscopy (BDS) and thermostimulated currents (TSC). These relaxation modes are associated with the glass transitions of adhesive and PET. The activation energy distribution determined by the TSC technique of fractional polarization can be associated with the adhesive chemical sequences manifestations and can be correlated with the adhesive properties.

The storage at room temperature of the adhesive tape involves the heterogeneity of the physical structure, characterized by glass transition dissociation. Thus, the correlation between the transitions and the dielectric relaxation processes evidences a segregation of the amorphous phases. This phenomenon is responsible of the adhesive properties evolutions. This amorphous phase heterogeneity affects the adhesive performances. These results have been discussed by the molecular mobility interpretations. So, the physical structure and the properties of the material have been linked to the chemical characteristics.

Reference
[1] Y.M. Boiko, G. Guérin, V.A. Marikhin and R.E. Prud'Homme. Polymer. 42, 8695 (2001).

Molecular dynamics in PVME hydrogels at sub-zero temperatures

R. Kisiel[1*], **M. Kozanecki**[1], **A. Schoanhals**[2], **M. Pastorczak**[1], **K. Koynov**[3], **L. Okrasa**[1], **H.J. Butt**[3], **K. Krysiak**[1], **J. Ulanski**[1]

[1] Department of Molecular Physics, Technical University of Lodz, Zeromskiego 116, 90-924 Lodz, Poland
[2] Federal Institute for Materials Research and Testing, Unter den Eichen 87, 12205 Berlin, Germany
[3] Max-Planck Institute for Polymer Research, Ackermannweg 10, 55-128 Mainz, Germany
*Email address: renata.pstrokonska@p.lodz.pl

From applicative point of view the most promising group of hydrogels are stimuli-responsive (particularly: thermo-responsive) materials [1]. Their main advantage is abrupt change in the properties in response to even small modification in environmental conditions. These materials are mostly synthesized from polymers exhibiting lower critical solution temperature (LCST) in water, and poly(vinylmethylether) PVME is an example of such polymer. In a case of crosslinked macromolecules LCST is manifested in a volume phase transition [2].

Systematic studies of hydrogels are commonly conducted in the range of temperature between 0-100°C, nevertheless, investigations of these materials at temperatures below freezing point of water seems to be also important. They should help to understand better phenomena involved in synthesis and applications of cryogels as well as lyophilization processes. From this point of view, molecular dynamics is especially interesting, because it may give valuable information helpful to design hydrogels with precisely define diffusive and/or mechanical properties.

An influence of temperature, crosslinking and swelling degrees on molecular dynamics in thermo-responsible PVME hydrogels was an object of performed investigations. BDS (including high frequency region 1MHz - 3GHz) and DMA were used to study hydrogels synthesized by electron beam irradiation of PVME (to obtain networks with different density of crosslinks various irradiation doses were applied). Investigations were performed at sub-zero temperatures.

Whereas, changes in mechanical modulus of the systems below 0°C relate to freezing and melting (also “pre-melting”) of ice, the high frequency BDS results revealed molecular relaxation process of unfrozen water. Shapes of temperature dependencies of mechanical modulus of the system and dielectric strength of water process, suggests that the water freezes in PVME gels rapidly, while the water melting is strongly influenced by the polymer network. The melting process extends from c.a. -20°C (glass transition of linear PVME) up to 0°C. It means that the molecular dynamics of polymer network and water molecules is interdependent in hydrogels (mobility of the network is stimulated by water molecules, and simultaneously structure and dynamics of water are dependent on polymer concentration). DMA results showed also that the molecular dynamics in PVME gels strongly depends on water content only for weakly swollen samples (below swelling degree 5).

References

[1] Chaterji S., Kwon I.K., Park K., *Smart Polymeric Gels: Redefining the Limits of Biomedical Devices,* Prog. Polym. Sci. 2007 (32) 1083–1122

[2] Gil E.S., Hudson S.M., *Stimuli-responsive polymers and their bioconjugates*, Prog. Polym. Sci. 2004 (29) 1173–1222

Molecular dynamics of miktoarm star block copolymers based on poly(butyl acrylate) and poly(ethylene oxide)

M. Makrocka-Rydzyk[a], A. Wypych[a], M. Jancelewicz[a], S. Jurga[a*]
[a]Department of Macromolecular Physics, Faculty of Physics, Adam Mickiewicz University
Umultowska 85, 61-614 Poznań, Poland
and
K. Matyjaszewski [b]
[b]Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh,
Pennsylvania 1521, USA
*Email address: zfmak@amu.edu.pl

Star polymers, consisting of many arms connected to a central core, represent a branched nanoscale material with compact structure, globular shape, and large surface area [1,2]. Introduction of various functional groups into the star polymers may significantly expand the potential applications of star polymers in various areas, such as: catalysis, optical imaging, drug delivery systems [1].

We have investigated the molecular dynamics of miktoarm (Fig.1), i.e. heteroarm star copolymers made by poly(butyl acrylate) (PBA) and poly(ethylene oxide) (PEO) arms connected to one core, using Broadband Dielectric Spectroscopy (BDS) and NMR techniques. The materials under study were synthesized by means of the atom transfer radical polymerization technique [2]. The molar ratios of PBA/PEO were: 0.80/0.20, 0.50/0.50, 0.20/0.80.

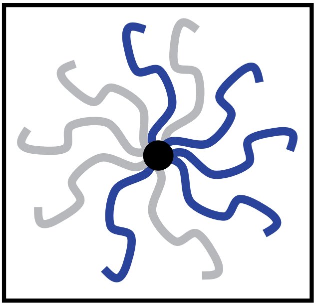


Fig. 1. Schematic structure of miktoarm star block copolymers

BDS measurements, performed in a wide temperature range, allowed to detect two relaxation processes in investigated compounds: α relaxation process - connected to segmental chain motions of polymer backbone and α_c relaxation - arising from constrained mobility of polymer chains in amorphous phase, which are confined by crystallites. In PBA/PEO 0.80/0.20 the crystallization process is partially restricted by high amount of amorphous PBA.

The investigations of NMR spin-lattice relaxation times (T_1) as a function of Larmor frequency, performed for all compounds, confirm dynamics of polymer chains in confined space below melting temperature (T_m), revealing dispersion of relaxation times, which obeys a characteristic for confined dynamics power law of $T_1 \propto \omega^{0.75}$ [3]. However above T_m the frequency dependence of T_1 is described by power laws: $T_1 \propto \omega^{0.5}$ and $T_1 \propto \omega^{0.25}$ at high and low frequencies, respectively. These results reflect chain dynamics, which can be explained on the basis of the renormalized Rouse model in terms of high-mode and low-mode number limits [4].

Acknowledgements
This work is supported by 6th Framework Programme under SoftComp Grant No 502235-2 and research grant No N N202 128536 (Poland).

References
[1] John E. Moses and Adam D. Moorhouse, Chem. Soc. Rev., 2007, 36, 1249–1262.
[2] Haifeng Gao and Krzysztof Matyjaszewski; Macromolecules, 2008, 41, 4250-4257.
[3] Reiner Kimmich and Esteban Anoardo, Prog. NMR Spectrosc. 2004, 44, 257-320.
[4] Nail F. Fatkullin and Reiner Kimmich; J. Chem. Phys. 1994, 101, 822-832.

Dynamics of Polyurethane Block Copolymers in the Undeformed and Deformed States

J. Runt[1*], H. Lee[1], D. Fragiadakis[2], A. Castagna[1], D. Martin
[1]Department of Materials Science and Engineering, Penn State University, University Park, PA 16802 USA
[2]Naval Research Lab, Washington DC 20375 USA
[3]AIBN, University of Queensland, St Lucia, QLD 4072, Australia
*Email address: runt@matse.psu.edu

Following from our research on the phase separated microstructure and unlike segment demixing of segmented polyurethane (PU) block copolymers,[e.g.1,2] we are exploring the dynamics of several families of these copolymers using broadband dielectric spectroscopy. In this paper we focus on PUs synthesized using a two-step polymerization method, having MDI – BDO hard segments and poly(tetramethylene oxide) [PTMO] soft segments (1000 g/mol). The dynamics of the segmental and local processes will be described, as will the behavior of a low frequency relaxation. The latter arises from interfacial (MWS) polarization and its strength decreases significantly with increasing temperature, disappearing at a temperature similar to that where the small-angle X-ray scattering from the phase separated microstructure disappears.

We will also describe initial findings of the role of uniaxial deformation on the dielectric relaxation behavior of several segmented PUs with PTMO soft segments. The α process varies significantly in location, strength, and relaxation breadth with increasing extension ratio (see Figure 1), in contrast to chemically crosslinked cis-1,4-polyisoprene. This behavior is in keeping with the larger effective crosslink density of the polyurethanes and the resulting constrained mobility of soft phase segments.

We would like to express our appreciation to the NSF Polymers Program for support of this research.

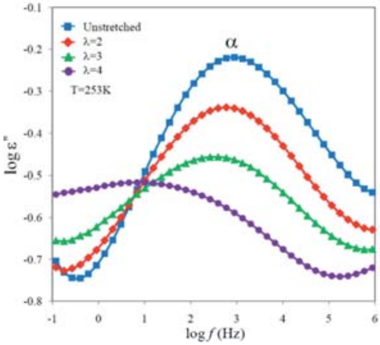


Figure 1. Dielectric loss factor at 253 K of the soft phase α process of a PTMO-based polyurethane with 32.5 wt% hard segments, as a function of extension ratio (λ).[3]

References

[1] R. Hernandez, J. Weksler, A. Padsalgikar, T. Choi, E. Angelo, J.S. Lin, L.C. Xu, C.A. Siedlecki, J. Runt, Macromolecules 41, 9767 (2008).
[2] T. Choi, J. Weksler, A. Padsalgikar, J. Runt, Polymer 50, 2320 (2009).
[3] H. Lee, D. Fragiadakis, D. Martin, J. Milne, A. Milne, J. Runt, Macromolecules In press (2010).

Simulation
-
Theory

Thursday 9/Sept
Room B

15:30 - 16:00	**G. D. Smith**
16:00 - 16:15	F. Affouard
16:15 - 16:30	Z. Ghallabi
16:30 - 16:45	J. Trzmiel
16:45 - 17:00	R.R. Nigmatulin
17:00 - 17:15	M. Yu Balakina
17:15 - 17:45	**J. Dyre**

Dynamics and Relaxation in Room Temperature Ionic Liquids: Molecular Dynamics Simulation Studies Using High Quality Polarizable Force Fields

Grant D. Smith[*], **Dmitry Bedrov and Oleg Borodin**

Department of Materials Science and Engineering, University of Utah, Salt Lake City, Utah, USA
*Email address: gsmith2@gibbon.mse.utah.edu

We have developed a high quality, quantum chemistry based polarizable potential for use in molecular dynamics simulations of room temperature ionic liquids (ILs). The quality and transferability of this force field has been demonstrated through extensive comparison of structural, thermodynamic and transport properties of a large number of ILs with experimental data. Recently, we have been conducting molecular dynamics simulations of ILs comprised of a diverse set of cations and anions utilizing this force field in order to better understand gigahertz to terahertz (nanosecond to picosecond) dynamics in these interesting and important materials. Our hope is to glean insight into the correlation between dynamics and nanoscale structure, as well as the role of cation and anion chemical structure on high frequency dynamics in relaxation processes in ILs. In light of these efforts, I will report on the results of our molecular dynamics simulation studies for a number of ILs. Included in the discussion will be results of our efforts to understand the contribution of rotational and translational motion to dielectric relaxation in these materials. I will also discuss the correlation between high-frequency relaxation, local structure and important bulk transport properties, including ionic conductivity, viscosity and Li^+ conduction in lithium salt doped ILs. The latter are of great interest for use as electrolytes in secondary lithium batteries. Finally, I will report on the relaxation of interfacial structure in ILs in contact with charged substrates (electrodes).

Debye process in ibuprofen glass-forming liquid: insight from molecular dynamics simulation

F. Affouard[1*], N. T. Correia[2]
[1]Unité Matériaux et Transformation (UMET) – UMR CNRS 8207 - UFR de Physique - BAT P5 - Université Lille 1, 59655 Villeneuve d'Ascq, France
[2]REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal
*Email address: Frederic.affouard@univ-lille1.fr

From dielectric spectroscopy (DRS) investigations, most of the molecular glass-formers show multiple non-simple exponential (non-Debye) relaxation processes. In most cases, the lowest frequency and dominant peak is identified to the so-called α-relaxation associated to the cooperative molecular motions and the glass transition. Some other higher frequency secondary processes corresponding to localized motions are also usually observed such as the so-called β-Johari-Goldstein and γ- processes. For unclear reasons, it is known for decades that some monohydroxy alcohols or amides hydrogen bonded (HB) glass-forming systems in which the -OH or the –NH group is sterically accessible behave differently. At the lowest frequency, they exhibit a surprising very intense peak corresponding to a purely exponential or Debye-type decay.

An interesting possibility to investigate the origin of relaxation processes in a different class of HB liquids is offered by racemic ibuprofen. This widely used pharmaceutical compound can be easily supercooled and form a glass. Molecular mobility of ibuprofen has been recently investigated by DRS covering a wide temperature and frequency range[1]. A rich relaxation map was obtained including a Debye type relaxation which unlike to that observed in monohydroxy alcohols and amides possesses an amplitude much lower than the α-process.

By means of Molecular Dynamics simulations, dynamical properties of racemic ibuprofen glass-forming liquid were investigated. The origin of the peculiar low amplitude Debye-type dielectric relaxation observed experimentally is addressed. Since this compound is composed of simple molecules possessing a carboxylic acid group O=C-O-H, it may form a rich linear/cyclic HB multimers distribution – cyclic dimers above all – in the liquid state. Fundamental differences thus exist between ibuprofen and alcohols in their dielectric properties**.** An explanation based on intra-molecular cis-trans isomerism of the carboxylic group is thus suggested. A comparison is made with the Debye-type relaxation found in microstructured monohydroxy alcohols.

References

[1] A. R. Bras, J. P. Noronha, A. M. M. Antunes, M. M. Cardoso, A. Schönhals, F. Affouard, M. Dionisio, N. T. Correia, J. Phys. Chem., 112, 11087 (2008).

Theoretical and experimental study of the composite based polyfluoride of vinylidene P(VDF)/barium titanate

<u>Z. Ghallabi</u>[1,2*] **, M. Arous**[1]**, A. Kallel**[1]**, I. Stevenson-Royaud**[2]**, G. Boiteux**[2] **and G. Seytre**[2]

[1] Laboratoire des Matériaux Composites Céramiques et Polymères, Faculté des Sciences de Sfax, 3018 Sfax, Tunisie
[2]Université Lyon1, UMR CNRS 5223 IMP, Laboratoire des Matériaux Polymères et des Biomatériaux, Bât. ISTIL, 15, Bd. Latarjet F-69622 Villeurbanne Cedex France

*Email address: zied.ghallabi@hotmail.com

Polyfluoride of vinylidene films, filled with barium titanate, are made by extrusion. The dielectric properties of these films are measured under various conditions. The evolution of the relative permittivity and dielectric rigidity according to the volumic fraction is modelled respectively by the theory of mixture and by a semi-empirical model. The mixtures are studied in broadband dielectric spectroscopy. The dielectric measurement results show that the effective dielectric constant of the composite is slightly dependent on the concentration of $BaTiO_3$. These films show interesting characteristics for an application of energy storage.

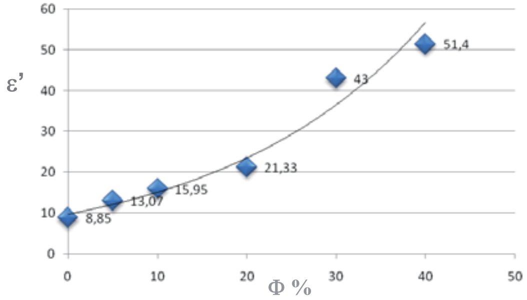


Fig.1. Volume fraction of $BaTiO_3$

Keywords

Composite material; Vinylidene fluoride polymer; Composite; Barium Titanates; Dielectric properties

Two-power-law relaxation processes in semiconductors possessing metastable defects

J. Trzmiel[1*], **K. Weron**[1]
[1]Institute of Physics, Wroclaw University of Technology. Wybrzeze Wyspianskiego 27,
50-370 Wroclaw, Poland
*Email address: Justyna.Trzmiel@pwr.wroc.pl

The non-Debye relaxation behaviour, frequently observed in various dielectric systems, is represented by a low- and high-frequency power-law dependency of the complex dielectric permittivity $\varepsilon(\omega)=\varepsilon'(\omega)-i\varepsilon''(\omega)$ on frequency:

$$\varepsilon(0)-\varepsilon'(\omega)\sim\varepsilon''(\omega)\sim(\omega/\omega_p)^m,\quad \omega\ll\omega_p$$

$$\varepsilon'(\omega)\sim\varepsilon''(\omega)\sim(\omega/\omega_p)^{n-1},\qquad \omega\gg\omega_p,$$

where ω_p denotes the loss peak frequency, $\varepsilon(0)$ - the static permittivity and the power-law exponents m and n fall in the range of (0, 1]. The two-power-law relaxation pattern, characteristic for dipolar complex systems, was observed by us in indium and gallium doped semiconducting mixed crystals $Cd_{1-x}Mn_xTe$ possessing deep metastable defects – the so called DX centers. The power-law exponents, obtained for these materials, satisfy relation m<1-n (see Fig.1.) which, unfortunately, cannot be interpreted by means of the well-known Havriliak-Negami function.

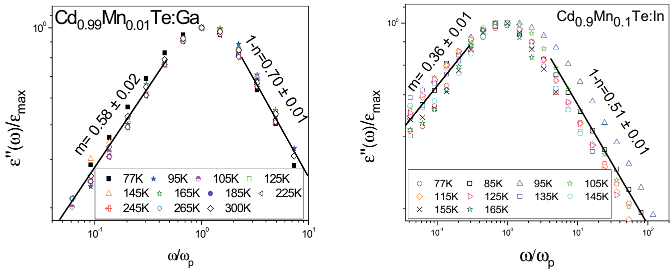


Fig.1. Absorption (imaginary) term of the complex dielectric permittivity $\varepsilon(\omega)=\varepsilon'(\omega)-i\varepsilon''(\omega)$ for $Cd_{0.99}Mn_{0.01}Te$:Ga and $Cd_{0.9}Mn_{0.1}Te$:In samples.

In order to explain the origins of such a relaxation behaviour we propose a correlated-cluster relaxation model leading to the generalized Mittag-Leffler relaxation function. We show that this function is able to reproduce relaxation patterns observed for the investigated $Cd_{0.9}Mn_{0.1}Te$:In and $Cd_{0.99}Mn_{0.01}Te$:Ga samples. The proposed model, taking into account the local randomness resulting from the microscopic anisotropy of the studied samples, allows one to investigate mutual correlations between the defects and brings into light the scale invariant spatio-temporal properties of the studied materials.

We believe that this study will broaden the knowledge on the properties of this important, from the practical point of view, class of semiconducting mixed crystals and also provide useful tools to find the microscopic origins of the two-power-law dielectric relaxation responses for which m<1-n.

Evidences of the fractional kinetics in temperature region: evolution of extreme points in dielectric spectra

R. R. Nigmatullin[1]
[1]Kazan State University. Theoretical Physics Department, 420008 Kazan, Russia
*Email address: nigmat@knet.ru

Based on a new approach that will be presented in detail in the extended paper one can find new evidences of existence of the fractional kinetics not only in the frequency range. One can find rather general principles of detection of different collective motions in temperature region. These principles can be expressed in terms of an algorithm (defined in the paper as an approach). This approach includes some steps that help to separate a couple of the neighboring collective motions (expressed in the frequency range as a linear combination of two power-law exponents) from each other and establish the temperature evolution of the extreme point that follows to the generalized Vogel-Fulcher-Tamman (VFT)-equation. This experimentally confirmed fact gives new evidences for supporting of the theory of dielectric relaxation based on the fractional kinetics[1] on the frequency/temperature domain. As an example for verification of this new approach the ibuprofen complex permittivity data measured in the wide frequency/temperature range were chosen. The reason of such selection was the following. It helps to compare the conventional study of this complex substance recently published in[2] and use possibilities of the developed approach that can add some new features to the picture obtained in the frame of the conventional treatment. We suppose that possibilities presented by new approach will be extremely useful for detection of different collective motions[3] in other substances studied by the method of broadband dielectric spectroscopy (BDS). We derived original expressions that generalize the well-known VFT-equation and applicable for temperature evolution of *any* extreme point (minimal or maximal one).

$$x_m(T) = \frac{\ln\left(\left|\frac{\sin(0.5\cdot\pi\nu_1)}{\sin(0.5\cdot\pi\nu_2)}\right|\right)}{\nu_2-\nu_1} + \frac{\nu_1\ln(\tau_1)-\nu_2\ln(\tau_2)}{\nu_2-\nu_1}, \tag{1}$$

$$Ly_m(T) \equiv 2\ln\left(\frac{y_c(x_m)}{2}\right) = \ln\left(\left|\sin(0.5\cdot\pi\nu_1)\cdot\sin(0.5\cdot\pi\nu_2)\right|\right) + \nu_1\ln(\tau_1) + \nu_2\ln(\tau_2).$$

Here the temperature dependence of characteristic relaxation times $\tau_{1,2}$ (T) and the power-law exponents $\nu_{1,2}$ (T) can be derived from new approach. Theoretical expressions (1) received the excellent confirmation at analysis of the randomly taken complex permittivity data for ibuprofen[3]. New approach generalizes and discovers important details missed in the traditional approach. In particular, this approach implies the following:

(a) that *any* maximal/minimal point (including the hidden ones) in analysis of complex permittivity spectra is *important*;

(b) it says also that the statement 'one peak should be associated with one relaxation process' is correct only for symmetric peaks.

References

[1] R.R. Nigmatullin. Physica B: Condensed Matter. 404 (2009) 255; R.R. Nigmatullin. Dielectric relaxation phenomenon based on the fractional kinetics: theory and its experimental confirmation. Phys. Scripta. T134 (2009) doi:10.1088/0031-8949/2009.

[2] A.R. Brás, J.P. Noronha, A.M.M. Autunes, M.M. Cardoso, A. Schönhals, F. Affouard, M. Dionísio, N. T. Correia, J. Phys. Chem. B 112 (2008) 11087.

[3] R.R. Nigmatullin, Ana R. Brás and N. T. Correia. Ividences of the fractional kinetics in temperature region: detection of ectreme points in ibuprofen. Communications in Nonlinear Science and Numerical Simulations (2010) (has been acccepted for publication).

Modeling of Quadratic Response and its Relaxation Stability for Nonlinear Optical Polymer Electret

M.Yu. Balakina
Institution of Russian academy of sciences A.E. Arbuzov Institute of organic and physical chemistry of Kazan Scientific Centre of RAS, Kazan, Russia
Email address: mbalakina@yandex.ru

Polymer material exhibiting electrical response due to the incorporated organic dipole chromophores is in the electret state resulting from the orientation of chromophore groups in the applied electric field. Material in the electret state is characterized by the macroscopic polarization which is determined by the orientational order of the chromophores. In the polymer electret organic chromophores are in the locally anisotropic polarizable deformable environment. New models and approaches are required for the description of the medium effect on the chromophore nonlinear optical (NLO) response.

In[1-3] we have proposed original analytical approach to the modeling of polymer electret NLO response, which is based on the special ansatz defining the cavity occupied by the chromophore in the material. The cavity is chosen to be conformal to the characteristic ellipsoid of the generalized permittivity tensor of the material, virtual medium inside the cavity being either isotropic or anisotropic. In the framework of the model the local electric field affecting the chromophore in the electret is obtained. This field depends on the applied electric field, macroscopic polarization of the electret, dielectric properties of the medium, as well as on the chromophore electric moment, multipole (quadrupole and octupole) contributions being taken into account in addition to the dipole contribution. The obtained equation establishes relationship between the electret macroscopic polarization and molecular electric characteristics of the chromophores (dipole moment, polarizability and hyperpolarizability). Analytical equations for the pyroelectric, piezoelectric and electrostrictive coefficients of the material are obtained on basis of polymer electret macroscopic polarization.

To study the stability of the polymer NLO electrets quadratic response, which is directly connected with the relaxation of chromophores orientation order, we have suggested an evolutional model accounting for the interrelation of electric, rheological and thermal processes in polymer material. The distinguishing feature of the model is the use of non-stationary equations taking into account pyroelectric, piezoelectric and electrostrictive effects.[2,3] Retardation of the response is described by the integro-differential operators of the special type; one of the models uses the so-called Kohlrausch-Williams-Watts stretched exponential functions. The main attention is given to the relaxation model of two-dimensional polymer film.

References

[[1]. M.Yu. Balakina. Chem Phys Chem 2006, 7, 2115-2125.
[2]. M.Yu. Balakina. J Non-Cryst Solids 2007, 353, 4432-4436.
[3]. M.Yu. Balakina. Russ.Chem.Bull., Int.Ed., 2008, V.57, №7, 1351-1355.

The work is performed under financial support of Russian Foundation for Basic Research (projects № 08-03-01108-a and № 09-03-00696-a).

Modeling ion conduction in disordered solids and other fundamental challenges

Jeppe C. Dyre[1*],
DNRF centre "Glass and Time", Roskilde University, Postbox 260, DK-4000 Roskilde, Denmark
*Email address: dyre@ruc.dk

There is still no simple and generally applicable model for ion conduction in non-crystalline solids like glasses, polymers, etc. It is not known whether or not such a model exists, but data from measurements of, e.g., the conduction's frequency and temperature dependence gives rise to optimism in this regard. One problem is whether - and in which sense - ion conduction may be modeled as the motion of non-interacting particles. This might be the case if the conducting entities are relatively rare, like for instance vacancies or some kind of interstitials. This paper reviews the recent progress on this front[1] and also discusses some other unanswered scientific questions that remain unanswered like how to define the mobile ion density, what are the origins of the mixed-alkali effect, of time-temperature superposition, and of the nearly constant loss.

References

[1] J. C. Dyre, P. Maass, B. Roling, and D. L. Sidebottom, Rep. Prog. Phys. 72, 046501 (2009).

Dielectric Developments

Friday 10/Sept
Room A

9:00 - 9:30	**R. Böhmer**
9:30 - 9:45	G. A. Swartz
9:45 - 10:00	V. V. Meriakri
10:00 - 10:15	A. Axelrod
10:15 - 10:30	B. A. Mazeo
10:30 - 10:45	B. Martin
10:45 - 11:00	M. Abdelguerfi
11:00 - 11:30	**M. Paluch**

Electrical cleaning of dielectric materials: Experimental method for spectral resolution enhancement and recent applications

C. Gainaru, R. Böhmer
Fakultät für Physik, Technische Universität Dortmund, 44221 Dortmund, Germany

The application of moderately large electrical fields to ion containing liquids and solids in combination with temperature cycling enables one to reduce the contribution of conductivity to dielectric loss spectra significantly, in some cases by up to three orders of magnitude, see Fig. 1.[1] This time-honored and simple,[2,3] yet widely unknown technique involves temperature cycling in conjunction with temporary exposure of the sample to an electrical bias field. Electrical purging was recently used profitably in studies of a diverse array of materials such as supercooled liquids, also viscous monohydroxy alcohols, overhydrated proteins, ion-doped clathrate hydrates, and normal-mode polymers. The efficiency of the current method is compared with alternative approaches that were suggested to mitigate the adverse effects that impurity-ion conductivity can have on the resolution of dielectric spectra. Here we will focus on the relative merits of procedures such as derivative analyses, the Kramers-Kronig transformation (KKT),[4] subtraction procedures, as well as the coating of electrodes with insulators. Finally, some limitations and prospects for further developments of the ion sweeping method are discussed.

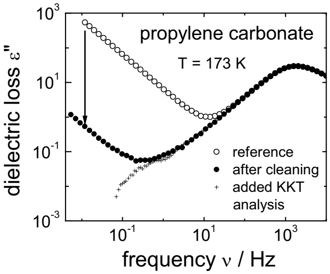


Fig.1. Dielectric loss of a supercooled liquid before and after electrical cleaning.

References
[1] C. Gainaru, R. Böhmer, G. Williams, Eur. Phys. J. B (submitted)
[2] e.g., P. Cebe, D.T. Grubb, Macromolecules 17, 1374 (1984)
[3] E.J.C. Kellar, G. Williams, V. Grongauz, S. Yitzchaik, J. Mat. Chem. 1, 331 (1991)
[4] M. Wübbenhorst, J. van Turnhout, J. Non-Cryst. Solids 305, 40 (2002)

*nano*Dielectric Spectroscopy (*n*DS) of polymeric systems by using Electric Force Microscopy

G.A. Schwartz[1*], R. Arinero[2], C. Riedel[1,2,3], P. Tordjeman[4], A. Alegria[1,5] and J. Colmenero[1,3,5]

[1]Centro de Física de Materiales, M. de Lardizabal 5, 20018 San Sebastián, Spain.
[2]Institut d'Electronique du Sud, Université Montpellier II, 34095 Montpellier, France.
[3]Donostia International Physics Center, M. de Lardizabal 4, 20018 S. Sebastián, Spain.
[4]Institut de Mécanique des fluids, 1 Allée du Prof. C. Soula, 31400 Toulouse, France.
[5]Dep. de Física de Materiales (UPV/EHU), Fac. de Química, 20080 S. Sebastián, Spain.

*Email address: schwartz@ehu.es

Broadband dielectric spectroscopy (BDS) has shown to be a powerful technique to study the molecular dynamics of polymers and glass forming systems over a huge frequency range (10^{-5}–10^{12}Hz) at different temperatures, pressures and under different environments. Although their well known exceptional features, the standard BDS techniques have a fundamental limitation: *they provide no spatial resolution*. To overcome this constrain we have been developing during the last years different approaches[2-5] that allow mapping the local dielectric permittivity of thin films by means of electrostatic force microscopy (EFM) with typical spatial resolution of about 20nm. The proposed experimental methods are based on the detection of both, the topography and the electric force gradient at a given value of the tip-sample distance. In this way we are able to image both the topography and the dielectric permittivity of polymer thin films. Besides the success of these methods they were limited to measure the static dielectric permittivity.
In this work, we present an extension of those methods to measure the local frequency response of thin films. Thus, by means of a standard AFM setup, we are able to measure both, the local dielectric loss spectra over more than four decades in frequency (2-3.210^4Hz) and the dielectric contrast image at a given frequency and temperature. We have tested our method on several systems; we have measured the segmental relaxation on both pure polymers and nanophase-separated polymer mixtures, the secondary relaxation on poly(methyl methacrylate) and the polymer dynamics in nanocomposites. This method seems to be an appropriate tool for approaching fundamental problems of soft matter and will open the door for studying the complex dielectric response in polymers, nano-structured materials, biological systems and soft matter in general.

References

[1] F. Kremer, A. Schönhals, *Broadband Dielectric Spectroscopy*, Springer (2002).
[2] C. Riedel, R. Arinero, Ph. Tordjeman, M. Ramonda, G. Lévêque, G. A. Schwartz, D. G. de Oteyza, A. Alegria, J. Colmenero, J. Applied Phys. 106, 024315 (2009).
[3] C. Riedel, R. Arinero, Ph. Tordjeman, G. Lévêque, G. A. Schwartz, A. Alegria, J. Colmenero, Phys. Rev. E 81, 010801 (2010).
[4] C. Riedel, G.A. Schwartz, R. Arinero, P. Tordjeman, G. Lévêque, A. Alegría, J. Colmenero, Ultramicroscopy doi:10.1016/j.ultramic.2010.02.024 (2010).

Beam Waveguide spectroscopy of Materials in Millimeter and Submillimeter Waves Ranges

V.V. Meriakri[*], **E.E. Chigrai, M.P. Parkhomenko**
Kotel'nikov Institute of Radioengineering and Electronics, Russian Academy of Sciences
Vvedenski sq. 1, Fryazino Moscow Reg. 141190, Russia
*Email address: meriakri@ms.ire.rssi.ru

For wavelengths λ longer than approximately 6-8 mm effective waveguide and resonator technique of materials properties measurement is elaborated. On the other hand for wavelengths shorter than 0.5 mm geometrical optical methods are available.
However, there are some difficulties in carrying out material investigation in the intermediate interval of wavelengths. The reason is that the waveguide technique is ineffective due to a decrease of the waveguide dimensions, gaps between waveguide and sample walls, on the other hand the optical technique is ineffective due to diffraction effect and as a result not allowing the use of geometrical laws of optics.
Therefore we suggested [1] for the measurement of material properties is to use quasi-optical lens beam waveguide transmits only the fundamental low-loss Gaussian type mode with enough small cross-sectional dimensions of a wave beam and large losses for higher order modes. In this case the incident on the plane-parallel specimen wave and the wave on the receiving aperture are the same and it is possible to estimate the measurement errors due to a thickness l of a plane-parallel specimen, inclination of its boundaries to the beam waveguide axis Ψ and cross-sectional dimensions of the specimen a and receiving aperture b. So for beam waveguide consisting of non-reflecting lenses with a and $b > 10\lambda$, $l \leq 1$ cm, $\psi \leq 0.2$, refractive index $n < 5$ the magnitude of errors in transmission $|t|^2$ and reflection $|r|^2$ coefficients are less than$5{\cdot}10^{-3}$, whereas in conventional free space measurements these values may be in this case more than 10^{-1}. Using this quasi-optical set up it was measured complex refractive indexes $n + ik$, in very wide intervals n from 1.05 to 20, $|t|^2$ from approximately 1 to 10^{-6}, $\tan\delta = 2nk/(n^2 - k^2)$ from 10^{-5} to 1, and $|r|^2$ from about 1 to 10^{-4} [1]. There were some new methods and instruments for investigation electromagnetic properties of materials elaborated: equal arm interferometer with sweep of frequency, method immersed in liquid sample, method using a change of liquid thickness, method matching dielectric plate, method for thin lossy films. There were investigated dielectric properties of many low-loss [2] and lossy media: non polar and polar liquids, including water solutions, human blood and skins [3], liquid crystals [4], dielectric and magnetic nano powders, polymers, including polymers with nano fillers (including carbon nano tubes).

References

[1] V.V. Meriakri, Moscow Univ. Phys. Bull., (USA), 47 (3), 81(1992) .
[2] V.V.Meriakri, vol. 12 of «Electrocomponent Science Monographs», London, NY, 117, (2001)
[3] V.V. Meriakri, E.E. Chigrai, D. Kim, I.P. Nikitin, L.I. Pangonis, M.P. Parkhomenko and J.H. Won, Meas. Sci. & Tech., IOP Publishing, 18, 977 (2007)
[4] V.V. Meriakri , E.E. Chigray , I.P. Nikitin, L.C. Pan , R. P. Pan, M.P. Parkhomenko, Proc. of the 34th Intern. Conf. on Infrared, Millimeter, and Teraherz Wave, Korea, (2009), IEEE Catalog Number CFP09IMM-CDR ISMB 978-4244-5417-4, www.irmmw-thz2009.org.

Analyte Detection in Solutions Using Coupled Antennae Impedance Spectroscopy (AIS)

A. Lichtenstein[1], A. Konevsky[1], N.Ferrera[1], D. Nuttman[1], J.Schreiber[2], N. Axelrod[1]

[1] Physical Logic Ltd. 31 Halekhi St., Bney-Brak 51200, Israel

[2] Physical Logic AG.

*Email address: noel@physical-logic.com

High throughput technologies and online monitoring require new label-free methods for real-time sensing of chemicals in the liquid phase.[1,2]

Antennae impedance spectroscopy (AIS) is a technique that interrogates a medium by radiating it with an electromagnetic (EM) field and measures the impedance of the antennae.[3] In a Coupled Antennae Impedance Spectroscopy (CAIS) setup two opposing antennae are based on both sides of a cuvette that contains the probed medium. The antennae response is broadband and allows both reflection and transmittance parameters (S11 and S12) to be measured.

AIS is ideally suited for industrial applications where non-contact, continuous and real-time monitoring of chemical processes and online determination of liquid composition is required.

We apply the CAIS method in the study of biomolecules: proteins (BSA) and saccharides (glucose , fructose, galactose, maltose, lactose and sucrose) soluble in water, electrolyte solution and electrolyte solutions containing human serum.

The antennae signal is measured by VNA in the frequency range from 1 MHz up to 6 GHz at room temperature. The analysis is performed by identifying frequency bands at which temporal changes of the averaged S-parameters are best correlated to the changes of the analyte concentration in cuvette. For each analyte, there is a unique set of frequency bands that can be used both for the identification and quantification of the analyte concentration in solution.

By using the CAIS technique, we were able to determine all examined biomolecule solutions, both quantitatively and qualitatively e.g.: we have demonstrated the ability to differentiate between monosaccharide's stereoisomers in solutions of water and PBS with millimolar resolution.

References

[1] U. Kaatze, Meas. Sci. Technol. 19, 112001, (2008)
[2] U. Kaatze and Y. Feldman, 17 R17–35, Meas. Sci. Technol. (2006)
[3] R. Nilavalan, G. S. Hilton and R. Benjamin, Electronics Letters, 35, 1771, (1999).

Overcoming electrode polarization by magnetic induction spectroscopy

B. A. Mazzeo[1*], **P. Getz**[1]
[1]Department of Electrical and Computer Engineering, Brigham Young University, 459 Clyde Building, Provo, UT, 84604, USA
*Email address: bmazzeo@ee.byu.edu

Electrode polarization is common in dielectric spectroscopy experiments through electrode contact with solution[1]. Because the polarization component is in series with observed phenomena, it complicates the interpretation of dielectric spectra. Electrode spacing, four-electrode methods, and dielectric coatings have all been considered to overcome polarization phenomena[2,3,4]. Additionally, numerical techniques are frequently employed to analyze data and remove the parasitic contribution[5]. Elimination of electrode polarization either numerically or physically is thus critical for proper interpretation of experimental spectra up to through the MHz range.

To avoid this parasitic contribution, electric fields parallel to the electrode surfaces may be induced by employing an alternating magnetic field. Measuring the response of the alternating magnetic field allows inference of the electrical properties of the liquid solution. The in-phase and out-of-phase components correspond to permittivity and conductivity contributions. High-permeability toroids and solenoids with gaps are used to confine magnetic field interrogation to the sample of interest. Numerical results are shown in Figure 1. Theoretical and experimental results, sensitivity, and practicality of this method are discussed and analyzed in comparison with traditional dielectric spectroscopy employing parallel electrode surfaces.

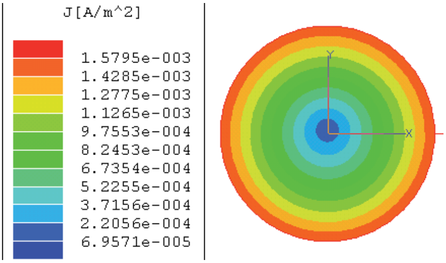


Fig.1. Eddy current simulation (Ansoft Maxwell SV) of 10 mm radius cylinders in an alternating magnetic field. The continuous material medium has a conductivity of 4 S/m and relative permittivity of 81. A magnetic field intensity of 1 A/m is applied to the cylinder. The eddy current is internal to the cylinder.

References

[1] McClendon, J. F. Journal of Biological Chemistry 43, 317 (1920)
[2] Schwan, H. P., Maczuk, J. Review of Scientific Instruments 31, 59 (1960)
[3] Schwan, H. P. *Physical Techniques in Biological Research,* Academic Press (New York) (1963)
[4] Richert, R. European Physical Journal B 68, 197 (2009)
[5] Feldman, Y., Polygalov, E., Ermolina, I. Polevaya, Y., and Tsentsiper, B. Measurement Science and Technology 12, 1355 (2001)

Kohlrausch relaxations by interacting and non-interacting dipoles in PVDF copolymer

B. Martin[*], **H. Kliem**
Institute of Electrical Engineering Physics, Saarland University
Campus, Building A5 1, D-66123 Saarbruecken, Germany
*Email address: b.martin@mx.uni-saarland.de

Thin films of PVDF copolymer are prepared by a Langmuir-Blodgett technique as metal-ferroelectric-metal structures. Small signal measurements in the frequency domain from the mHz range up to the MHz range show a power law for the dielectric permittivity $\varepsilon'(\omega) \sim \omega^{-\beta(T)}$. In the time domain we find a depolarization current $j(t) \sim t^{-\alpha(T)}$. From these measurements alone it cannot be distinguished clearly whether the dipoles in these systems relax independently of each other or if these dipoles are interacting.

To discriminate between interacting and non-interacting dipole systems a field reversal exeperiment is carried out. With a long positive small signal voltage pulse of 1000 s both the fast and the slow dipoles in the ferroelectric system are oriented in positive direction. Now, the voltage pulse is reversed for a short time of 20 s to align the fast dipoles in negative direction. Afterwards, a short circuit is applied to the structure and the total depolarization current is measured. This current crosses zero at a time t_{meas} since the fast and the slow dipoles relax in opposite direction.

On the other hand with the numerical superposition of three time-shifted depolarization currents it is for linear time-invariant systems possible to model the total current after a pulse sequence as described above. This superposition yields also a zero crossing t_{sup} which is identical to t_{meas} only if the system is linear and time-invariant, i.e. if the dipoles do not interact[1,2].

A measured time difference $\Delta t = t_{meas} - t_{sup}$ in dependence of the temperature for PVDF copolymer is shown in Fig. 1. For low temperatures in the ferroelectric state we find $\Delta t \neq 0$ indicating an interacting dipole system. For higher temperatures in the paraelectric state the interaction is lost and we find $\Delta t \approx 0$. Thus, it can be concluded that the small signal relaxational response resulting in the permittivity $\varepsilon(\omega)$ is coupled to the large signal ferroelectric behavior resulting in the hysteresis curve.

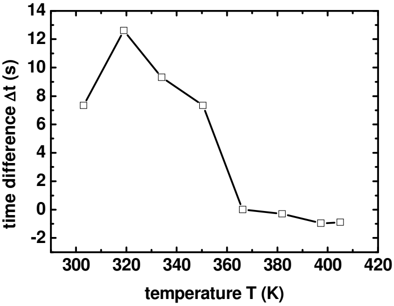


Fig.1. Time difference $\Delta t = t_{meas} - t_{sup}$ for different temperatures.

References

[1] T.C. Guo and W.W. Guo, IEEE CEIDP Ann. Rep., 29 (1982).
[2] M. Kuehn and H. Kliem, phys. stat. sol. (b) 244, 1418 (2007).

New dielectric techniques developed by time domain reflectometry

M. Abdelguerfi[*]**, A.Soualmia***
[*] Faculté de Physique Equipe Spectroscopie Diélectrique USTHB
BP 32 El Alia Alger, Algerie

*Email address :meriemsoualmia@yahoo.fr
a_soualmia@yahoo.fr

Dielectric Spectroscopy is the most fundamental and applied aspects used to describe molecular motions and relaxation process of different kinds of dielectric substances. Its principal characteristic is the wide frequency range over which dielectric matter may respond to an applied electromagnetic field and the observed dielectric response is related to molecular events caused mostly by charge migration and dipole orientation

It is known that migration of charges gives rise to dielectric losses by conductivity(ionic polarization process) and dipole orientation gives rise to dielectric losses by relaxation process (polar polarization process)

Dielectric Spectroscopy applicability is the study of direct correlations between the response of real system that is a dielectric sample and an idealized equivalent model circuit which can describe ionic and polar polarization that give dielectric properties experimentally by measuring the conductivity and the complex dielectric permittivity over the necessary frequency range. Because the whole field of dielectric spectroscopy covers an unusually wide frequency range, a large number of laborious frequency domain techniques may then be required.

However for some decades Time Domain Reflectometry has seemed to be the alternative to the point by point approach in the Frequency Domain; that is obviously due to the fact that in only one measurement, with a single time domain signal applied as a flash to a dielectric sample then we can get a same nature time domain response of the sample

Moreover TDR techniques provide a more intuitive and direct look at the dielectric characteristics of the material. In fact, direct response analysis defines the ionic and polar aspects of the dielectric sample. They offer of course rapid, non destructive, in situ and automated measurements; they also allow predictions and more interpretations.

The aim of the present paper is to gain an improved understanding of the characteristic parameters which describe the dielectric losses model; in the other hand an approach of models describing the dielectric properties and the electrical conductivity

and automated measurements; they also allow predictions and more interpretations.

The aim of the present paper is to gain an improved understanding of the characteristic parameters which describe the dielectric losses model; in the other hand an approach of models describing the dielectric properties and the electrical conductivity

Keywords: *Time Domain Spectroscopy, permittivity, conductivity relaxation.*

Study of Kinetics of Tautomerization Process in some Pharmaceutically Important Molecules – New Application of BDS.

Marian Paluch*, Żaneta Wojnarowska, Patryk Włodarczyk and Kamil Kamiński
Institute of Physics, University of Silesia, ul. Uniwersytecka 4, 40-007 Katowice, Poland
*Email address: marian.paluch@us.edu.pl

There are a number of chemical compounds that readily convert to other isomers when melted or dissolved in a solvent. This phenomenon is known as tautomerization process. The tautomerization phenomenon becomes important problem in pharmacy because various isomers may characterize with different pharmacological activity. In this presentation we will show that the broadband dielectric spectroscopy can be successfully used for monitoring of the mutarotation process of some pharmaceutically important molecules. Basing on these measurements one can construct the kinetic curves and determine the activation energy of this process [1].

References

1. P. Wlodarczyk, K. Kaminski, M. Paluch, J. Ziolo, J. Phys. Chem. B **113** 4379 (2009)

6TH INTERNATIONAL CONFERENCE ON
BROADBAND DIELECTRIC
SPECTROSCOPY AND ITS APPLICATIONS

www.dielectric2010.com
07 - 10 MADRID
SEPTEMBER 2010

Biological Materials (III)

Friday 10/Sept
Room A

12:00 - 12:15	F. Bruni
12:15 - 12:30	M. Vogel
12:30 - 12:45	A. Caduff
12:45 - 13:00	S. Cerveny
13:00 - 13:30	**A. P. Sokolov**
13:30 - 13:45	**CLOSING CEREMONY**

Two dynamic crossovers in protein hydration water

F. Bruni[1*], M. G. Mazza[2], K. Stokely[2], S. E. Pagnotta[3], H. E. Stanley[2], G. Franzese[4]
[1]Dip. di Fisica, Univ. Roma Tre. Rome, Italy. [2]Center for Polymer Studies and Dep. of Physics, Boston University, Boston, Massachusetts, USA. [3]CSIC-UPV/EHU– Materials Physics Center MPC, Donostia-San Sebastian, Spain. [4]Dep. de Física Fonamental, Universitat de Barcelona, Barcelona, Spain.
*Email address: bruni@fis.uniroma3.it

We study the dynamics of the hydrogen bond network of a percolating layer of water molecules adsorbed on globular lysozyme protein by measuring the temperature dependence of the relaxation time of water protons with dielectric spectroscopy. We observe two dynamic crossovers: (i) at *T*~252 K, which we assign to water protons fluctuations along the growing hydrogen bond network; (ii) at *T*~181 K which we interpret as arising from a structural ordering of the water network (Fig. 1). We support this interpretation by comparing our experimental results with calculations on a cell model of water, showing that the two crossovers correspond to two maxima in the specific heat, associated with two structural changes of the hydrogen bond network: the formation of the network at higher *T* and its reordering at lower *T*.
The likely occurrence of quantum effects on the water proton dynamics over the protein surface is suggested, combining dielectric spectroscopy and deep inelastic neutron scattering experiments.

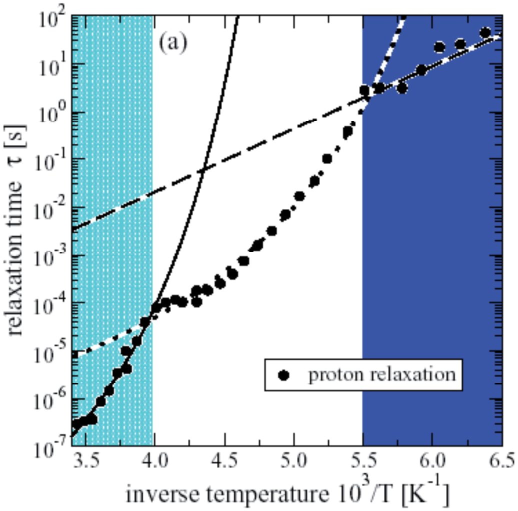


Fig.1. Dielectric relaxation time of water protons (H_3O^+) as a function of inverse temperature for hydrated powders of globular protein Lysozyme. Water content is *h*=0.30 gH_2O/g dry protein.

Comparison of results from nuclear magnetic resonance and dielectric spectroscopy on the temperature-dependent dynamics of protein hydration waters

M. Vogel[*], **S.A. Lusceac**
Institut für Festköperphysik, Physikalisches Institut, Technische Universität Darmstadt.
Hochschulstraße 6, 64289 Darmstadt, Germany
*Email address: michael.vogel@physik.tu-darmstadt.de

Nuclear magnetic resonance (NMR) and broadband dielectric spectroscopy (BDS) yield valuable information about molecular rotational motion. In particular, BDS provides access to molecular dynamics in very broad time and temperature ranges. In NMR, a broad time window can be covered when combining results from spin-lattice relaxation (~ps), line-shape (~μs), and stimulated-echo (~ms) experiments. Furthermore, detailed insights into the geometry of rotational motions are available from NMR line-shape and stimulated-echo analyses. Here, we demonstrate that, for studies of complex molecular dynamics in disordered materials, it is particularly useful to apply BDS and NMR in combination.

We exploit the capabilities of such approach to investigate the temperature-dependent dynamics of water in various types of soft confinements, in particular, in the hydration shells of the proteins myoglobin, elastin, and collagen. We find that the time scales of water reorientation obtained from NMR and BDS are nicely consistent.[1-5] The results yield strong evidence against a sharp crossover in the temperature dependence of the correlation time τ, which was reported in previous neutron scattering work[6] and taken as evidence for the existence of a fragile-to-strong transition for protein hydration water. Exploiting the good agreement between BDS and NMR data, we use the temperature-dependent distributions of correlation times $G(\log \tau)$ determined in BDS as input for ^{2}H NMR line-shape and stimulated-echo analyses performed in the framework of computer simulations.[2-5] This approach allows us to determine the temperature-dependent mechanism for the rotational motion of protein hydration water. The analysis indicates that water performs isotropic rotational jumps down to temperatures of about 200 K, i.e., in rigid elastin and collagen matrices. For the hydration water of myoglobin, there is a crossover from isotropic reorientation to anisotropic reorientation upon cooling, which occurs in the vicinity of the glass transition temperature of the protein at about 200 K. The low-temperature reorientation of protein hydration waters involves large jump angles on the order of the tetrahedral angle.[1,2]

References

[1] M. Vogel, Phys. Rev. Lett. 101, 225701 (2008).
[2] S.A. Lusceac, M. Vogel, and C.R. Herbers, Biochim. Biophys. Act. 1804, 41 (2010).
[3] H. Jansson and J. Swenson, Biochim. Biophys. Act. 1804, 20 (2010).
[4] C. Gainaru, A. Filmer, and R. Böhmer, J. Phys. Chem. B 113, 12628 (2009).
[5] C. Gainaru, A. Filmer, R. Böhmer, S.A. Lusceac, M. Rosenstihl, and M. Vogel (in preparation).
[6] S.-H. Chen, L. Liu, E. Fratini, P. Baglioni, A. Faraone. E. Mamontov, Proc. Natl. Acad. Sci. 103, 9012 (2006).

Chronobiology, dielectric characterisation and the relevance to non invasive in vivo monitoring of biophysical parameters

A. Caduff[1*], P. Zakharov[1], A. Megej[1], F. Dewarrat[1], M. Talary[1]
[1] Solianis Monitoring AG, Leutschenbachstrasse 46, 8050 Zurich, Switzerland
[2] Applied Physics Dept., The Hebrew University of Jerusalem, 91904, Israel

*Email address: andreas.caduff@solianis.com

With the increasing availability of miniaturization of circuitry and low powered micro controllers in vivo, real time dielectric spectroscopy for physiological monitoring with highly portable devices has increasingly become of great interest [1-3]. Such sensor concepts have recently been presented [1-2], integrating different dielectric and optical sensors on one substrate, allowing a wide frequency band electromagnetic characterization of human skin and underlying tissue [1-2]. This Multisensor measures the magnitude and phase at different frequency points between 1 kHz and 2 GHz, combined with 3 different optical wavelengths, temperature and acceleration. A total of 19 different sensors signals can be recorded, transmitted and displayed in real time.

Skin as a complex multilayered heterogeneous dielectric with its own dynamic and structure brings a new challenge in dielectric spectroscopy as a new hierarchy of complexity [4]. This is shown to be the case for challenging applications like non invasive glucose monitoring (NIGM), where different effects with different underlying physical mechanisms can significantly affect the electromagnetic properties of the respective tissue under test.

Chronobiology has seen increasing attention with respect to skin dynamics is. A field where researchers are looking at body rhythmicities with different magnitudes and cycle periods [5-6]. Dermal chronobiological cycles have been indentified that modulate e.g. water migration, blood perfusion characteristics, lipid secretion, skin temperature, sweat secretion or skin thickness to just name a few [5-6]. These parameters expose a wide spectrum of periods that can overlay in sequence or even in combinations with the effective parameters of interest.

The impact of these cycles on the dielectric and optical properties with the underlying mechanisms on human tissue is shown and current strategies to control and combine in suitable ways are presented.

References

[1] Non-invasive glucose monitoring in patients with Type 1 diabetes: a Multisensor system combining sensors for dielectric and optical characterisation of skin. Caduff A et al. Biosens Bioelectron. 2009 May 15;24(9):2778-84.
[2] Scheffler M et al. Wrist-wearable medical devices: technologies and applications. Med Device Technol. 2003 Sep; 14(7):26-30.
[3] Vuorela T, Vanhala J, Hyttinen J. Design and Implementation of a Portable Long-Term Physiological Signal Recorder. IEEE Trans Inf Technol Biomed. 2010 Feb 17.
[4] S. Gabriel, R. W. Lau, C. Gabriel, Phys. Med. Biol. 41, 1996.
[5] Mehling A and Fluhr JW. Chronobiology: biological clocks and rhythms of the skin. Skin Pharmacol Physiol. 2006;19(4):182-189.
[6] Latreille J, Guinot C, Robert-Granie C, Le F, I, Tenenhaus M and Foulley JL. Daily variations in skin surface properties using mixed model methodology. Skin Pharmacol Physiol. 2004;17(3):133-140.

Hydration water dynamics in cement based materials and deoxyribonucleic acid (DNA)

Silvina Cerveny[1], S. Arrese-Igor[1], J, Dolado[4], A. Alegría[1,2], J. Colmenero[1,2,3]
1 Centro de Fisica de Materiales (CSIC, UPV/EHU)-Materials Physics Center, Paseo Manuel de Lardizabal 4, 20018, San Sebastián, Spain
2 Depto. de Física de Materiales, UPV/EHU, Facultad de Química, San Sebastián
3 Donostia International Physics Center, San Sebastián, Spain
4 LABEIN-Tecnalia, Parque Tecnológico de Bizkaia, Derio, Spain

*Email address: sceryeny@ehu.es

The dynamics of water in confined geometries at low temperatures (110-260K) is one of the great challenges that have fascinated the scientific community due to its significant repercussion in several fields of biological, chemical and physical sciences. In particular, the dynamics of confined water is one of the hot topics in the physics of condensed matter as revealed by several publications, contradictory results, and the lack of a coherent frame [1]-[4]. In particular, it has been recently reported the existence of a crossover near T_{cross} = 220K from high-T non-Arrhenius to low-T Arrhenius behavior in several systems [2a,3b,5] and interpreted as a transition from the high density to low density phase of supercooled water (fragile to strong transition - FST). The existence of this crossover is a current hot topic of debate.

In this work we present a different approach to the problem by studying two different systems: hydration water at the surface of deoxyribonucleic acid (DNA) and water in calcium silicate hydrate (C-S-H), the most important hydration product of cement based materials. In spite of the fact that these two systems are substantially different, similarities can be found in the behavior of water dynamics when studied by broadband dielectric spectroscopy (10^{-2} to 10^{8}Hz) in the low temperature range (110-280K). We will show in this work that the origin of the apparent FST can be understood in the frame of a merging between two different relaxations at T_{cross}. This experimental fact indicates that no sign of a fragile-to-strong transition happens in these two systems.

References

[1] Sjostrom J, et al J. Chem Phys 128, 154503 (2008); Yoshida K, et al J. Chem Phys 129, 054702 (2008)
[2] L. Liu et al., Phys. Rev. Lett. 95, 117802 (2005) ; Swenson J, Phys. Rev. Letters 97, 189901 (2006); Cerveny S, et al Phys. Rev. Letter 97 189802 (2006)
[3] W. Doster et al, Phys. Rev. Letter 104, 098101 (2010); Chen et al Proc. Natl. Acad. USA 103, 9012 (2006)
[4] M. Vogel. Phys. Rev. Letter 101, 225701 (2008)
[5] Y Zhang et al, J. Phys.: Condens. Matter 20 (2008) 502101

Dynamics of Biomolecules: Combining Dielectric and Neutron Scattering Spectroscopy

A. P. Sokolov
Department of Chemistry, University of Tennessee, Knoxville, TN 37996-1600, USA
and Chemical Sciences Division, ORNL, Oak Ridge, TN, USA
*Email address: sokolov@utk.edu

Dynamics of biological macromolecules (proteins, RNA, DNA) spread over very broad frequency range. Understanding microscopic mechanisms controlling motions and activity of biomolecules remains a great challenge. In this talk we present analysis of dielectric and neutron scattering data of protein lysozyme, tRNA and DNA. Combination of dielectric and neutron scattering measurements helps to identify various relaxation processes and follow their behavior in a broad temperature range [1,2]. Presented analysis provides assignment of dielectric relaxation processes that disagree with traditional interpretations.

Our analysis reveals strong difference in temperature dependence of relaxation processes in proteins and nucleic acids (RNA, DNA) [2]. Moreover, we demonstrate that dynamics of hydration water also depend strongly on biomolecule. These results contradict to the traditional view of ‘slaved’ dynamics, which assumes that the dynamics of biomolecules is controlled by dynamics of hydration water. It appears that both, biomolecule and its hydration water, have mutual influence.

[1] S. Khodadadi, S. Pawlus, A. Sokolov, J. Phys. Chem. B 112, 14273 (2008).
[2] S. Khodadadi, et al., Biophys.J. 98 (April 2010, in print).

Poster Session

Wednesday 8/Sept
Thursday 9/Sept
11:15-13:30
Claustro

Dielectric study in methacrylate-endcapped caprolactone/poly(ethylene glycol) methacrylate copolymer networks

R. Sabater i Serra[1*], **J.L. Escobar Ivirico**[1,2], **A. Andrio Balado**[3], **M. Monleón Pradas**[1,2,4], **M. Salmerón-Sánchez**[1,2,4], **J.L. Gómez Ribelles**[1,2,4]
[1]Centro de Biomateriales e Ingeniería Tisular. Universitat Politècnica de València, 46022 València, Spain
[2]CIBER de Bioingeniería, Biomateriales y Nanomedicina (CIBER-BBN), Valencia, Spain
[3]Departament de Física, Universitat Jaume I, 12071 Castelló, Spain
[4]Centro de Investigación Príncipe Felipe, 46013 València, Spain
*Email address: rsabater@die.upv.es

Methacrylate-endcapped caprolactone (CLMA) and poly(ethylene glycol) methacrylate (PEGMA) networks were obtained by radical polymerization. Copolymer networks with different compositions were prepared (CLMA/PEGMA: 70/30, 50/50 and 30/70). Dielectric relaxation spectroscopy was employed, along with differential scanning calorimetry, to investigate segmental dynamics in the system. Both the glass transition and the main dielectric relaxation of the CLMA/PEGMA copolymer networks are located between those of the corresponding homonetworks. Copolymer networks show a secondary relaxation process at temperatures below -50ºC, which can be assigned to the overlapping of the corresponding secondary processes for the homopolymer networks: γ_{CLMA}-relaxation is related to the local mobility of caprolactone units[1-2] in CLMA and γ_{PEGMA}-relaxation is assigned to the twisting motions within ethylene glycol moiety in PEGMA[3-5]. Fig. 1 shows the temperature dependence of ε'' at $1{\cdot}10^4$ Hz where the main relaxation and the secondary relaxation processes in both homopolymer and copolymer networks can be observed.

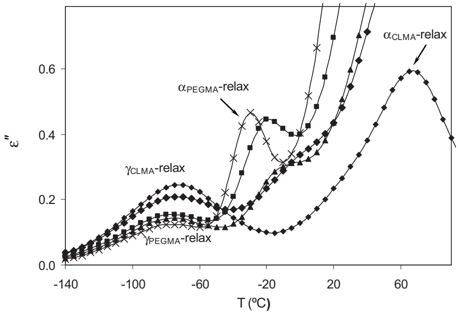


Fig.1. Isochronal curves at 1-10^4 Hz.

References
[1] R. Sabater i Serra, J.L. Escobar Ivirico, J.M. Meseguer Dueñas, A. Andrio Balado, J.L. Gómez Ribelles, M. Salmerón Sánchez. Eur. Phys. J. E. 22, 293 (2007).
[2] M. Grimau, E. Laredo, M.C. Perez, A. Bello. J. Chem. Phys. 114, 6417 (2001)
[3] M. T. Viciosa, A. R. Brás, J.L. Gómez Ribelles, M. Dionisio. Eur. Poly. J. 44, 155 (2008)
[4] M. T. Viciosa, M. Dionisio. J. Non-Cryst. Solids. 44, 155 (2008)
[5] R. Sabater i Serra, M.T. Viciosa Plaza, M. Dionisio, A. Andrio Balado, J.M. Meseguer Dueñas, J.L. Gómez Ribelles. J. Non-Cryst. Solids. 356, 616 (2010).

Dielectric Spectroscopy and Phase Behavior of Side Chain Liquid Crystalline Copolymers

Y.Hepuzer Gursel[1], H. Cinkaya[2], O.Kamer[2], F.Salehli[2]*
[1]Chemistry Department, Faculty of Science and Letters, Istanbul Technical University,
Maslak 34469, Istanbul, Turkey.
[2]Physics Department, Faculty of Science and Letters, Istanbul Technical University,
Maslak 34469, İstanbul, Turkey.
*Email address: salehli@itu.edu.tr

Previous investigations of liquid crystalline (LC) homopolymers with cyanobyphenyl side chains show that above glass transition (T_g) phase transition sequence strongly depend on side chains length [1]. Recently was found that transformations of mezophases are reflected on the temperature evolution of α- and β-relaxation times in the cyanobyphenil polyacrilates [2].The aim of the present work is to investigate how a degree of cooperativity of mezogenic side chains influences the mezophase transformations and dielectric relaxation properties in LC copolymers. For this purpose LC copolymers in which acrylate segment with cyanobyphenil side chain alterating with maleic anhidrit segment in the backbone were sentezed. Dielectric measurements were carried out by Novocontrol BDS in the frequency range of 10^{-2}Hz - 10^{7}Hz in a wide temperature interval with the support of by DSC and polarized light microscopy.

Above the glass transition temperature (T_g=283K) in LC11 maleic anhidrit copolymer (LC11MAC) the phase transition sequence at 314K, 368K and 425K have been observed on the low frequency $\varepsilon'(T)$ on the heating run. At room temperature the small size fan-like structure that coexists with quenched regions are observed in polarized light in LC11MAC.Above 314 K the LC texture become bright with blue / orange regions,suggesting the existence of two kinds of fan-like structure in the sun mezophase: The frustration of the LC texture is observed at temperatures ~380K. Thus the temperature interval between two peaks of $\varepsilon'(T)$ at 368K and 425K can be considered as temperature region of co-existing of izotropic phase and microregions of LC copolymer.

In the $\varepsilon''(\omega)$ spectra well defined δ- and α-relaxation processes were clearly observed above T_g. Both relaxation processes are described well by Havriliak-Negami relation. The δ-relaxation peaks are measured in whole polymeric state between 283K-368K, whereas the α-relaxation mode is active only in the limited temperatures adjacent to T_g. The α-relaxation mode is embedded at T>335K due to increasing level of $\varepsilon''(\omega)$, indicating that copolymeric backbone became essentialy ''soft'' before formation of LC texture. Two stages in the temperature evolution of $\tau^{\alpha}(T)$, which obeys to the VFT relation, have been observed. The anomaly of $\tau^{\alpha}(T)$ coincides with transition at 314K.

In the $\tau^{\delta}(T)$ evolution the three stages were observed with increasing temperature. In the first, between T_g and 314K , and the third stages between 353K-368K the $\tau^{\delta}(T)$ exibits the VFT evolution, whereas in the second stage, between 314K-353K, the Arhenius type of evolution takes place. The third stage of $\tau^{\delta}(T)$, where the fast motions of mezogenic side chains take place coincides with the fluidity processes of LC texture observed in polarized light. We can therefore conclude that the mitigation of the copolymeric backbone is the reason of microphase separation into two kinds of fan-like structure in LCMAC.

References

[1] S.G. Kastromin, V.P. Shibaev, Visokomolekularniye Soedineniya, 41B(11), 1854, (1999).
[2] F.Salehli, S.Yildiz, H.Ozbek, E.Uykur, Y.Hepuzer Gursel, Y.Yuksel Durmaz, Polymer, in press, doi 10.1016/j.polymer.2009.12.029.

Effect of gamma-irradiation on the electret properties of poly-L-lactid

T. Yovcheva[*], M. Marudova, A. Viraneva, E. Gencheva, N. Balabanov, G. Mekishev
Department of Experimental Physics, University of Plovdiv, 24 Tzar Assen Str., 4000 Plovdiv, Bulgaria.
*Email address: temiov@uni-plovdiv.bg

Electret stability of poly-L-lactide (PLA) films, gamma-irradiated up to 100 kGy has been investigated by measuring the surface potential during the storage period. PLA samples – 40 µm thick films, were prepared by casting of solution and then irradiated in a ^{60}Co radiation facility, in air, at room temperature, at a dose rate of 0.25 kGy/h, to absorbed doses of 5, 25, 50 and 100 kGy. After that they were charged in a positive and negative corona discharge conventional corona triode system (5kV). The sample surface potential was measured by the method of the vibrating electrode with compensation. The time dependences of the sample surface potential under room conditions were studied for 30 days. After this period steady state values of the surface potential were established for all of the samples. The structural changes during the irradiation were estimated by viscometric determination of the molecular weight and some thermal characteristics of the films – glass transition temperature, temperatures and enthalpies of cold crystallization and melting and degree of crystallinity.

The values of the surface potential of the irradiated samples, independently of the corona polarity and irradiation dose, were higher in comparison with the non-irradiated samples. This effect could be related to the decrease of the molecular weight of PLA during the irradiation, which was estimated by the decrease of the intrinsic viscosity and melting temperature of the samples. Random chain scission and appearance of end radicals is the most probable result of the irradiation process. The highest values of the surface potential were achieved for samples irradiated at 5 kGy. DSC-thermograms of the samples indicated the highest glass transition temperature and crystallinity of these samples. The crystal structure is related to unhomogeneities in the PLA structure, which could behave like charged traps and lead to stability of the surface potential. Therefore, preliminary gamma-irradiation of the PLA samples could be used as a method for increasing of the surface charge.

It was found out that the surface potential of positively charged PLA films was higher than that for the negatively charged.

The effect of low pressure on the surface potential drop was also investigated. It was ascertained that preliminary storage of the samples at 0.1 mbar pressure led to stability of the electric charge.

Pressure effect on the polymer electrets films behaviour

A. Viraneva[*], T. Yovcheva, E. Gencheva, G. Mekishev
Department of Experimental Physics, University of Plovdiv, 24 Tzar Assen Str., 4000 Plovdiv, Bulgaria.
*Email address: asia83@uni-plovdiv.bg

In the present paper the dependences of the surface potential decay on the pressure under which the electrets were stored and on the storage time were studied.

Polypropylene (PP) samples, 20µm thick, and Polylactic acid (PLA) and poly (ethylene terephtalate) (PET) samples, 40µm thick, charged in a positive or a negative corona were studied. Each sample was placed on a metal pad. The samples were charged to different initial surface potential, by means of a conventional corona triode system. The corona voltage was ±5kV and the grid voltages of the same polarity were 350V, 500V, 650V, 800V and 950V. Charging of electrets was performed under room conditions. After charging the initial surface potential V_0 was measured using the method of the vibrating electrode with compensation, by which the estimated error was better than 5%. After that the electrets were placed into a vacuum chamber under various low pressures for 30 minutes. The pressures in the vacuum chamber were in the range from 0.1mbar to 1013 mbar. After removing the electrets from the vacuum chamber, their surface potentials V were measured again and the normalized surface potentials V/V_0 were calculated.

The results obtained show that charge decay is different for different polarity of the corona voltage (positive or negative) and for different materials (PP, PLA and PET). The dependence of the normalized surface potential V/V_0 on the normalized pressure p/p_0 for all the samples were described by the following equation [1]:

$$\theta = a + \frac{1}{2} b \left(1 + erf \left(\frac{x - c}{\sqrt{2d}} \right) \right)$$

where $\theta = V/V_0$, p_0 is atmospheric pressure, $x = \log(p/p_0)$, and a, b, c, d are constants for each material. The parameters a, b, c, d were calculated and compare for different corona polarity and materials. Processes of desorption from the electret surface due to the electric field are assumed to occur [2].

The dependences of normalized surface potential on the time of storage under room conditions were studied for a month for two sets of samples, charged in a negative corona. For the first set the electrets were stored under room conditions after producing and for the second one they were preliminary placed under low pressure at 0.1mbar for 30 minutes. The results obtained show that the electrets, which have been placed preliminary under low pressure are more stable.

References
[1] A. P. Viraneva, T. A. Yovcheva, E. S. Pisanova, E. A. Gencheva, G. A. Mekishev, AIP Conference Proceedings, 382-388 (2010).
[2] A.P.Viraneva, T.A.Yovcheva, E.A.Gencheva, G.A.Mekishev, JNCS 356, 560-563 (2010).

Influence of the gas media on the stability of corona charged polypropylene films stored at low pressures

G. Mekishev[*], T. Yovcheva, A. Viraneva, E. Gencheva
Department of Experimental Physics, University of Plovdiv, 24 Tzar Assen Str., 4000 Plovdiv, Bulgaria.
*Email address: mekishev@uni-plovdiv.bg

The influence of different factors as humidity, laser irradiation, temperature, pressure, and gas media on charge decay has been studied in order to obtain stable electrets for numerous applications [1-3].

In the present paper the influence of the gas media in which electrets have been obtained on the electrets behavior of samples stored at low pressures was investigated.

Non-metalized samples of 20μm thick polypropylene (PP) film were studied. Initially the PP film was cleaned with alcohol in an ultrasonic bath for 4 minutes, washed in distilled water, and dried under room conditions. The 30mm diameter samples were cut from that cleaned film. All the samples were put onto the same diameter metal pads. The samples were charged in corona discharge in different gas media by a trielectrode system consisting of a corona electrode (needle), a grounded plate electrode, and a grid placed between them. The used gases were O_2, N_2, Ar, CO_2 and dry air. Negative or positive voltage of 5kV was applied to the corona electrode, and negative or positive voltages of 500V and 800V were applied to the grid, respectively. Thus, the electrets were charged to potentials limited by the grid potentials as stated above. Electrets surface potential was measured by the method of a vibrating electrode with compensation.

After charging the initial surface potential V_0 was measured. Then the samples, together with their metal pads, were placed into a vacuum chamber, consisting of an isolated base and a jar bell, when the pressure was decreased step by step from 1013mbar to 0.1mbar. At each pressure the samples were stored for 1 minute. Then the electrets were removed from the vacuum chamber, the surface potential V was measured again and the normalized surface potentials V/V_0 were calculated.

The results obtained show that the gas media in which the corona discharge occurs has a significant influence on the initial surface potential and the charge decay behaviour at low pressures. The decay of the surface potential depends on the sort of the gases. The difference in the effects of gas media on the rate of charge decay of the electrets was supposed to be due to different kinds of surface traps, which arise from the interaction between gas ions and sample surfaces.

References

[1] L. Herous, M. Nemamcha, S. Saad, J. of Eng. and Appl. Sci. 1, 329-334 (2006).
[2] C. Gang-Jin, X. Hui-ming, Z. Chun-feng, J. of Zhejiang Univ. Sci. 5, 923-927 (2004).
[3] G. A. Mekishev, T. A. Yovcheva, A. P. Viraneva, JNCS, 353, 4453-4456 (2007).

Influence of fragility on polymer cold crystallization

A. Sanz, A. Nogales, T.A. Ezquerra
Instituto de Estructura de la Materia, CSIC. Serrano 119, Madrid 28006, Spain
*Email address: asanz@iem.cfmac.csic.es

The first order phase transition by which a supercooled amorphous polymer material transforms into a semicrystalline one continues to be a challenging central problem of polymer physics affecting other fields including material properties and protein crystallization. Although substantial progress has been made in understanding polymer crystallization over the past four decades several aspects of this process remain open. In particular, the influence of chain cooperativity, dynamic fragility and correlated motions on polymer crystallization remain unclear. Here we show the existence of a correlation between nucleation kinetics and dynamic fragility when the crystallization process takes place in the proximity of the glass transition temperature.

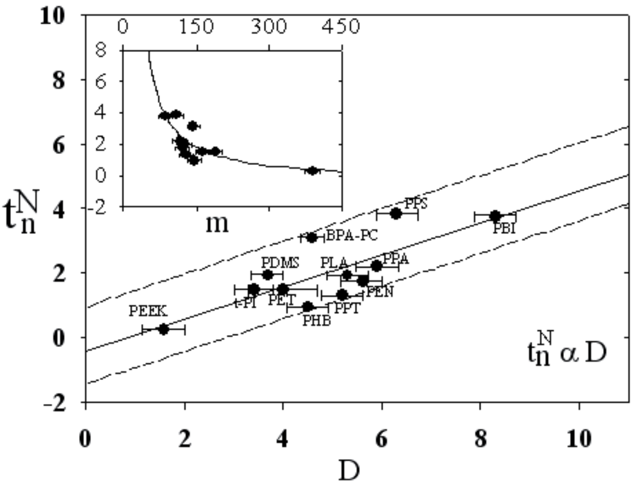


Fig.1. Values of normalized nucleation time factor for different polymers as a function of their corresponding fragility strength values D. Continuous line is the best linear fitting. The inset shows the same data as a function of the fragility index m .

References

[1] A. Sanz, A. Nogales, T. A. Ezquerra Macromolecules, 43, 29 (2010).

Influence of the Crystalline Structure in the Segmental Mobility of Semicrystalline Polymers: Poly(triethylene terephthalate)

I. Martín-Fabiani, A. Linares, A. Sanz, A. Nogales, T.A. Ezquerra
[1]Instituto de Estructura de la Materia, CSIC. Serrano 119, Madrid 28006, Spain
*Email address: imartinf@iem.cfmac.csic.es

The influence of the characteristic nanostructure of semicrystalline polymers on the segmental dynamics has been studied by dielectric spectroscopy (DS) in poly(triethylene terephthalate) (PTT) samples with different degree of crystallinity. In the investigated temperature range (from -100°C to +200 °C), three processes have been identified as maxima in the imaginary part of the complex dielectric permittivity including local, segmental and Maxwell-Wagner-Sillars relaxations. The shape of the relaxations has been analyzed on the basis of the Havriliak-Negami formalism. Simultaneous X-ray scattering and dielectric spectroscopy measurements revealed that, during cold crystallization, crystalline lamellae tend to be homogeneously distributed along the sample. A significant amount of rigid amorphous phase is formed during cold crystallization, and its location is assigned to the crystal-amorphous interface. The formation of the rigid amorphous phase during cold crystallization is less effective for poly(trimethylene terephthalate) than for other similar aromatic polyesters like poly(ethylene terephthalate). The mobile amorphous phase, giving rise to the dielectric α relaxation, is mainly located between consecutive crystalline lamellae. The segmental dynamics of the amorphous phase seems to be restricted by the growing crystals during both primary and secondary crystallization.

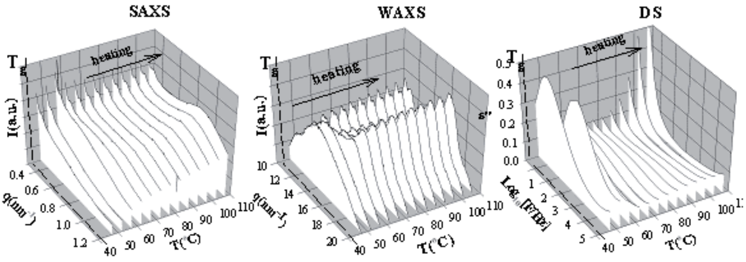


Fig.1. Non isothermal crystallization of initially amorphous PTT followed by SAXS, WAXS and DS at selected temperatures. WAXS and SAXS intensities are represented as a function of scattering vector q. The DS panel shows the evolution of the dielectric loss ε'' with frequency.

References
[1] A. Sanz, A. Nogales, T. A. Ezquerra Macromolecules, 43, 671(2010)

Phase behaviour and dynamics in a symmetric Polystyrene-block-Poly(ethyl methacrylate) Copolymer

A. Sanz*, D. R. Rueda, T. A. Ezquerra and A. Nogales
Instituto de Estructura de la Materia, CSIC, C/ Serrano 121, 28006, Madrid, Spain
*Email address: asanz@iem.cfmac.csic.es

The phase behavior of a diblock copolymer based on poly(styrene) and poly(ethyl methacrylate) is studied in the weak segregation limit[1]. The unmixing of the blocks into a lamellar morphology takes place during heating and the lower critical ordering transition (LCOT) is located approximately at 168 ºC. Fine control of the inter-layers thickness in the ordered phase is achieved by annealing with time-temperature dependence above the LCOT. The irreversibility of the microphase separation makes possible the freezing of the layered structure into room temperature. Therefore, we present a simple way to produce a diblock copolymer with a layered structure controlling on demand the size of the inter-layers spacing in a wide range from 35 nm up to above 50 nm. We are also able to obtain a fine control of the lamellar thickness by controlling temperature and time during isothermal annealing treatments above the LCOT.

Broadband dielectric spectroscopy has been used to study selectively the dynamics of the poly(ethyl methacrylate) chains in both mixed and phase separated PS-b-PEMA copolymers. Compared with a poly(ethyl methacrylate) homopolymer, the α relaxation describing the segmental dynamics shows slower relaxation times and changes in the apparent activation energy (dynamic fragility).

The figure 1 describes the evolution with temperature and time of the inter-layers spacing a in a microphase separated (initially mixed) film of PS-b-PEMA during successive heating and cooling cycles. Following each heating run the sample was annealed at 190 ºC for a selected time (15 s, 45 min, and 1 h, for the 1st, 2nd and 3rd cycle, respectively).

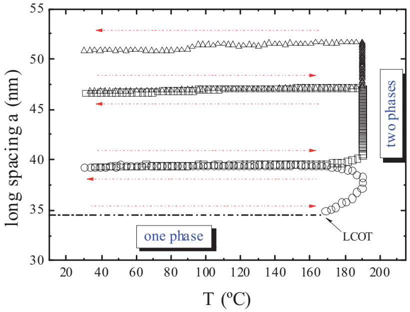


Fig.1. Long period as a function of temperature and time for microphase separated diblock PS-b-PEMA

References

---

[1] F. S. Bates. Science. 251, 898 (1991)

On the use of insulating electrodes in dielectric spectroscopy measurements

S.E. Pagnotta[1*], **S. Cerveny**[1], **A. Alegría**[1,2], **J. Colmenero**[1,23], **F. Bruni**[4]
[1]Centro de Física de Materiales (CSIC-UPV/EHU) - Materials Physics Center MPC, San Sebastián, Spain.
[2] Departamento de Física de Materiales, Universidad del País Vasco (UPV/EHU), Facultad de Química, San Sebastián, Spain.
[3] Donostia International Physics Center, San Sebastián, Spain.
[4]Dipartimento di Fisica "E. Amaldi", Universitá degli Studi "Roma Tre". Roma, Italy.

*Email address: sckpagns@ehu.es

Broadband dielectric spectroscopy is a powerful experimental method to investigate the dynamical behavior of a sample through the analysis of its frequency dependent dielectric response. This technique is based on the measure of a complex quantity (i.e., admittance or impedance) as a function of frequency of a sample sandwiched between two electrodes. In the case of solid protonic conductors, such as ice or hydrated powdered proteins, often insulating layers are inserted between the metal electrode and the sample. In this way it is possible to eliminate free exchange between electronic and protonic charge carriers at the sample–electrode interface, which eventually would lead to a conductivity beyond the level intrinsic in the sample behaviour. However the use of this experimental setup require a carefull data analysis and data reduction in order to extract useful and reliable informations from the measured spectra, which is inevitably distorded by the presence of the insulating layer as recently discussed by several authors[1,2].

In order to account for this distortion, here we present a fitting procedure that is developed and tested against dielectric spectroscopy data collected on different samples, with different conduction properties, and measured with and wihtout the use of insulating electrodes.

References

[1] F. Bruni, S.E. Pagnotta. Phys. Chem. Chem. Phys. 6, 1912 (2004).
[2] R. Richert, Eur. Phys. J. B 68, 197 (2009).

Dielectric properties of poly(2-hydroxyethoxyethylmethacrylamide-co-oxyethylenemethacrylate)s

M.B. Redondo[1], M. Carsí[1], P. Ortiz-Serna[1], M.J. Sanchis[1], R. Díaz-Calleja[1], E. Riande[2], J. Guzmán[2] ,F. García[3]

[1]Instituto de Tecnología Eléctrica, Departamento de Termodinámica Aplicada, ETSII,
Universidad Politécnica de Valencia, Valencia, Spain

[2] Instituto de Ciencia y Tecnología de Polímeros (CSIC) Juan de la Cierva 3, 28003,
Madrid, Spain

[3]Universidad de Burgos, Plaza Misael Bañuelos s/n, 09001 Burgos, Spain

*Email address: marefo@ite.upv.es

Thermal behaviour of a copolymer series of 2-hydroxyethoxyethylmethacrylamide and oxyethylenemethacrylates[1] has been studied by differential scanning calorimetry (DSC). Poly(2-hydroxyethoxyethylmethacrylamide) exhibits the glass transition in the vicinity of 200º C, close to its decomposition temperature. The two copolymers analyzed (90/10 and 95/5) present the glass transition temperature close to -50ºC. Broadband dielectric spectroscopy has been used to study the influence of the composition on the dielectric properties of the copolymer. [1] Dielectric measurements have been performed in the temperature and frequency ranges 133 - 423K and 10^{-2}–10^{8} Hz, respectively. The loss permittivity spectra of the copolymer series show the existence of two relaxations processes associated with local molecular motions. These processes were characterized by using the Havriliak-Negami and Fuoss-Kirkwood empirical equations[2]. The shape and relaxation times of the two absorptions were correlated with the molecular composition of the copolymer.

References

[1] S. Kalakkunnath, D. S. Kalika, H.Lin, R.D.Raharjo, B.D. Freeman, Macromolecules 40, 2773 (2007); Polymer 48, 579 (2007).

[2] S. Havriliak, S. Negami Polym. 8 (1967) 161–210; J Polym Sci, Polym Symp 14 (1966) 99; Fuoss R, Kirkwood JE. J Am Chem Soc. 63:385–9 (1941)

Dipolar and Ionic Relaxations of Poly(methacrylate)s Containing Dimethoxy-Phenyl Side Groups

M.J. Sanchis[1], M. Carsí[1], P. Ortiz-Serna[1], G. Domínguez-Espinosa[1], R. Díaz-Calleja[1], E. Riande[2], L. Alegría[3], L. Gargallo[3], D. Radic´[3]

[1] Instituto de Tecnología Eléctrica, Departamento de Termodinámica Aplicada, ETSII, Universidad Politécnica de Valencia, Valencia, Spain
[2] Instituto de Ciencia y Tecnología de Polímeros (CSIC) Juan de la Cierva 3, 28003, Madrid, Spain
[3] Departamento de Química Física, Pontificia Universidad Católica de Chile, Santiago, Chile

*Email address: jsanchis@ter.upv.es

This work reports a comparative study of the response of poly(2,3-dimethoxy benzyl methacrylate), poly(2,5-dimethoxy benzyl methacrylate) and poly(3,4-dimethoxy benzyl methacrylate)[1] to electrical perturbation fields over wide frequency and temperature windows with the aim of investigating the influence of the location of the dimethoxy substituents in the phenyl moieties on the relaxation behavior of the polymers. The dielectric loss isotherms above T_g exhibit a blurred relaxation resulting from the overlapping of secondary relaxations with the glass-rubber or α relaxation. At high temperatures and low frequencies, the α relaxation is hidden by the ionic conductive contribution to the dielectric loss. A usual, the real component of the complex dielectric permittivity in the frequency domain increases with decreasing frequency until a plateau is reached corresponding to the α glass-rubber relaxation. However, at high temperatures, the real permittivity starts to increase again with decreasing frequency until a second plateau is reached, a process that presumably reflects a distributed Maxwell-Wagner-Sillars relaxation[2] or α' absorption. The α and α' processes appear respectively as asymmetric and symmetric relaxations in the loss electrical modulus isotherms in the frequency domain. To facilitate the deconvolution of the overlapping absorptions, the time retardation spectra of the polymers were computed from the complex dielectric permittivity in the frequency domain using linear programming regularization parameter techniques[3]. The spectra exhibit three secondary absorptions named, in increasing order of time, γ, γ' and β followed by the α relaxation. At long times the α' relaxation, well separated from the α absorption, appears. The replacement of the hydrogen of the phenyl group in position 2 by the oxymetyl moiety enhances the dielectric activity of the poly(dimethoxy benzyl methacrylate)s.

References

[1] L. Gargallo, M.I. Muñoz, D. Radic´ Polymer 27, 14161419 (1986).
[2] Maxwell, J.C. *Electricity and Magnetism*, Clarendon, Oxford 1893; Wagner, K.W. Arch. Elektrotech, 2, 371 (1914); Sillars, R.W.Inst. Electr. Eng., 80, 378 (1937)
[3] Domínguez-Espinosa, G.; Ginestar, D.; Sanchis, M. J.; Díaz-Calleja, R.; Riande, E. J. Chem. Phys, 129, 104513 (2008); Press, W.H.; Teukolsky, S.A.; Vetterling, W.T.; Flannerty, B.P. *In The Art of Scientific Computing*, 2nd ed.; Cambridge University Press: New York, 1992; Chapter 18. Morozov, V.A. *Methods for Solving Incorrectly Posed Problems*; Springer: New York, 1984.

Broadband Dielectric Spectroscopy of Poly(methyl methacrylate-co-(1,4,7,10-tetraoxacyclododecan-2-yl) methyl methacrylate) membranes

M.B. Redondo[1], P. Ortiz-Serna[1], M. Carsí[1], M.J. Sanchis[1], R. Díaz-Calleja[1], E. Riande[2], J. Guzmán[2], F. García[3], J.M. García[3]

[1]Instituto de Tecnología Eléctrica, Departamento de Termodinámica Aplicada, ETSII, Universidad Politécnica de Valencia, Valencia, Spain
[2] Instituto de Ciencia y Tecnología de Polímeros (CSIC) Juan de la Cierva 3, 28003, Madrid, Spain
[3]Universidad de Burgos, Plaza Misael Bañuelos s/n, 09001 Burgos, Spain

*Email address: marefo@ite.upv.es

Polymers containing crown ethers in their structure, offer great possibilities to be useful as metal ions catalysis, ion-exchange membranes, molecular imprinting compounds, surfactans, et.[1]. The dielectric relaxation behaviour of two membranes of poly(methyl methacrylate-co-(1,4,7,10-tetraoxacyclododecan-2-yl) methyl methacrylate) (10/90 and 25/75) has been studied using Broadband Dielectric Spectroscopy in the frequency range 10^{-2} to 10^{8} Hz and temperature window 148 -383K. The spectra apparently show three strongly overlapped relaxations obscured at high temperature and low frequencies by an important conductive contribution. Taking into account that compliance relaxation processes are better defined in the retardation time spectra than in the loss spectra in the frequency domain, the analysis of the overlapped dielectric relaxations was carried out by means of retardation time spectra[2] obtained from the complex dielectric permittivity in the frequency domain using a Tikhonov regularization technique[3]. Deconvolutions of the overlapping peaks in the retardation spectra were performed using Havriliak-Negami type empirical equations[4]. Dipole correlation functions were calculated from the Retardation Spectra and subsequently, the Williams ansatz was analyzed[5].

References

[1] C.J. Pedersen, The Discovery of the crown ethers. Nobel lecture 8 (1987); N.J. Turro, P.L. Kuo. J. Phys. Chem. 90, 837-841 (1986)
[2] Riande, E.; Díaz-Calleja, R. *Electrical Properties of Polymers* Dekker, New York, 2004, Chap. 8; Kremer, F., Schönhals, A. *In Broadband Dielectric Spectroscopy* , Springer: Berlin 2003
[3] G. Domínguez-Espinosa D. Ginestar, M.J. Sanchis, R. Díaz-Calleja, E. Riande, J.Chem. Phys. 129, 104513, (2008)
[4] S. Havriliak, S. Negami Polym. 8, 161–210 (1967); J Polym Sci, Polym Symp 14, 99 (1966)
[5] G. Williams, Adv. Polym. Sci. 33 (1979) 60,; G. Williams, in *Keynote Lectures in Selected Topics of Polymer Science*, edited by E. Riande CSIC, Madrid, 1995, Chap. 1

Molecular dynamics of 2,2,2-trifluoroethylacrylate polymers investigated by dielectric spectroscopy

M. Raihane [1], E. G. Merino[2], S. Atlas[1], A. Belfkira[1], M. Dionísio[2], N. Correia [2*]

[1] Laboratory of Bioorganic and Macromolecular Chemistry-Faculty of Sciences and Technologies (FST) -Av. A. Khattabi, BP.549, 40000 Marrakech, Morocco

[2] REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa, 2829-516 Caparica, Portugal.

*Email address: n.correia@dq.fct.unl.pt

High dielectric constant polymers are becoming crucial components in advanced electronic devices, such as memory and gate dielectrics for integrated circuits, stationary power generation, and miniature capacitors for telecommunication[1]. Polymers containing polar substituents such as cyano and fluoro groups are of interest in the development of advanced electrical and optical materials because of the large dipole moment arising from their polar substituents (C-CN and C-F) [2,3]. Combining fluorinated monomers and comonomers bearing cyano groups should induce a synergetic effect on the properties for the resulting copolymers [4].

To develop new dielectric polymers containing CN and F groups with strong dipole moments, the radical copolymerization of acrylonityrile (AN) with 2,2,2-trifluoroethyl acrylate (ATRIF) as a fluorinated comonomer initiated by AIBN have been reported in this present work. The homopolymer of ATRIF was also prepared. The NMR analysis has shown that the molar percentage of AN in the copolymer was 58 mol %.

Both copolymer, poly(AN-co-ATRIF), and homopolymer, Homo-ATRIF, were dielectrically characterized over a frequency range from 10^{-1} to 10^{6} Hz, and in a temperature range from 223 to 393 K. The dominating relaxation process detected in both materials was the α-relaxation, associated with the dynamic glass transition. A significant shift of the dielectric loss curves for lower frequencies/higher temperatures of poly(AN-co-ATRIF) relative to the homopolymer was observed, revealing an hindered mobility originated by the inclusion of acrylonitryle groups in the copolymer.

A VFT temperature dependence of the relaxation times (τ) was found, as characteristic of cooperative processes. The extrapolation of the VFT equation to τ=100 s allowed to estimate a glass transition temperature (T_g) for each material, which differ ~ 40 K, the one of the copolymer being higher (308 K) in accordance with the shift in the isotherms. The study was complemented by differential scanning calorimetry, from which the T_g values determined, respectively 273 and 313 K for the homo and copolymer, are in good agreement with those dielectrically obtained.

Acknowledgments: The authors thank the financial support to the Action of Cooperation (Maroc/Portugal) 415/CNRST/Marrocos.The authors thank also the Swedish Research Links Programme for the framework "International Research Grant" Sweden - MENA (Middle East and North of Africa) (Ref: VR 2008-6002) between FST (Marrakech) and KTH (Stockholm).

References

[1] (a) R.C.G. Naber, C. Tanase, P.W. Blom, F.J.Touwslager, S. Setayaesh, D.M. de leeuw, Nat. Mater. 4, 243 (2005). (b) A. Meskini , M. Raihane , I. Stevenson-Royaud , G. Boiteux , G. Seytre , B. Ameduri J of Non-Crystalline Solids 356, 688–694 (2010).

[2] Gerhard-Multhaup R. Ferroelectrics;75:385–92 (1987).

[3] Koizumi S, Tadano K, Tanaka Y, Shimidzu T, Kutsumizu S, Yano S. Macromolecules. 95, 6563 (1992)

[4] A. Meskini, M. Raihane, B. Ameduri, C. Hakme, D. Sage, I. Stevenson, G. Boiteux, G. Seytre, H. Kaddami, Eur. Polym. J. 45, 804 (2009).

Crystal growth in low density poly(ethelene) observed by use of ion motion

Y. Anada
Department of Business and Information Systems, Faculty of Business Administration
and Information Science, Hokkaido Information University.
59-2 Nishi-Nopporo, 069-8585 Ebetsu,
Japan
Email address: anada@do-johodai.ac.jp

The knowledge of the crystal growth mechanism of polymer is remarkably developed by Lauritzen-Hoffman theory.[1] After this theory, the existence of density fluctuation or ordered structure in the non-crystalline part in polymers have been pointed out.[2,3] On the other hand, an approach of broad band spectroscopy has been made for this matter recently. In the time development of the permittivity at a constant temperature, an initial increase of permittivity was observed before an decrease of permittivity.[4,5] Although the decrease of the permittivity is considered to be originated from spherulite growth, the increase of permittivity is presumably related to the initial stage of crystallization. In these studies, this phenomenon is investigated by using the dipole of polymers as if it is a dynamic probe for polymer aggregation. On the other hand, the ions naturally existing in the free space in polymer may be used as a dynamic tracer to research the mechanism of this phenomenon. In the previous study,[6,7] the increase and decrease processes in the time development of permittivity of low density poly(ethylene) (LDPE) is investigated by electrical broad band spectroscopy method. The Avrami equation was applied to permittivity data and the Avrami index were estimated. As the experiment was carried out only at one temperature in the previous study, the knowledge obtained in the experiment is limited to consider the crystal growth. In this study, the permittivity was observed at plural temperatures in order to obtain more information. Other experimental conditions are the same as before. Melting temperature of the present sample of LDPE is ca.110 degree centigrade. As a result of experiment, the Avrami index was estimated at 2.9 in average for the permittivity-decrease process at the three different temperatures, 94, 97 and 100 degree centigrade. The value of the index corresponds with three-dimensional growth in the inhomogeneous nucleation.[8] Therefore, it is considered that the spherullite growth was detected by ion motions. For the permittivity-increase process, the Avrami index was estimated at 2.4 in average. Although this value is a little larger than that for the two-dimensional crystal growth, this result suggests that the ion motion in the initial process is related to the lamella growth.

References

[1] J. I. Lauritzen, J. D. Hoffmann. J. Res. NBS 31,1680(1959).
[2] N. V. Pogodina, S. K. Siddiquee, J. W. van Egmond, H. H. Winter. Macromolecules 32(4),1167(1999).
[3] Z. D. Wang, B. S. Hsiao,E. B. Sirota, P. Agarwal, S. Sirinivas. Macromolecules 33(3), 978(2000).
[4] G. R. Saad, A. A. Kansour,A. H. Hamed. Polymer 38,4091(1997).
[5] A. Wurm, R. Soliman, C. Shick. Polymer 44,7467(2003).
[6] Y. Anada. Abstract of 5th BDS 2008. 168(2008).
[7] Y. Anada. Proceedings of 7th EMSES, 51(2009).
[8] T. Hatakeyama, F.X. Quinn. Thermal Analysis, Baffins Lane, Chichester, John Wiley & Sons, (1999).

Low k dielectric materials in electronic interconnect devices

I. Abuetwirat
Faculty of Electrical Engineering and Communication Technická 8, 616 00 Brno, Czech Republic
*Email address: butwiratines@Yahoo.com

The continuing improvement in the microelectronic integrated circuit (ISc) is to a large extent the result of reduction in the device size. This enables an increase in the device packing density[1] in the single chip and the processing speed. An emerging factor that may disrupt this trend[2] is the propagation delay and power dissipation within the chip, due to resistance capacitance (RC) coupling become significant. Several developments are in progress on vapour deposition of Polytetrafluoroethylene (PTFE) to reduce C, and to implement high conductive metal to reduce R. Dielectric spectroscopy has proven very useful for studying the conformation, structure and the dynamic of polymer system[3]. Dielectric constant and loss tangent of PTFE sheet with thickness 0.15 mm have been measured at room temperature by using commercial impedance analyzer with frequency range from 2o Hz to1 MHz. A low dielectric has been observed as a bout 2.1.at 1 MHz.

References

[1] M. Kremer. The Search of Low- Dielectric Constant Materials. (Leipzig) D(04103), 3 (1989).
[2] D.Shamiryan,T. Abell, F. Lacopi, K. Maex.Low-k Dielectric materials. Materialtoday.vol 7 34(2004)
[3] G. Schaumburg. Novocontrol Provides Application notes on Dielectric Spectroscopy, 4 (1989)

Dielectric Properties of Poly (2-ethoxyethyl methacrylate-co-2,3 dihydroxypropyl methacrylate) Membranes

M. Carsí [1*], P. Ortiz-Serna[1], M. B. Redondo[1], R. Díaz-Calleja[1], M. J. Sanchis[1], E. Riande[2], J. Guzmán[2].

[1]Instituto de Tecnología Eléctrica, Departamento de Termodinámica Aplicada, ETSII,
Universidad Politécnica de Valencia, Cno. De Vera s/n, 46022. Valencia, Spain
[2]Instituto de Ciencia y Tecnología de Polímeros (CSIC),
Juan de la Cierva 3, 28003, Madrid, Spain

*Email address: mcarsi@ter.upv.es

The dielectric relaxation behavior of a serie of copolymers membranes of 2-ethoxyethyl methacrylate (EEMA) and 2,3 dihidroxypropylmethacrylate (DHPMA) has been studied using broadband dielectric spectroscopy (DRS) in the frequency domain of 10^{-2} to 10^{8} Hz and at temperatures between 123 and 473 K. The influence of the composition on the dielectric properties of the copolymers is described[1-2, 6].

The loss permittivity spectra of the copolymer series shows the existence of almost three relaxations processes in the temperature-frequency range studied. At high temperature and low frequencies, the isotherms representing the dielectric loss as a function of frequency show important conductive contribution overlapping the loss factor. The alpha process, associated with the dynamic glass transition, is resolved from the dielectric spectra by modelling with Havriliak-Negami (HN) function[3-4]. Moreover, the secondary relaxations, beta and gamma processes, has been conveniently analysed in terms of the empirical Fuoss-Kirkwood (FK) equation.

The alpha process corresponds to the cooperative relaxation correlated to the glass transition and arises from main-chain cooperative micro-brownian motions and follows Vogel-Fulcher-Tammann (VFT) behavior[5]. On the other hand, the local beta process originates from side-chain rotation of the asymmetric side group about the C-C bond connecting it to the polymer backbone. In the lower temperature range, these copolymers show one more relaxation, the gamma relaxation, that can be attributed to the response of the ethoxy group in the side chain.

References

[1] McCrum N. C., Read B. E., Williams, G. Anelastic and Dielectric effects in polymeric solids. Wiley, London 1967; Kremer, F., Schönhals, A. Broadband Dielectric Spectroscopy Springer Verlag, Berlin 2003.
[2] Riande, E.; Díaz-Calleja, R. Electrical Properties of Polymers, Marcel Dekker, New York, 2004.
[3] Havriliak S, Negami S. Polymer, 8,161–210 (1967)
[4] Havriliak S, Negami S. J Polym Sci, Polym Symp, 14, 99–117 (1966)
[5] Vogel HZ. Phys.;22:645 (1921). Fulcher GS. J. Am. Ceram. Soc. 8 339(1925); Tamman G, Hesse WZ. Anorg. Allg. Chem. 156, 245 (1926)
[6] G. Williams, Adv. Polym. Sci. 39, 59 (1979)

Assessment of mechanical and dielectric characteristics of polyethylene/polar seed hair systems

S. Aradoaei[1*], R. Darie[2], I. Spiridon[2], R. Ciobanu[1]
[1]Technical University of Iasi. Blvd. D. Mangeron 53, 700050 Iasi, Romania
[2]Romanian Academy, "Petru Poni" Institute of Macromolecular Chemistry. 41 A Gr. Ghica Voda Alley, 700487, Iasi, Romania
*Email address: asteor@yahoo.com

Nowadays, the growing environmental awareness throughout the world has triggered a paradigm shift towards designing environmentally friendly materials. The interest in cellulose fibers as reinforcement agents in composite materials with polymer matrices has increased dramatically in the last decades, the main reasons associated with this upsurge being their renewable and ubiquitous character, good mechanical properties, low density, low cost and recyclability.

In the present work, several blends containing different types of polyethylene and poplar seed hair have been obtained by melt processing. The influence of the natural component amount on the processing, mechanical and dielectric behavior of the studied bio-composites has been evaluated [1].

References

[1] S. Aradoaei, R. Darie, G. Constantinescu, M. Olariu, R. Ciobanu. Modified lignin effectiveness as compatibilizer for PET/LDPE blends containing secondary materials, NOC 14511, (2010).

Morphology and dielectric properties of some LDPE/PA blendes in present of compatibilizers

R. Darie[1*], S. Aradoaei[2], R. Ciobanu[2], C. Vasile[1],
[1]Romanian Academy, "Petru Poni" Institute of Macromolecular Chemistry. 41 A Gr. Ghica Voda Alley, 700487, Iasi, Romania
[2]Technical University of Iasi. Blvd. D. Mangeron 53, 700050 Iasi, Romania
*Email address: ucadarie@yahoo.com

Interest in blending polyethylene with polyamide is due to the differences in their properties, mainly the barrier properties. Polyethylene transmits oxygen and hydrocarbons but it is resistant to moisture. Polyamide is highly sensitive to moisture but a good oxygen barrier. Thus, the main applications of the two polymers are in packaging films and containers requiring low permeability. Another disadvantage of polyamides is their low resistance to stress in the presence of sharp notches or cracks, commonly evaluated as notched impact strength. To overcome this deficiency, polyamides have been blended with several types of impact modifiers, typically elastomeric or low modulus type olefinic polymers. Compatibilizers, which reduce the interfacial tension and stabilize the dispersed structure, can be added to improve the properties of polyethylene/polyamide blends [1].

In order to improve the compatibility in a polymer blend composed of two normally incompatible constituents as LDPE and PA6, a small amount of rubbery phase and different types of compatibilizers have been added, in other words, applying reactive compatibilization cumulated with the impact modification, because LDPE presents poor reactivity and PA contains carboxyl and amino- end groups as well as amidic bonds. In a previous study the efficiency of some compatibilizers upon thermal and impact properties has been proved [2]. In this work, the compatibilization effect was evaluated by analyzing the melt processing, morphology and dielectric properties.

References

[1] M.K. Akkapeddi, Commercial polymer blends, in Polymer Blends Handbook, Vol 2, Utracki, L.A. (ed.), Kluwer Academic Publisher, Dordrecht, 1023-1115 (2002).

[2] R.N. Darie, C. Vasile, M. Kozlowski. The effect of compatibilization in the reactive processing of the low density polyethylene/polyamide 6/EPDM blends", Polimery, 51 (9), 656-661 (2006).

Study of the nanostructure of phase-separated polymer mixtures by using Electrostatic Force Microscopy

M.M. Kumali[1*], G.A. Schwartz[2], A. Alegría[1], J. Colmenero[1-3]

[1]Dep. de Física de Materiales UPV/EHU, Fac. de Química, 20080 San Sebastián, Spain.
[2]Centro de Física de Materiales, M. de Lardizabal 5, 20018 San Sebastián, Spain.
[3]Donostia International Physics Center, M. de Lardizabal 4, 20018 S. Sebastián, Spain.

*Email address: mmkummali001@ikasle.ehu.es

Single as well as multi-components polymer thin films are of great interest because their properties can be very different from bulk, and directly related to many important surface phenomena such as coating, adhesion, surface friction and lubrication among others[1]. In particular, the nanostructure of thin films of non-miscible polymer blends has recently created great interest[1-4]. One of the most useful approaches typically used for studying the polymer distribution in thin films is atomic force microscopy (AFM). This technique is very versatile and allows measuring the size and distribution of the different phases in heterogeneous polymer blends. However, AFM measurements are typically limited to topographic or phase imaging (related with the surface mechanical properties) which give partial information about the distribution of the polymer chains in the blend. To overcome this constrain we have studied the nanostructure of phase-separated polymer mixtures using a recently developed experimental approach that allows imaging the local dielectric permittivity of thin films by means of electrostatic force microscopy (EFM)[5-7]. This experimental method is based on the detection of both, the topography and the electric force gradient at different values of the tip-sample distance. In this work we analyze by means of EFM the nanostructure of thin films of polystyrene (PS) and poly(vinyl acetate) (PVAc) blends with different thicknesses and thermal treatments. We will show that the dielectric response not only is fully decoupled from the topography, but also gives additional information about each polymer phase as well as the interphase.

References

[1] H. Ogawa, T. Kanaya, K. Nishida, G. Matsuba, J.P. Majewski, E. Watkins, J. Chem. Phys. 131, 104907 (2009).
[2] H. Ogawa, T. Kanaya, K. Nishida, G. Matsuba, Polymer 49, 254 (2008).
[3] H.J. Chung, R.J. Composto, Phys. Rev. Lett. 92, 185704 (2004).
[4] H. Ogawa, T. Kanaya, K. Nishida, G. Matsuba, Polymer 49, 2553 (2008).
[5] C. Riedel, R. Arinero, Ph. Tordjeman, M. Ramonda, G. Lévêque, G. A. Schwartz, D. G. de Oteyza, A. Alegria, J. Colmenero, J. Applied Phys. 106, 024315 (2009).
[6] C. Riedel, R. Arinero, Ph. Tordjeman, G. Lévêque, G. A. Schwartz, A. Alegria, J. Colmenero, Phys. Rev. E 81, 010801 (2010).
[7] C. Riedel, G.A. Schwartz, R. Arinero, P. Tordjeman, G. Lévêque, A. Alegría, J. Colmenero, Ultramicroscopy doi:10.1016/j.ultramic.2010.02.024 (2010).

Combined DDS and TSC studies of dipolar relaxations in PEEK

A. Leonardi[1], **E. Dantras**[1,*], **C. Lacabanne**[1]

[1]Laboratoire de Physique des Polymères, Institut Carnot CIRIMAT, Université Paul Sabatier, 31062
Toulouse 9, Cedex, France
*Email address: dantras@cict.fr

Poly(ether-ether-ketone), PEEK, is an attractive high performance thermostable thermoplastic polymer with properties strongly dependent upon crystallinity and morphology. The potential to control thermal history through processing conditions makes it of interest in the study of structure/properties relationships. To ensure the amorphous nature of PEEK, DSC analyse gave rise to the step of the heat flow associated with the thermodynamic glass transition and an exothermic peak due to cold crystallization.

Morphology of PEEK has been described with a 'three-phase model' [1] [2] containing the crystallites, the mobile amorphous and the rigid amorphous fractions highly constrained by crystallites.
The temperature dependence of molecular mobility of PEEK has already been characterized by Thermally Stimulated Current (TSC) [3] and Dynamic Dielectric spectroscopy (DDS) [4] [5] [6]. Dielectric properties were often hampered by dissipative losses due to ohmic conduction. A Kramers-Kronig transform [7] was used to allow the calculation of dielectric relaxation losses ε''_{KK} from the real part $\varepsilon'_{T(\omega)}$ of the complex permittivity obtained by DDS.

Secondary dipolar relaxations have been revealed: they are associated to non-cooperative localized mobilitys. The main α relaxation, occurring close to the glass transition temperature and following a VFT equation, was attributed to delocalized cooperative motions of the free amorphous phase. At higher temperature, the relaxation α_c has been attributed to the rigid amorphous phase.

The aim of this work is to study the dynamic behaviour of PEEK over a broad dynamic range by combining DDS and TSC. Results provide a phenomenological model explaining heterogeneity of amorphous PEEK and improve the knowledge of molecular/dynamic structure relationships.

[1] S.Z.D. Cheng, M.Y.Cao, B.Wunderlich, Macromolecules 19, 1868 (1986)
[2] BB. Sauer, B.S. Hsiao, Polymer 36, 2553 (1995)
[3] M. Mourgues-Martin, A. Bernes, C. Lacabanne, J. of Thermal Analysis 40, 697 (1993)
[4] P. Huo, P. Cebe, Macromolecules 25, 902 (1992)
[5] A. Nogales, T.A. Ezquerra, Macromolecules 32 2301 (1999)
[6] A. A. Goodwin, J.N. Hay, Polymer science Part B 36, 851 (1998)
[7] P.A.M. Steeman, J. Van Turnhout, Colloid polym Sci 275, 106 (1997)

Relation between the electromechanical response and the dielectric breakdown of Poly(ethylene naphthalene 2,6-dicarboxylate) (PEN) films under high DC electrical field

N. Lahoud[1,2], **B. Zegnini**[3], **J. Martinez-Vega**[1,2*]
[1]Université de Toulouse ; UPS, INPT ; LAPLACE (Laboratoire Plasma et Conversion d'Energie) ; 118 route de Narbonne, F-31062 Toulouse cedex 9, France
[2]CNRS ; LAPLACE ; F-31062 Toulouse, France
[3]University of Laghouat, BP 37 G, route de Ghardaïa, Laghouat 03000, Algeria
*Email address: juan.martinez@laplace.univ-tlse.fr

Under dc electrical field, induced mechanical stresses are responsible for highly localized mechanical deformations in Poly(ethylene naphthalene 2,6-dicarboxylate) (PEN) films and thus have an important participation to the ageing process of these materials[1]. The heterogeneity of the structural material response under the application of an electrical field is shown by using an optical strain measurement technique combined to the Scanning Electron Microscopy (SEM). By means of the optical technique, the induced mechanical deformation has been quantified for different distances from the final breakdown area. The level of the electro-mechanical induced deformation is larger when approaching the final breakdown zone even for fields much lower than the breakdown field. This observation relates, in a straightforward way, the local induced strain to the breakdown phenomenon. Using the SEM technique, the damage on the sample surface caused by the dielectric breakdown and presented by a small perforation on the samples surface is shown for samples with different crystallinity degrees. The results show that the hole diameter depends on the crystallinity degree. These results confirm several studies and models which have highlighted the role of microdomains in the ageing mechanism and dielectric breakdown of insulating materials[2]. Finally, the effect of the electrical field loading mode on the mechanical response of samples is presented. In this purpose two loading modes are treated: the gradually increasing step voltage and the polarization/depolarization modes. At high fields, the level of the induced deformation is higher for the successive steps application mode as shown in Fig.1.

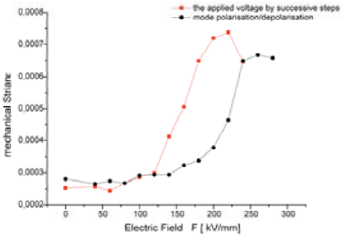


Fig.1 The effect of the electrical field loading mode on the induced deformation

References
[1] B. Zegnini, N. Lahoud, L.Boudou, J. Martinez-Vega, J. Appl. Polym. Sci., 110, 23 (2008).
[2] N.Lahoud, L. Boudou, J. Martinez-Vega, J. Non-Cryst. Sol., 356, 652 (2010).

P-21

Influence of the nature of the solvent on the secondary and structural relaxations of PMMA

N. Suárez[1*], **N. Salazar Serge**[2], **J. L. Feijoo**[3], **and M. Hernández**[1]
[1]Departamento de Física, [2]Departamento de Química, [3]Departamento de Materiales
Universidad Simón Bolívar, Caracas, Venezuela
*Email address: nsuarez@usb.ve

This work is related to the study of the influence of the nature of the solvent on the thermal and dielectric properties of solution-cast films of poly(methyl mathacrylate) (PMMA). Four solvents were used to prepare the films, toluene, dichlorometane, tetrahydrofuran and acetone. Figure 1 shows the dielectric thermal stimulated depolarization spectra (TSDC) of the PMMA films prepared with the different solvents and the compressed molded sample. Similar to the data previously reported by Kalogeras et.al[1], the figure exhibits a broad secondary relaxation signal, and long-range conformational changes of the polymer backbone. (A) displays the secondary relaxations whose intensity and profile vary with the selected solvent. The glass transition is shown at higher temperaturas (B) as a huge peak, with intensity and temperature position (Tg) variations among the different solvents. The whole spectra of the cast samples exhibit evident intensity attenuation as compared to the molded film. A lower value of Tg is also a common feature among the cast samples. Comparable Tg trends have been obtained by Differential Scanning Calorimetry (DSC) technique. Traces of the different solvents are expected to reside in relatively strong binding sites [1], e.g., hydrogen bonded to C=O groups. The measured amount of the remnant acetone, dichlorometane, toluene, and tetrahidrofuran solvents, obtained by nuclear magnetic resonance (NMR), is 0.30, 0.40, 9.00, and 14.00% respectively. The samples with higher solvent contents exhibit lower Tg values. The retained solvent molecules, trapped inside the PMMA films, affect the dynamics of the segmental and the localized dielectric relaxations. This effect differs in function of the nature and the amount of the solvent, and it could be partly explained by acid-base interactions between PMMA and the solvents[2].

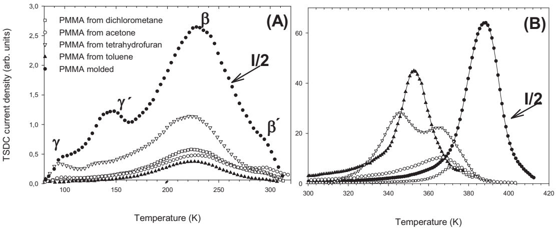


Fig.1. Low temperatura (A), and High temperature (B) dielectric spectra of PMMA

References

[1] I. M. Kalogeras, E. R. Neagu, and A. Vassilikou-Dova; *Macromolecules* **37**, 1042 (2004).
[2] S. Bistac, J. Schultz, *Mat. Sci. & Eng.*, **31** 347 (1997).

α- and β- Dielectric Relaxations in Fluorinated Methacrylate Polymers and Copolymers of Vinylidene Cyanide

S. Capaccioli[1*], V. Castelvetro[2], P.A. Rolla[1], M. Raihane[3], S. Atlas[3] and A. Meskini[3]
[1] Dipartimento di Fisica, Università di Pisa, Largo Pontecorvo 3, 56127 Pisa, Italy
[2] Dipartimento di Chimica, Università di Pisa, via Risorgimento 35, 56126, Pisa, Italy
[3] Laboratoire de Chimie Bioorganique et Macromoléculaire, Université Cadi Ayyad, Faculté des Sciences et Techniques, Avenue Abdelkrim Khattabi, BP 549- 40000 Marrakech, Morocco
*Email address: Simone.Capaccioli@df.unipi.it

Polymers containing highly polar substituents are of potential interest for the development of advanced electrical and optical materials[1,2]. Particularly interesting cases are the combinations of cyano-containing monomers such as methacrylonitrile (MAN), acrylonitrile (AN), and vinylidene cyanide (VCN) with either captodative or fluorinated comonomers, recently synthesized by our group[3,4]. Within this class, we recently compared the dynamic and thermal properties of the fluorinated methacrylate homopolymer 2,2,2-trifluoroethyl methacrylate (MATRIF) and its copolymer with VCN, characterized by dielectric spectroscopy and differential scanning calorimetry (DSC). The complex permittivity $\varepsilon=\varepsilon'-j*\varepsilon''$ was determined over a wide range of temperatures (120 K-450 K) and frequencies (1 mHz-10 MHz). Both systems show a very complex scenario, characterized by three relaxation processes: a slower one, due to the structural α-relaxation, whose relaxation time has a Vogel-Fulcher-Tamman (VFT) temperature behaviour, attaining a time of 100 s close to the calorimetric glass transition temperature Tg. Structural α-relaxation was found much slower in VCN copolymer than in MATRIF, with Tg=371 K, 40 K higher than for the MATRIF. Larger steepness or fragility index was also found as well as a broader relaxation shape, all indicating a more cooperative behaviour. The two faster secondary relaxations β- and γ-, active also in the glassy state, show a different behaviour: β-one is faster has with a smaller activation energy for VCN copolymer, while the γ-one is very similar in both homo- and co-polymer. The substitution with VCN causes a larger timescale separation at Tg between α- and β-relaxation, in good agreement with the Coupling Model prediction, according to a pattern already observed in a series of PS/BMA copolymers[5]. Additionally, for the VCN copolymer, another VFT-like process was found in the same temperature range of the glass transition, slower than α-one and overlapped by the d.c. conduction arising from ionic impurities. The total value of the dielectric strength Δε has been determined and compared to the values reported for similar cyano-contaning copolymers: comparatively high values of dielectric strength Δε were found, suggesting substantial piezo or pyroelectric properties, due to the combined contribution of CN dipoles orientation and the synergistic effect of fluorinated groups.

References

[1] R. Gerhard, R. Muhlhaupt, Ferroelectrics 75, 385-392 (1987).
[2] S. Miyata, M. Yoshikawa, S Tasaka S, M.Ko, Polymer J 12:857-860 (1980)
[3] M. Raihane, JP Montheard, G Boiteux, Macromol Chem Phys 201, 2365 (2000).
[4] A. Meskini, M. Raihane, B. Ameduri, C. Hakme, D. Sage, I. Stevenson, G.Boiteux, G.Seytre, H. Kaddami, Eur. Pol. J. 45, 804-812 (2009)
[6] K.L. Ngai, Macromolecules, 32, 7140-7146 (1999)

Molecular motion of mechanically degradated poly(ethylene terephthalate) PET studied by off-resonance NMR techniques

M. Baranowski[1*], A. Woźniak-Braszak[1], K. Jurga[1],
J. Jurga[2], K Hołderna-Natkaniec[1]
[1]Faculty of Physics, Adam Mickiewicz University, Umultowska 85,
61-606 Poznań, Poland,
[2]Institute of Materials Technology, Poznań University of Technology, Piotrowo 3,
61-138 Poznań, Poland.
*Email address: mikbar@amu.edu.pl

This article presents the study of molecular motions of poly(ethylene terephthalate) (PET) which were mechanically degradated to simulate the recycling process by solid-state ^{1}H NMR techniques. This polymer have a great commercial and industrial application in fibers, food containers, bottles, pharmaceutical packagings, toys etc.

The NMR techniques were used to investigate the molecular dynamics. The estimation of relaxation times in the rotating frame off-resonance $T_{1\rho}^{off}$ for PET was performed on homemade 30,2 MHz pulse spectrometer by measuring the recoveries of magnetization at the effective field B_e without sample overheating[1,2]. The results of measurements were presented[3] as a function of angular frequency and realized at a constant angle Θ equal to 10°.

The spin-spin proton $T_{2\rho}^{off}$ relaxation times were carried out on a special unique homemade pulse spectrometer operating at 30.2 MHz with special NMR probe which is characterised by high homogeneity of magnetic field. The experiments[4] were realized at a constant magic angle Θ equal to 54,7°.

The estimation of on-resonance $T_{1\rho}$ relaxation times in rotating frame for PET was also performed on the same pulse spectrometer. The obtained rates of off-resonance relaxation times as a function of angular frequency were matched to the equation

$$\frac{1}{T_{1\rho}^{\mathrm{off}}} = \frac{K}{4}\sin^2\Theta J(\omega_e,\tau_c,\theta) + \frac{1}{T_1},$$

using the following density function given by Davidson and Cole formula:

$$J(\omega_e,\tau_c,\theta) = \frac{2\alpha}{\omega_e}\left[\frac{\sin(\theta\arctan(\omega_e\tau_c))}{\left(1+\omega_e^2\tau_c^2\right)^{\frac{\theta}{2}}}\right],$$

where $K = 64\cdot10^{-50}\ \mathrm{m^6/s^2}$ for protons, ω_e is the effective frequency, τ_c is upper cut-off correlation time, θ is the width of the distribution of correlation times and T_1 is the spin-lattice relaxation time in the laboratory frame.

References

[1] J. Jurga, A. Woźniak-Braszak, Z. Fojud, K. Jurga, Solid State NMR 25, 47 (2004).
[2] K. Jurga, Z. Fojud, A. Woźniak-Braszak, Solid Nuclear Magnetic Resonance 25, 119 (2004).
[3] A. Woźniak-Braszak, M. Szostak, J. Jurga, K. Jurga, A. Piekarz, M. Baranowski, J. Appl. Magn. 29, 221 (2005).
[4] J. S. Blicharski, Acta Physica Polonica, A41 (1972).

P-24

On the influence of the space charge on the characteristics of the phase transition in ferroelectric polymers

V. Kochervinskii[1], I. Malyshkina[2*], M. Shcherbina[1], N. Bessonova[1]
[1]Karpov Institute of Physical Chemistry, Vorontsovo Pole 10, 105064 Moscow, Russia
[2]Moscow State University, Phys. Dept., Leninskie Gory, 119991 Moscow, Russia
*Email address: malysh@polly.phys.msu.ru

The work is devoted to the study of the isotropic films of copolymer of vinylidene fluoride and tetrafluoroethylene VDF/TFE 94/6 with different thermal history. One of the samples (1) was prepared by crystallization at room temperature from the acetone low-boiling solvent. Samples 2 and 3 were prepared by crystallization from the melt under pressure at various cooling regimes. 100 nm thick Al electrodes have been deposited by thermal evaporation. Dielectric properties have been measured in wide temperature (20÷160°C) and frequency (10^{-1}÷10^{7} Hz) range by means of Novocontrol Concept 40 setup.

It was shown earlier, that in this type of films a huge dielectric dispersion is observed at high temperatures, which is related to the space charge relaxation[1-3]. On the other hand, these copolymers are ferroelectrics, and ferroelectric to paraelectric phase transition, which according to structural data[4] proceeds near the melting temperature, should be observed here. Since the space charge relaxation is registered in the same temperature range, the task was to follow its effect on the electrophysical characteristics around the Curie temperature. It is known that this transition is accompanied by dielectric anomalies. We analyzed temperature dependencies of dielectric permittivity ε' at various frequencies of the electric field. The analysis shows that the temperature peak of ε' can be observed only on frequencies above some critical value. For the sample 1 it is 1 kHz, and the ferroelectric to paraelectric phase transition appears to be the transition of the first type, since the peak temperature at cooling is lower than at heating. The $\varepsilon'(T)$ peak for samples 2 and 3 is observed only at frequencies higher than 10 kHz.

Comparison of the conductivity σ in the region of low-frequency plateau for all films in the state of the melt (at 160°C) shows that it differs greatly. Thus the thermal history of preparation of the films manifest itself as a memory effect. This leads to the suggestion that the hysteresis effects for ε' and σ in the region of the Curie temperature depend essentially on equilibrium of the structure of the initial film. The analysis shows, that one can judge about the approach to equilibrium state by generation of spherulites at crystallization. There were no such structures in the sample 1 in initial state and consequently we can consider the structure of the film to be far from equilibrium. In case when the film (in initial state) is crystallized with formation of spherulites (sample 3), the hysteresis in $\sigma(T)$ and $\varepsilon'(T)$ is essentially smaller. As a consequence, it was obtained that for the sample 3 ferroelectric to paraelectric phase transition is of the second type. Estimates show that approach to the equilibrium state of initial films affects Curie–Weiss constants as well.

References

[1] V.V. Kochervinskii, I.A. Malyshkina, G.V. Markin, N.D. Gavrilova, N.P. Bessonova. J. Appl. Polym. Sci. 105, 1101 (2007).
[2] V. Kochervinskii, I. Malyshkina. Journal of Non-Cryst. Solids 356, 564 (2010).
[3] V. Kochervinskii, I. Malyshkina, N. Gavrilova, S. Sulyanov, N. Bessonova. Journal of Non-Cryst. Solids 353, 4443 (2007)

Study on molecular motions and phase separation in polyEGDM/LBH semi-interpenetrating network

M. Makrocka-Rydzyk[1], K. Wegner[1], A. Wypych[1], S. Jurga[1] and E. Andrzejewska[2]
[1]Department of Macromolecular Physics, Faculty of Physics,
Adam Mickiewicz University, Umultowska 85, 61- 614 Poznan, Poland
[2] Institute of Technology and Chemical Engineering, Poznan University of Technology,
M.Skłodowskiej-Curie Sq., 60-965 Poznan, Poland
*Email address: zfmak@main.amu.edu.pl

Highly crosslinked polymers produced from multifunctional (meth)acrylate monomers due to their high structural stability, increased resistance to solvents and improved mechanical stability have found broad range of applications including coatings, information storage systems, spherical lenses and dental biomaterials [1]. The improvement in mechanical properties of the material may be obtained through its blending with elastomer. Semi-interpenetrating polymer network (semi-IPN), comprising at least one polymer network and one linear polymer held together by permanent entanglements (Fig.1), may be regarded as polymer blend. Such special kind of polymer blending ensures a significant improvement in the morphological stability of the system in comparison with simple blends [2].

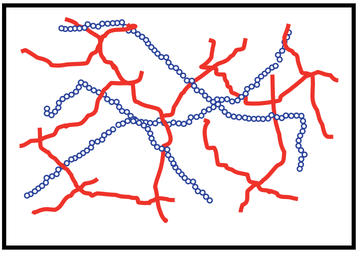


Fig.1. The semi-IPN structure

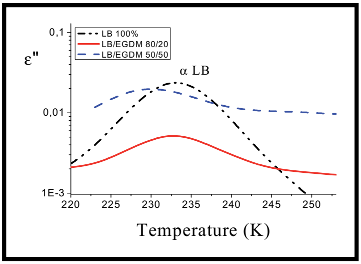


Fig.2. Isochronal plots of imaginary part of complex dielectric permittivity (ε”) at 1Hz measured for LBH/polyEGDM compounds.

The goal of our studies was to determine the molecular dynamics of semi-IPN compounds, which have been made by photopolymerization of crosslinkable ethylene glycol dimethacrylate (EGDM) in the immediate presence of low molecular weight polybutadiene (LB). Samples of different compositions i.e. 80/20; 50/50 and 20/80, as well as LB and polyEGDM homopolymers, have been studied by means of Broadband Dielectric Spectroscopy (BDS).

The molecular dynamics of semi-IPN systems reflects the molecular behaviour of neat LB. The relaxation processes connected with glass transitions of LB (α LB) and EGDM (α EGDM) have been found. The decrease of LB glass transition temperature (α LB), with increasing amount of EGDM in semi-IPN system, is observed (Fig.2).

Acknowledgements:

This work is supported by research grants: No N N202 128536 and No 32-061/2010-DS (Poland).

References:

[1] J. E. Dietz, N. A. Peppas; Polymer 38 (1997) 3767-3781.
[2] L.H. Sperling, D. Klempner, L.A. Utracki (Eds.), Interpenetrating Polymer Networks, American Chemical Society, Washington, 1991

Polymer functionalization as a tool to selectively study component dynamics in miscible polymer blends by dielectric spectroscopy

Sandra Plaza-García[1,2,3*], Reidar Lund[1], Angel Alegría[2,3], Juan Colmenero[1,2,3], Jonathan Janoski[4], and Roderic P. Quirk[4].
[1]Donostia International Physics Center. Paseo Manuel de Lardizabal 4, 20018 San Sebastián, Spain
[2]Centro de Física de Materiales (CSIC-UPV/EHU), Paseo Manuel de Lardizabal 5, 20018 San Sebastián, Spain
[3]Departamento de Física de Materiales, Universidad del País Vasco (UPV/EHU), Apartado 1072, 20080 San Sebastián, Spain
[4]Institute of Polymer Science and Polymer Engineering, The University of Akron, Ohio 44325-3909
[*]Email address: splaza001@ikasle.ehu.es

Polymer functionalization involves the inclusion of specific chemical groups covalently attached to the chain. When functionalizing polystyrene chains with cyano (-CN) functional groups, the dielectric relaxation strength increases due to the high dipole moment. Earlier we found that CN-functionalized polystyrenes exhibit overall physical properties (T_g, viscosity, etc) similar to the H-functionalized analogs while the dielectric strength nearly increases an order of magnitude[1,2]. Here the functionalization is used to selectively study the component dynamics in miscible polymer blends. The system selected was PS/PVME and by using either PS-H/PVME or PS-CN/PVME mixtures, both the PS and PVME contributions can be separated out unambiguously. The results shown here are focused on blends having a low concentration of the fast component (25%PVME), which gives rise to a strong dynamic asymmetry, i.e. a large disparity in the component dynamics. In this way we could directly study the relation between the PS dynamics in the blend and the confinement effects detected on the PVME molecular motions (see Fig 1).

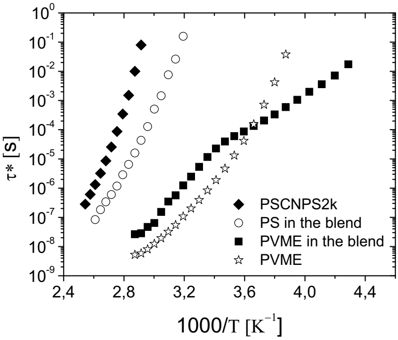


Fig 1.Arrhenius plot of the characteristic relaxation times of the segmental dynamics of the pure polymers and the components in the 75/25 miscible blend.

References

[1] R. Lund, S. Plaza-García, A. Alegría, J. Colmenero, J. Janoski, S. R. Chowdhury, R. P. Quirk. Macromolecules 42, 8875-8881 (2009)
[2] R. Lund, S. Plaza-García, A. Alegría, J. Colmenero, J. Janoski, S. R. Chowdhury, R. P. Quirk. Journal of Non-Crystalline Solids 356, 676-67 (2010)

Kinetics of curing reaction for selected epoxy resins described in terms of changes in ionic conductivity

M. Włodarska[1*]
[1]Institute of Physics, Technical University of Lodz, 90-924 Lodz, Poland.
*Email address: magdaw@p.lodz.pl

The aim of this work is to describe changes in ionic conductivity which occur during the curing reaction. A series of mixtures based on mesogenic epoxies as well as standard epoxy resins are analysed in the course of curing. In all observed cases the reaction is accompanied by visible and systematic evolution of the conductivity. The speed of these changes depends on composition of the mixture and temperature of curing process and it is connected with changing properties of the material, because final properties of epoxy resins, both liquid-crystalline and traditional ones, are largely affected by the method and conditions of curing. Physical properties of a resin undergo fundamental changes during cure. Initially, when cross-linking density is low, the resin remains brittle and soluble, even though it begins to solidify. As the density of links increases, properties of the resin change irreversibly, it becomes non-melting and insoluble[1]. In studies on the curing process a method developed by Gillham is often used, which is based on analyzing changes in vitrification temperature[2,3]. This technique is based on correspondence between conversion rate and temperature of glass transition, which can be verified experimentally[2]. Beyond traditional methods of studying reaction progress, it has been discovered that broadband dielectric spectroscopy (DRS) can also be useful for monitoring these reactions. This procedure was applied to various systems, including epoxy-amine ones, by a number of researchers[4,5,6]. These studies were focused on changes in mobility of dipoles during the reaction[7]. The technique can be extended by representing experimental data in terms of electric modulus, which enables tracking of reaction progress also through observation of ionic mobility[8]. This approach proved to be useful, because changes in ionic conductivity are well visible on the plots of electric modulus vs. time observed in the low frequency range at the temperatures applied in measurements – relaxation processes are partially visible at high frequencies[7]. It was found that in studied systems DRS technique is appropriate for describing behavior of polymeric materials in the course of curing, because it allowed drawing conclusions about the reaction dynamics at different temperatures by monitoring of ionic mobility during the reaction.

References

[1] Z. Brojer, Z. Hertz, P. Penczek, Żywice epoksydowe (Warszawa: WNT) (1982).
[2] G. Wisanrakkit, J.K. Gillham, J. Appl. Polym. Sci., 41, 2885 (1990).
[3] S.L. Simon, J.K. Gillham, J. Appl. Polym. Sci., 46, 1245 (1992).
[4] S.D. Senturia, N.F. Sheppard, Adv. Polym. Sci., 80, 1 (1986).
[5] D.E. Kranbuehl, M. Hoff, J. Godfrey, R. Hoffman, Polym. Eng. Sci., 26, 338 (1986).
[6] G. Williams, I.K. Smith, P.A. Holmes, S. Varma, J. Phys.: Cond. Matter, 11, A57 (1999).
[7] M. Włodarska, G. Bąk, B. Mossety-Leszczak, H. Galina, T. Pakuła, J. Non-Cryst. Solids, 353, 4371-4375 (2007).
[8] M. Włodarska, B. Mossety-Leszczak, G.W. Bąk, H. Galina, Scientific Bulletin Łódź, Tech. University No 1010, Physics 28, 95-102 (2007).

Dielectric response of cured epoxy resins based on biphenyl group in wide range of temperature

M. Włodarska[1*], B. Mossety-Leszczak[2], A Maj[1], G. W. Bąk[1], H. Galina[2], M. Izdebski[1].**

[1]Institute of Physics, Technical University of Lodz, 90-924 Lodz, Poland.
[2]Department of Industrial and Materials Chemistry, Rzeszow University of Technology
35-959 Rzeszow, Poland
*Email address: magdaw@p.lodz.pl, **Email address: mossety@prz.rzeszow.pl

In this work we investigated dielectric response of cured epoxy resins based on biphenyl group[1]. This group often induces liquid crystalline properties in the materials, so properties of curing product for this type of monomers could be more complex than for traditional epoxy resins[2,3]. In this research two monomers were used with the same mesogen but with long and short symmetric tails[1]. They were cured with standard amines (DDM, DMAP). Temperature and time of the curing process were established through dielectric, thermal and optical analysis, for each mixture separately. We tried to determine rather low temperature of curing, at which the process did not run very fast but reaction started and continued its progress. For all materials dielectric monitoring during isothermal cure was done. The evolution of conductivity with time, which could be observed as a relaxation peak in electric modulus representation[4], was easily seen in all the cases. Small differences in the dynamics of the curing process were observed in different mixtures. In particular, when the monomers with long aliphatic chains were used, the changes of conductivity peak were very well seen during the first hour and then they stabilised and remained practically constant afterwards. This behaviour also had influence on the dielectric properties of the curing products, for example materials based on the monomer with short tails needed additional post-curing at a higher temperature. Although generally dielectric response is similar in all materials, differences can be seen in the details. At lower temperatures quite high relaxation process is seen in all products, its low activation energy pointed towards a β-process, which appears in many polymers[5]. The Havriliak-Negami formula was fitted to the data and characteristic parameters of the observed relaxation processes were compared in detail. These β-processes are usually attributed to molecular motions of particular dipolar groups in the system, and in our materials it could be connected with carboxyl groups in central segments of the monomers. At higher temperatures quite high conductivity was observed in all materials, which greatly decreased at lower temperatures (below 100°C). The character of this conductivity drop was similar in all investigated products. This behaviour could be connected with changes in the properties of the material and it is also correlated with DSC measurements. The conductivity of all resins was also obtained from current/voltage characteristic.

References

[1] B. Mossety-Leszczak, H. Galina, M. Włodarska, G. W. Bąk. Przemysł Chemiczny 85(8-9), 956 (2006).
[2] J.Y. Lee, J. Jang. Polymer 47, 3036 (2006)
[3] P. Castell, A. Serra, M. Galià, M. Giamberini, C. Carfagna. J. Polym. Sci. A: Polym. Chem. 41**,** 1 (2003).
[4] P.B. Macedo, C.T. Moynihan, R. Bose, Phys. Chem. Glasses, 13(6), 171 (1972).
[5] F. Kremer, A Schönhals. Broadband Dielectric Spetroscopy (Berlin: Springer), (2003).

Molecular dynamics and structure of poly(styrene-b-isoprene) diblock copolymers studied by BDS and NMR

J. Jenczyk, M. Makrocka-Rydzyk, A. Wypych, S. Głowinkowski, S. Jurga*
Department of Macromolecular Physics, Faculty of Physics,
Adam Mickiewicz University, Umultowska 85, 61-614 Poznań, Poland.
*Email address: zfmak@amu.edu.pl

Block copolymers are under great research interest due to their current and potential applications. Properties of these systems depend on individual blocks characteristics and on the interaction between the components[1].

We have investigated three nearly symmetric poly(styrene-b-isoprene) diblock copolymers: PS(11500)-b-PI(10500)→SI1, PS(45000)-b-PI(46000)→SI2 and PS(135000)-b-PI(131000)→SI3.

Broadband Dielectric Spectroscopy (BDS) and Nuclear Magnetic Resonance (NMR) studies were performed to characterize molecular motions in copolymers and their neat components. The molecular dynamics in copolymers reflects the molecular behaviours of neat PI and PS. The observed relaxations are (Fig.1): (a) primary relaxation (α-processes) due to segmental motions, relevant to the glass transition for PI and for PS parts of copolymer, (b) conformal interfaces relaxation arising from coherently ordered microstructure[2] (c) relaxation assigned to normal mode motions of PI chains, which involve the fluctuations of the end-to-end vector (visible in BDS measurements) and (d) relaxation originated in the rotation of methyl groups (observed only in NMR experiments). It appeared that the flexible polyisoprene and stiff polystyrene blocks in copolymer influence one another in terms of molecular dynamics. As a result the increase of the glass transition temperatures (T_g) for PI chains for all copolymers, in comparison with neat PI, was observed. Moreover, there is a substantial broadening in the distribution of relaxation times of both: the normal mode and glass transition processes in copolymers in comparison with neat PI. This effect is more pronounced for the copolymer of higher molecular weight.

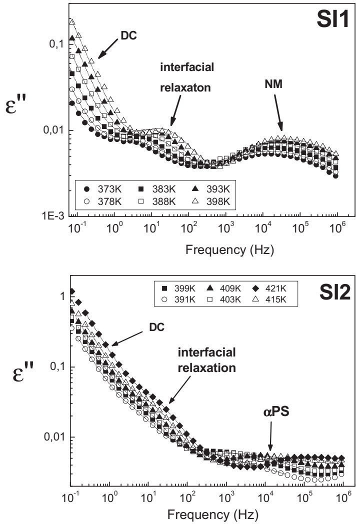


Fig. 1. Frequency dependence of the dielectric loss ε″ for SI1 and SI2 diblock copolymers.

Acknowledgements
This work is supported by 6th Framework Programme under SoftComp Grant No 502235-2 and research grant No N N202 285438 (Poland).

References

[1] I.W. Hamley. Developments in Block Copolymer Science and Technology (2004) John Wiley&Sons, Ltd.
[2] K. Karatasos, S. H. Anastasiadis, G. Floudas, G. Fitas, S. Pispast, N. Hadjichristidis, T. Pakula. Macromolecules 29, 1326 (1996).

Sub-glass relaxations in novel aromatic polyimides with application on gas separation process.

C. Álvarez[1*], C. García[1], M. Calle[1], A. E. Lozano[1], J. G. de la Campa[1], J. de Abajo[1]
[1]Instituto de Ciencia y Tecnología de Polímeros (CSIC).
Juan de la Cierva 3, 28006 Madrid, Spain
*Email address: cristina.alvarez@ictp.csic.es

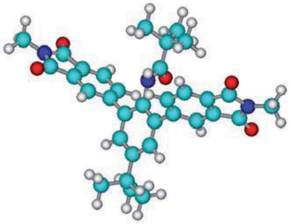


Fig.1. Molecular modelling of 5´-*t*-butyl-2´-pivaloylimino-3, 4, 3´´, 4´´-*m*-terphenyl dimethylimide.

Aromatic polyimides are considered as promising materials for gas separation processes. The most orthodox way to improve their properties in this field is to increase *fractional free volume* (FFV) by introducing bulky side groups and to increase at the same time the *rigidity* of the main chain, because the use of structures with high rigidity results in a strong size sieving ability. In this work, new polyimides based on monomers derived from m-terphenyl dianhydride have been studied. The presence of *tert*-butyl or/and pivaloylimino groups in the central ring (see example in Fig.1) should bring about both effects (increase of FFV and rigidity) [1,2]. In general, polyimides obtained from these dianhydrides and commercial diamines, such as 2,4,6-trimethyl-*m*-phenylendiamine and 2,2-bis(4-aminophenyl)hexafluoropropane, have shown O_2/N_2 separation characteristics close to the Robeson limit [2,3].

The high gas permeability of these polymers is in agreement with its high FFV. However, no direct correlation has been found between FFV and permeability parameters. This fact seems to indicate that the diffusivity of these polyimides is not controlled only by the global FFV but also the distribution of free volume elements (holes). It is known that the diffusivity of a gas molecule in an amorphous matrix can be described by a jumping-mechanism between neighbouring holes through the temporal opening of channels by thermal fluctuations of the matrix. In glassy state, sub-glass relaxations are responsible for these fluctuations. Thus, we present a comparative study of the dielectric relaxation behaviour of this family of polyimides in order to get a better understanding on how bulky pendant groups influence on molecular motions and their potential relationship to gas transport process.

Acknowledgements. Financial support from CSIC (PIE 200860I066) and MICINN (MAT 2007-62392) is acknowledged.

References

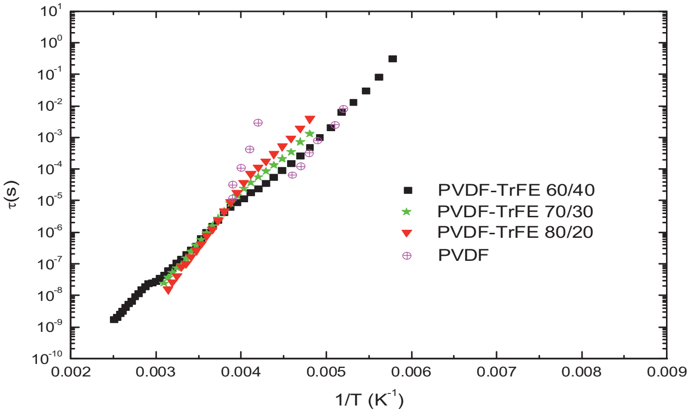
[1] C. García, A. E. Lozano, J. G. de la Campa, J. de Abajo, Macromol. Rapid Commun., 24, 686 (2003).
[2]M. Calle, A. E. Lozano, J. G. de la Campa, J. de Abajo, Macromolecules, 43, 2268 (2010).
[3] J. de Abajo, J. G. de la Campa, A. E. Lozano, J. Espeso, C. García, Macromol. Symp., 199, 293 (2003).

Origin of the β relaxation in PVDF based ferroelectric polymers. Confinement effects?

A. Nogales*, **A. Sanz, T.A. Ezquerra**
Soft Condensed Matter Group. Instituto de Estructura de la Materia, CSIC. Serrano 121, Madrid 28006, Spain
*Email address: a.nogales@iem.cfmac.csic.es

In recent years, the possibility of fabricate polymer based ferroelectric memories has drawn attention into Poly(vinylidene fluoride) and its copolymers with trifluoro ethylene P(VDF-TrFE). Due to the technological necessity of miniaturization of the devices, investigations are nowadays concentrated on the dynamic and static properties of P(VDF-TrFE) nanoscale systems, such as Langmuir Blodgget, thin films or nanoimprinted samples. However, from a dynamical point of view, there are still many fundamental open questions on the bulk systems. Understanding these effects may provide some hints about the nanoscale confinement impact on the technologically usable properties of these ferroelectric polymers.

In these work, we present Broad Band Dielectric Spectroscopy results on a series of P(VDF-TrFE) copolymers where the concentration of TrFE ranges from 0 to 40%. The relaxation map of this series of samples is rather peculiar, since exhibits a continuity across the studied temperature range of the relaxation time of processes with, in principle, very different origin: subglass local motion, segmental relaxation and ferro-to para transition.



References
[1] S. Ducharme S and A. Gruverman Nat Mater **8** 9-10 (2009)
[2] Z. Hu, M Tian, B. Nysten, A. M. Jonas. Nat Mater 8 62-7 (2009).
[3] P. Sharma, T. Reece, D. Wu, V.M. Fridkin, S. Ducharme, A Gruverman J. Phys.-Condes. Matter 21, 485902, (2009)
[4] A. V. Bune, V. M. Fridkin, S. Ducharme, L. M. Blinov, S. P. Palto, A. V. Sorokin, S. G. Yudin, A. Zlatkin, Nature, 391, 874 (1998).

The study of space charge relaxation in polyethylene terephthalate by using the final thermally stimulated discharge current method

E. R. Neagu[1*], C. J. Dias[1], M. C. Lança[1], R. Igreja[1], P. Inácio[1]
and J.N. Marat-Mendes[1]
[1]Departamento de Ciência dos Materiais, Secção de Materiais Electroactivos (I3N/CENIMAT), Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516, Caparica, Portugal

*Email address: neagu@dcm.fct.unl.pt

The thermally stimulated discharge current (TSDC) method allows us to study the dielectric relaxation in low mobility materials. On of the inconveniences is the fact that the method is sensitive to both dipolar and space charge (SC) effects. To overpass this inconvenience we have proponed a variant to this method, namely the final thermally stimulated discharge current (FTSDC) technique, to analyze charge trapping/de-trapping and transport in insulating materials [1]. The aim of this work is to analyze space charge relaxation in polyethylene terephthalate by using the final thermally stimulated discharge current method. It is known that for a polarized material the decay of polarization during the isothermal discharge step, for a dipole characterized by a relaxation time τ_k and a saturation polarization P_{0k}, is given by

$$P_k(t_c, t_{di}) = P_{0k}\left[1-\exp(-\frac{t_c}{\tau_k})\right]\exp(-\frac{t_{di}}{\tau_k})$$

where t_c is the charging time and t_{di} is the discharging time. By decreasing the value of t_c and by increasing the value of t_{di} the experimental conditions can be selected so that the FTSDC is mainly determined by the space charge de-trapping [2, 3]. Actually, by choosing the values for t_c and t_{di} we control the maximum value of the relaxation time τ_k still active in the discharging process and the maximum current related to dipole randomization. Consequently, by diminishing significantly the contribution of the dipole randomization to the measured current the effects related to space charge relaxation can be studied.

The main concern will be dedicated to answer the question: what relaxations can be observed above the glass transition temperature?

References

[1] E. R. Neagu and J. N. Marat-Mendes, Japan J. Appl. Phys. 40, 1160 (2000).
[2] E. R. Neagu and R. M. Neagu, J. Appl. Phys. 100 (7), art. no. 074107 (2006).
[3] E. R. Neagu, J. Appl. Phys. 97, 4 (2005).

Electro-thermal poling of silver ion conducting glasses with antibacterial properties

J. Kruempelmann, B. Roling
Department of Chemistry, University of Marburg, Hans-Meerwein-Straße, D-35032 Marburg
Germany
Email address: kruempej [at] staff [dot] uni-marburg [dot] de

Phosphate and borate based silver ion conducting glasses provide a useful means of releasing silver ions incorporated into the glass network in a controlled manner. The antibacterial effect of the silver ions is the reason for their varied applicability in healthcare products[1]. We investigate electrochemical processes in silver doped phosphate and borate based glasses during electro-thermal poling. In the electro-thermal poling technique, a dc voltage is applied to the material for a time interval at a specific temperature[2]. The applied voltage causes movements of the silver ions and leads to the formation of a silver depleted layer under the anode and a silver enriched layer under the cathode. When the glass is cooled down the surface charges are stored in the material. By means of impedance spectroscopy, the effect of electro-thermal poling on the differential capacitance and conductivity of the silver ion conducting glasses is investigated. In order to differentiate between the capacitance of the anode and cathode, blocking and non-blocking electrodes are used. Non-blocking electrodes are subject to dissolution or growth processes whereas blocking electrodes are inert. The injection of silver ions from the non-blocking anode into the glass causes changes of the morphology of the interfacial boundary between the solid electrode and the glass[3]. The complete injection of silver ions leads to the formation of air gaps between the electrode and the glass. We discuss the usage of different electrode materials with respect to the impedance spectra during electro-thermal poling.

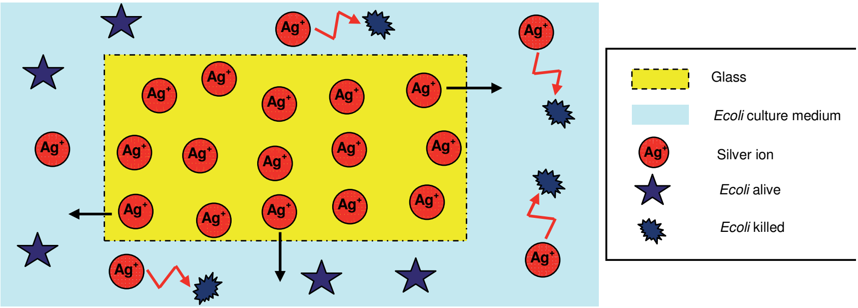


Fig. 1: Antibacterial effect of silver ion conducting glasses

References

[1] V. Simon, C. Albon, S. Simon, Journal of Non-Crystalline Solids 354 (2008) 1751
[2] C.R. Mariappan, B. Roling, Solid State Ionics 179 (2008) 671-677
[3] J. Janek, Solid State Ionics, 131 (2000) 129

Investigations of the nonlinear ionic conductivity in mixtures of ionic liquids with molecular solvents

J. Kirchberg*, **B. Roling**
Department of Chemistry, University of Marburg, Hans-Meerwein-Str., D-35032 Marburg
*Email address: kirchbe3 [at] staff [dot] uni-marburg [dot] de

Ionic liquids (ILs) and their mixtures with molecular liquids are of interest as electrolytes for electrochemical cells, such as thin-film batteries, supercapacitors, fuel cells, and dye solar cells.[1-3] The addition of molecular liquids to ILs leads, in general, to a decrease of the viscosity and to an increase of the ionic conductivity. After additional dissolution of lithium salts in such mixtures, fast lithium ion transport is expected.

While the linear electrical properties of ionic liquids and of mixtures are well studied, there are up to now no studies on nonlinear ion transport and dynamics under the influence of high electric fields, which are present in thin-film batteries.

Here, we investigate the nonlinear ionic conductivity of mixtures containing low concentrations of ILs in molecular solvents. At low IL concentrations, the dissolved ions should be isolated, and it should be possible to use them as probes for studying the dynamics of the solvent molecules. For the nonlinear conductivity spectroscopic measurements, we apply high ac fields and analyse higher harmonics in the ionic ac currents.

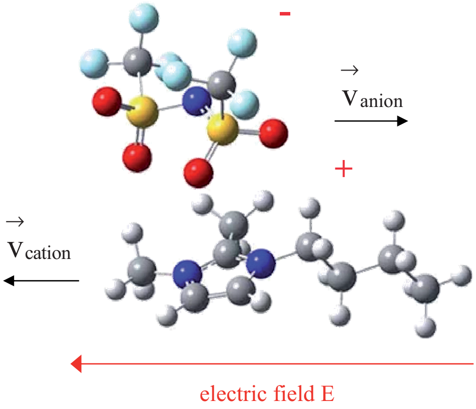


Fig.1: Typical ionic liquid under the influence of an electric field.

References

[1] M. Armand, F. Endres, D. MacFarlane, H. Ohno, B. Scrosati, *Nat. Mater.* **2009**, *8*, 621.
[2] P. Simon, Y. Gogotsi, Nat. Mater. **2008**, *7*, 845.
[3] A. Guerfi, M. Dontigny, P. Charest, M. Peticlerc, M. Lagacé, A. Vijh, K. Zaghib, *J. Power Sources* **2010**, *195*, 845.

Colloidal Dispersions of Nanoparticles in Ionic Liquid

C. Roesser[*], R. Roling
Department of Chemistry, Philipps-University of Marburg, Hans-Meerwein-Str.,
35032 Marburg, Germany
*Email address: Roesser2 [at] staff [dot] uni-marburg [dot] de

Room temperature ionic liquids (RTIL) are organic salts with outstanding properties, such as a wide electrochemical window, good chemical and thermal stability, and very low volatility. Due to their high safety performance, ILs are a promising class of electrolytes for future power sources and electrochemical devices. The gelation of ILs by the addition of nanoparticles result in interesting properties. These new solid electrolytes exhibit forming ability, transparency and flexibility, and can be used as electrolytes for high performance dye-sensitized solar cells (DSSCs)[1].

The ionic transport and viscoelastic properties of these nanocomposite ion gels depend on their microstructure. The formation of the gels is controlled by the physical-chemical properties of the solid-liquid interface.[2,3]

In this work we investigate the influence of the surface chemistry on the formation process and the ionic transport properties of ion gels. The study of the behaviour of such complex dispersed systems requires use of several complementary characterisation methods. An important aspect of the gelation effect is agglomeration of nanoparticles. A visual approach to studying the arrangement of particles and size of clusters is a statistic analysis of TEM micrographs. A comparison between the experimental observation and theoretical predictions of computer simulations[4] contains a reference to the interacting forces among the colloidal particles. To gain more information about the particle charge in ionic liquids, we added an imidazolium based IL to different silica suspensions and studied the surfactant property of the IL by measuring the zeta-potential. The translational self-diffusion coefficient of IL cations and anions in the gel were obtained by means of PFG NMR. A comparison of diffusion data and ac conductivity measurements, which can be related via the Nernst-Einstein equation, provide estimates of ionic association.

References

[1] P. Wang, S. M. Zakeeruddin, P. Comte, I. Exnar, and Michael Grätzel, J. Am. Chem. Soc. 125, 1166 (2003).
[2] K. Ueno, K. Hata, T. Katakabe, M. Kondoh, and M. Watanabe, J. Phys. Chem. B, 112, 9013, (2008).
[3] T. Umecky, Y. Saito, Y. Okumura, S. Maeda, and T. Sakai, J. Phys. Chem. B, 112, 3357, (2008).
[4] A. L. R. Bug, S. A. Safran, G. S. Grest, and I. Webman, Phys. Rev. Lett. 55, 1985 (1985).

Ammonia-hydrates: Ionic liquids and solids

H. Didzoleit, C. Gainaru, R. Böhmer
Fakultät für Physik, Technische Universität Dortmund, 44221 Dortmund, Germany

Hydrated ammonia plays an important role for the dynamics of some icy worlds in our solar system [1,2]. However, little is known about the low-temperature dynamics of ammonia water mixtures. These could play an important role in cryo-vulcanism, calling for laboratory studies of this system.

At moderately low NH_3 concentrations the mixtures with H_2O can be readily supercooled [3]. In the present work the dynamics of these ionic liquids was studied mostly using broadband dielectric spectroscopy, roughly up to the dihydrate composition. Comparison of our results is made with those from diffusion studies and from other hydrated glass formers [4].

At still lower ammonia concentrations NH_3 vitrification is strongly impeded by a large crystallization tendency of the doped ice system. Here, ammonia acts as an impurity generator in ice thus introducing various kinds of defects in its hexagonal crystal lattice. The presence of defects breaks the ice rules locally thereby speeding up the proton dynamics. The concentration dependence of these effects is discussed.

References

[1] R. D. Lorenz, Icarus 136, 344 (1998).
[2] see e.g., www.wired.com/wiredscience/2009/07/enceladusammonia/
[3] G. Vuillard, Publ. Sci. Univ. Alger. B3, 80 (1957)
[4] S. Cerveny, A. Alegría, J. Colmenero, Phys. Rev. E 77, 031803 (2008)

Dielectric properties of Zn-ZnO multilayer systems deposited on non-woven substrate.

M. Jaroszewski[*], **J. Pospieszna, J. Ziaja**
Wrocław University of Technology, Dept. of Electrical Engineering, 50-370 Wrocław, Poland
*Email address: maciej.jaroszewski@pwr.wroc.pl

Technology of deposition of metal layers on different types of wovens has been of strong interest lately[1,2]. Especially interesting is use of thin metal layers to shield the electromagnetic fields[3] and biological filtering. Wovens have extremely developed specific surface and deposited metal layers will have it as well, what highly improve screening or filtering properties[4].

In the paper, we report on dielectric properties of Zn-ZnO-polypropylene fabric composite. The dielectric parameters vary depending on the parameters of the plasma generating process. Measurements of the complex admittance of the composites were performed in the frequency range between 40 Hz and 15 MHz.

This publication was prepared with the key project – POIG no. 01.03.01-00-006/08 co-financed from the founds of European Regional Development Found within the framework of the Operational Programme Innovative Economy.

References

[1] M.S. Sarto, R. Li Voti, F.Sarto, M.C.Larciprete, IEEE Trans. on EMC, vool.47, No 3, August 2005.
[2] K. Bula, J. Koprowska, J. Janukiewicz, Fibres & Textiles in EE, Vol. 14, No. 5 (59) (2006) pp.75 – 79,
[3] Pospieszna J., Electrical Review, Conferences, No 1, (2006).
[4] J. Ziaja, J. Koprowska, J. Janukiewicz; FIBRES & TEXTILES in Eastern Europe January / December / A 2008, Vol. 16, No. 5 (70) pp. 64-66

Temperature-dependent cyclic voltammetry on different RTIL based on FAP-anions

T. Jänsch*, M. Drüschler, B. Roling.
Department of Chemistry, University of Marburg, Hans-Meerwein-Straße,
35032 Marburg, Germany
*Email address: jaenscht[at]students.uni-marburg.de

Nowadays, room temperature ionic liquids (RTIL) are much more developed than the first ionic liquids described in the early 20th century. A wide range of possible cation – anion combinations leads to RTIL with specific properties for nearly every use. Compared to common organic solvents used in synthesis and analytics, RTIL exhibit attractive advantages like lower volatility and combustibility, intrinsic high ion conductivity and high thermal and chemical stability. These properties qualify ionic liquids as solvents for electrochemical applications, for example to obtain nano-structered surfaces as thin films by electrodeposition[1]. Nevertheless, the electrochemical properties of RTIL have not been investigated exhaustively yet. In particular, their use as electrolytes requires an electrochemical window as broad as possible. In recent studies, the influence of several impurities has been investigated by means of cyclic voltammetry. The absorption of water as ubiquitous impurity in even hydrophobic RTIL is of great interest and has been studied for several ionic liquids at different temperatures. Depending on the composition of the RTIL, a dramatic decrease of the electrochemical window has been reported, especially for ionic liquids based on hexafluorophosphate-anions $[PF_6]^-$ [2]. There are also indications that an increase in temperature might have the same effect on the electrochemical window. As the thermal stability of ionic liquids is quite high in general, the electrochemical stability at elevated temperatures needs to be investigated to ensure save technical applications. In order to investigate the temperature-dependence of the electrochemical window, several samples of RTIL based on the electrochemically stable tris(pentafluoroethyl)trifluorophosphate anion $[FAP]^-$ were subjected to cyclic voltammetry at different temperatures. To this end, a home-made measurement cell was used affording temperature-control above ambient temperature.

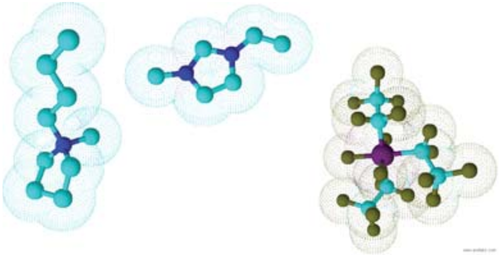


Fig.1. Components of the investigated RTIL: 1-butyl-1-methylpyrrolidinium cation, 1-ethyl-3-methylimidazolinium cation, tris(pentafluoroethyl)trifluorophosphate anion

References
[1] F. Endres, S. Zein, Phys. Chem. Chem. Phys. 8, 2101 (2006).
[2] A. O'Mahony, D. Silvester et al., J. Chem. Eng. Data 53, 2884 (2008).

Polymeric Lithium Electrolytes based on Ionic Liquids

B. Huber*, B. Roling
Department of Chemistry, University of Marburg, Hans-Meerwein-Straße,
35032 Marburg, Germany
*Email address: huberb[at]staff[dot]uni-marburg[dot]de

Lithium electrolytes, based on mixtures of alkyl carbonates or non conducting polymers with lithium salts, have been studied for several years. They are widely used as liquid or gel-like electrolytes[1].

We report new polyelectrolytes which overcome some of the drawbacks of the systems mentioned above, such as leakage problems and physical instabilities of the gels. These imidazolium bis(trifluoromethanesulfonyl)imide (TFSI) based electrolytes are polymerized ionic liquids (IL), showing most of the advantages of IL, such as thermal and electrochemical stability as well as high ionic conductivity.

In addition to previous works[2], our major attention is an enhancement of the lithium transference number. Promising strategies are the immobilisation of imidazolium cations in the polymer chain, usage of new lithium salts with weakly coordinating anions[3] and addition of suitable zwitterions[4,5].

Also the correlation between the microstructure of the polymers and their conductivity properties is of special interest. In addition to a comprehensive structural polymer analysis, we investigated the electrochemical and conducting properties by CV, ac impedance spectroscopy and pulse field gradient NMR.

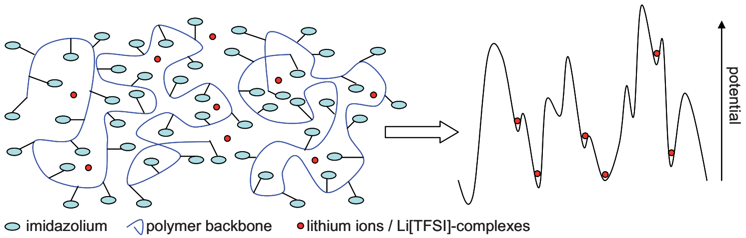


Fig. 1. Schematic depiction of an imidazolium based polyelectrolyte and a potential landscape.

References
[1] J. Shin, W. Henderson, S. Passerini, J. Electrochem. Soc., 152, A978 (2005).
[2] R. Marcilla, F. Alcaide, H. Sardon, J. A. Pomposo, C. Gonzalo, D. Mecerreyes, Electrochem. Commun., 8, 482 (2006).
[3] T. Linder, J. Sundermeyer, Chem. Commun., 2914-2916 (2009).
[4] M. Yoshizawa, M. Hirao, K. Ito-Akita, H. Ohno, J. Mater. Chem., 11, 1057 (2001).
[5] C. Tiyapiboonchaiya, J. Pringle, J. Sun, N. Byrne, P. Howlett, D. MacFarlane, M. Forsyth, Nature Materials, 3, 29-32 (2004).

A dielectric spectroscopy study on ionic liquid microemulsions

Z. Chen*, R. Nozaki
Dielectrics Laboratory, Department of Physics, Faculty of Science, Hokkaido University, 060-0810 Sapporo, Japan
*Email address: czdrs2006@hotmail.com

Ionic liquids (IL) have received increasing attention as neoteric “green solvents” and have been widely applied to fields such as chemical reactions, separations, and electrochemical applications. Recently, IL-based microemulsions have become highly concerned[1], which show notable advantages over the traditional ones in the preparation of nanoparticles as well as interesting microstructures[1,2]. The microstructure and the formation mechanism of this kind of microemulsion are still less understood. In this regard, dielectric study is highly desirable.

Dielectric measurements were carried out on bmimBF4/TX-100/Toluene mixtures in this work. By changing the fraction of the components, the microstructures of the mixtures change from IL-in-oil type via bicontinuous to oil-in-IL[3]. Fig.1 shows the dielectric behaviors of these three different types of microemulsions. The obvious difference between different types of microemulsions is a result of the change of their microstructures. The IL-in-oil type microemulsion is more interesting than the others, because IL is confined in a nanosize space where long-range conductance is forbidden. Therefore, the dielectric behaviors of IL droplets are expected to provide valuable information on the mechanism of ionic polarization of IL, which is far from well understood.

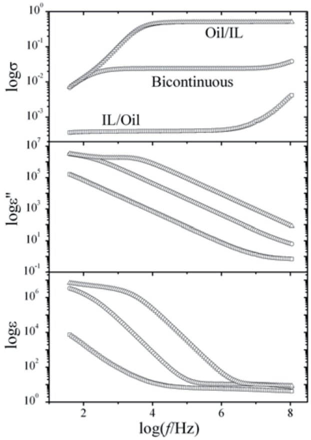


Fig.1. Permittivity and conductivity spectra of IL/TX-100/Benzene systems with different microstructure.

References

[1] Z. Qiu, J. Texter, Curr. Opin. Colloid Interf. Sci. 252, 13 (2008).
[2] T.L. Greaves, C.J. Drummond, Chem. Soc. Rev., 1709, 37 (2008).
[3] Y. Gao, S. Wang, *et al.*, J. Colloid Interf. Sci., 612, 301 (2006).

The dielectric and transport properties of anisotropic polymer electrolytes

A. Greenbaum (Gutina)[1*], Yu. Feldman[1], K. Shvartsman[2], D. Golodnitsky[2],
E. Peled[2], S. Khatun[3], P. Stallworth[3], S. Greenbaum[3]
[1]The Hebrew University of Jerusalem. Department of Applied Physics,
Edmond J.Safra Campus, 91904 Jerusalem, Israel
[2]Tel-Aviv University. Ramat Aviv, 69978 Tel-Aviv, Israel
[3]Hunter College of CUNY, Park Avenue 695, 10065 NY, USA
*Email address: Anechka@vms.huji.ac.il

Success in the development of high-conductive polymer electrolytes (PE) for all-solid-state lithium and lithium-ion batteries depends on finding a way to form new crystalline structures. These structures promote cation transport decoupled from the segmental relaxation of the host polymer and have enhanced inter- and intrachain mobility of Li+. The main goal of this study is to investigate the influence of homogeneous/gradient magnetic field (HMF/GMF) and aromatic dipeptide nanotubes (ADNT) filler on morphology, conductivity and dielectric properties of polyethylene oxide (PEO) - based lithium triflate ($LiCF_3SO_3$) polymer electrolytes.

Dielectric properties of the materials were investigated using Broad Band Dielectric Spectrometer (NOVOCONTROL BDS 80) in wide frequency (0.1 Hz - 1 MHz) and temperature (-100 ^{0}C ÷ 55 ^{0}C) ranges. Casting of LiTf:P(EO)$_3$-ADNT under a gradient magnetic field (GMF) created by NdFeB magnets, resulted in additional conductivity enhancement and changes in dielectric spectra of the material.

The results of the dielectric measurements together with PE characterization by a variety of techniques (HRSEM, MDSC, XRD, FTIR, NMR) furnish insights into the mechanism of crystallization and ion conduction in ordered helical-type polymer systems.

Dielectric relaxation in double potassium yttrium orthophosphate $K_3Y(PO_4)_2$ doped by ytterbium ions

S. Szulia[1*], H.A. Kołodziej[1], M. Kosmowska[1], G. Czupińska[2]

[1] Faculty of Chemistry, University of Wrocław
[2] Department of Inorganic Chemistry, Wrocław University of Economics
*Email: sylwia.szulia@o2.pl

Electric properties were scrutinized in double potassium yttrium orthophosphates $K_3Y_{(1-x)}Yb_x(PO_4)_2$ (x=0.01, 0.05). Both compounds were synthesized by means of solid phase reaction by sintering a stoichiometric mixture of the initial orthophosphates. of YPO_4, K_3PO_4 and Yb_2O_3 at 1200 ˚C for 4 hours. The obtained orthophosphate were melted in closed platinum-rhodium tube in the argon atmosphere at 1440 ºC.

Electric permittivity and dielectric loss measurements have been performed on polycrystalline samples in the temperature range -50 °C – 120 °C and frequency range 1kHz – 1MHz by means of HP 4282A impedance meter. Samples were made as pellets 10 mm in diameter and about 1-2 mm thick. Copper-foil electrodes were affixed to the prepared pellets. Before experiment, samples were annealed at a temperature of 170˚C in vacuum in order to decrease the amount of water absorbed from the air thus a number of electric charges is also reduced rather substantially. The frequency and temperature dependence of electric properties were analyzed by theoretical models of dielectric relaxation in order to obtain information abut molecular dynamic of our solids in external electric field.

Dielectric relaxation of aqueous salts solutions with negative hydration of ions

A. Kobelev, A. Lileev, A. Lyashchenko
N.S. Kurnakov Institute of General and Inorganic Chemistry of RAS, 119991 Moscow,
Leninsky prosp., 31, Russia.
E-mail address: sumkin@amik.ru, aklyas@mail.ru

The negative hydration is understood as increase in mobility of water molecules in the first sphere of ions (in terms of Samoilov's theory). Most brightly its features can be displayed in KI and CsI aqueous solutions. We studied complex dielectric permittivity (ε' and ε") of KI (0.5, 1.0, 2.0, 3.0, 4.0 m) and CsI (0.5, 1.0, 1.5, 2.0, 2.4, 2.75 m) aqueous solutions at temperatures 288, 298, 308, 313, 323K in the frequency range of dispersion of dielectric permittivity of water and solutions. Measurements were carried out by the method of thin dielectric rode in a waveguide at frequencies 7, 10, 13, 16, 19, 22, 25 GHz. The low-frequency (1 KHz) specific conductivity was measured to calculation of ionic losses. At high concentration especially at higher temperatures and low frequencies the contribution of ionic losses is high, therefore accuracy of determination of dipole losses, static dielectric constant and dielectric relaxation time is lower.

One relaxation process observed in the investigated solutions that described by the Debye or Cole-Cole equations. The values of static dielectric permittivity (ε_S) characterizing the electrostatic contributions to hydration of ions are calculated with use of the experimental data of high-frequency permittivity and dipole losses. The decrease of ε_S values occurs with KI and CsI concentration increase. For concentrated solutions the values of static dielectric permittivity at 298K reduce to ~40-50, whereas in pure water ε_S ~80. As ionic radius Cs^+ is more than ionic radius K^+ the decrease of ε_S values is expressed more poorly in the case of CsI solutions. The temperature coefficient of ε_S is equal to zero in high concentrated solutions, and probably changes a sign in case of KI solutions.

The values of dielectric relaxation time (τ) reflecting the changes of water molecules mobility in hydration shells of cations and anions are found. In KI and CsI solutions τ decreases with salt concentration. In case of CsI solutions the decrease of τ is weaker. Using the Eyring theory of absolute reaction rates the values of activation enthalpy ($\Delta H_\varepsilon^{++}$) of dielectric relaxation process were calculated from temperature τ dependences. $\Delta H_\varepsilon^{++}$ decrease for all investigated solution. The reducing of τ and $\Delta H_\varepsilon^{++}$ values testifies to structure breaking effect of initial water H-bond net. It appears stronger in comparison with other similar systems (KOH, KCl) and it is caused by the maximal negative hydration of cations K^+ and Cs^+ and anion I^- which do not form hydrate complexes in solution. Thus iodide-anion is the strongest breaker of water structure among other anions. Character and a sign of concentration dependence of τ change at higher temperatures and high salt concentrations when initial water structure is disturbed by thermal. In this case the hydration interactions of ions are more pronounced. They cause increase of τ values and probably the transition from negative to positive hydration of ions in potassium iodide and cesium iodide solutions occurs at temperatures 313-323K.

This work is supported by the grants of Presidium RAS and RFBR N 08-03-00095

Characteristic hopping lengths and molecular volumes of imidazolium-based ionic liquids

J. R. Sangoro*, C. Iacob, and F. Kremer
Institute of Experimental Physics I, Linnéstr. 5, 04103, Leipzig, Germany
*Email address: sangoro@physik.uni-leipzig.de

Translational diffusion in bis(trifluoromethylsulfonyl)imide-based glass-forming ionic liquids (ILs) is investigated in a wide frequency and temperature range by means of Broadband Dielectric Spectroscopy (BDS), and Pulsed Field Gradient Nuclear Magnetic Resonance (PFG NMR) [1-3] as shown in Fig. 1. It is experimentally shown that in the time-scale characterizing the cross-over from sub-diffusive to diffusive ion dynamics, the hopping lengths are of the order of molecular diameters determined from quantum-chemical calculations [3]. This provides a direct means – via Einstein-Smoluchowski relation – to determine diffusion coefficient by BDS over more than 8 decades unambiguously and in quantitative agreement with PFG NMR measurements. Unprecedented possibilities in the study of charge transport and dynamic glass transition are thus opened.

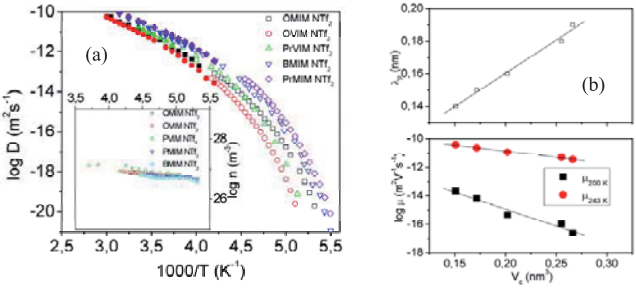


Fig. 1: (a) Diffusion coefficients determined from broadband dielectric spectra (open symbols) upon applying the Einstein-Smoluchowski equation for a series of ionic liquids based on bis(trifluoromethylsulfonyl)imide anion as well as the diffusion coefficient measured by PFG NMR (filled symbols) versus inverse temperature. Inset: the effective number density of charge carriers as a function of inverse temperature. (b) The experimentally obtained hopping lengths (upon combining PFG NMR and BDS) versus the sum of molecular volumes of anions and cations obtained from quantum chemical calculations for the different ionic liquids based on the same bis(trifluoromethylsulfonyl)imide anion. The calculations are carried out in the temperature ranges spanned by both techniques. The mobility at two selected temperatures are also compared to the computed volumes.

References

[1] *Broadband Dielectric Spectroscopy*, edited by F. Kremer and A. Schönhals, Springer (2003).

[2] J. R. Sangoro, A. Serghei, S. Naumov, P. Galvosas, J. Kärger, C. Wespe, F. Bordusa, and F. Kremer, Phys. Rev. E 77, 051202 (2008); J. R. Sangoro et al, J. Chem. Phys. 128, 214509 (2008) ; J. R. Sangoro, C. Iacob, A. Serghei,C. Friedrich, F. Kremer, *Phys. Chem. Chem. Phys.* 11, 913 (2009).

[3] J. R. Sangoro et al, (2010) Submitted.

Dielectric Strength of Polaron Process as Effective Dipole Correlation Factor in Ferroelectric $KTaNbO_3$

Shimon E. Lerner[1*], **Paul Ben Ishai**[1], **Michal Mierzwa**[2],
Marian Paluch[2], **Aaron J. Agranat**[1], **and Yuri Feldman**[1]

[1]Hebrew University of Jerusalem, Givat Ram, 91904 Jerusalem, Israel
[2]Institute of Physics, Silesian University, Bankowa 12, Katowice 40-007, Poland
*Email address: shimon.lerner@mail.huji.ac.il

The dielectric properties of a Polaron process present in $KTaNbO_3$ crystals were measured (10^{-2}-10^{6}Hz, at 300-375 °K) using Broadband Dielectric Spectroscopy. An analysis was then performed utilizing dielectric theory and the insight provided through the Kirkwood-Fröhlich molecular models[1]. At the same time, the theoretical parameters of such small Polarons have been well studied using the simple Holstein model[2]. Combining these two very different approaches, based on comparing them in terms of free energy, gives rise to many new insights, including a new definition for an electron hopping Kirkwood correlation factor. These insights were then tested by using hydrostatic pressure (up to 7.5kbar) to gently perturb the system and observe the outcome in terms of the Cole-Cole $\alpha(ln\,\tau)$ behavior. The Polaron dynamics, as reflected through the dipolar correlations and free electron carrier concentrations, can thus be accurately monitored from a dielectric standpoint.

References

[1] H. Fröhlich, Theory of Dielectrics, Clarendon Press, (1949).
[2] T. Holstein, Ann. Phys. (N.Y.) 8, 325 (1959).

Behavior Dielectric Properties of Ceramic System (SiO_2-Fe_2O_3-MoO_3) Added to V_2O_5 with Temperature Variation

C.C.Silva [1*], T. S. M. Fernandes [1]; M. A. S. Silva[1]; M.M. Costa[2] and A.S.B. Sombra[1]

[1] Telecommunications and Materials Science and Engineering Laboratory (LOCEM),
Department of Physics, UFC, Campus do Pici, Fortaleza – CE, Brazil
* ccsilva@fisica.ufc.br
[2] Physics Department - Federal University of Mato Grosso – UFMT

The sensitivity characteristics of metal–oxide ceramics[1,2] have been extensively investigated in recent years. The metal tin dioxide (SnO_2) is well-known material for various applications including preparation of semiconductor devices such as gas sensors[3,4] humidity sensors[4,5] and varistor[6-10]. SnO_2–Co_3O_4–Nb_2O_5–Cr_2O_3 ceramic material exhibits not only varistor properties discussed in the literature but also humidity-sensitive properties. The objective of this work was to investigate the structural and dielectric characteristics of stoichiometric quantities of ceramic system SiO_2-Fe_2O_3-MoO_3 added of V_2O_5 through reaction of the solid state. The ceramic system was prepared by solid state method (SS) in a planetary high energy ball milling (BM) (Fritsch Pulverisette 7). Stoichiometric quantities of SiO_2 (Aldrich, 99.8%), Fe_2O_3 (Vetec, 97%), MoO_3 (Vetec, 99%) V_2O_5 (Aldrich, 99.9%) were wet milled with alcohol during 3h with a rotational speed of 370 rpm and then sinterized at 1300ºC during 1h in a conventional furnace with a rate of 5 °C/min, where a heating ramp at 450ºC during 1h was used to remove any gas present in the samples. The samples **A** (SiO_2-Fe_2O_3-MoO_3), **BV** (SiO_2-Fe_2O_3-MoO_3 + 0.3% weigh V_2O_5) **CV** (SiO_2-Fe_2O_3-MoO_3 + 0.5% weigh V_2O_5) and **DV** (SiO_2-Fe_2O_3-MoO_3 + 0.7% weigh V_2O_5) were studied by X-ray diffraction (XRD) and dielectric measurements with temperature variation. The presence of nanocrystals was confirmed by X-ray diffraction. Dielectric measurements and loss in the 10^{-1} - 10^{6} Hz frequency range, with temperature variation (30, 40, 50), have been performed to compare whether there were improvements in the ceramic system with the V_2O_5 addition and which presented the best result.

References

[1] U. Lampe, J. Gerblinger and H. Meixner, Sensors and Actuators B 26, 97-104 (1995).
[2] Y. Shimizu, M. Shimabukuro, H. Arai and T. Seiyama, Chem. Lett. 7, 917-920 (1985).
[3] T. Seiyama, A. Kato, K. Fujiishi and M. Nagatani, Anal. Chem. 34, 1502-1503 (1962).
[4] B.M. Kulwicki, J. Am. Ceram. Soc. 74, 697-708 (1991).
[5] E. Traversa, Sens. Actuators B 23, 135-156 (1995).
[6] A.B. Glot, A.M. Chakk, B.K. Chernyi and A.Ya. Yakunin, Inorg. Mater. 10, 1866-68 (1974).
[7] A.Ya. Yakunin, B.K. Chernyi, A.M. Chakk and A.B. Glot, Inorg. Mater. 12, 803-805 (1976).
[8] A.B. Glot, Inorg. Mater. 20, 1522-1523 (1984).
[9] A.B. Glot and A.P. Zlobin, Inorg. Mater. 25, 274-276 (1989).
[10] P.N. Santosh, H.S. Potdar and S.K. Date, J. Mater. Res. 12, 326-328 (1997).
[11] S.A. Pianaro, P.R. Bueno, E. Longo and J.A. Varela, Ceram. Int. 25, 1-6 (1999).

Slow molecular mobility and calorimetric studies in the amorphous solid state of some imidazolium ionic liquids derivatives

H. P. Diogo[1*], **J. J. Moura-Ramos**[2], **S. S. Pinto**[2]
[1]Centro de Química Estrutural, Complexo Interdisciplinar,
Instituto Superior Técnico, 1049-001 Lisboa, Portugal
[2]Centro de Química-Física Molecular, Complexo Interdisciplinar,
Instituto Superior Técnico, 1049-001 Lisboa, Portugal
*Email address: hdiogo@ist.utl.pt

The knowledge of the time scales of molecular motions is needed for a better understanding of the amorphous solid state. The quenching of a disordered system down to below the glass transition temperature, Tg, often results in a glassy state (non-ergodic). This non-equilibrium situation induces structural relaxation, i.e. drives the system towards lower free energy states of the landscape, giving rise to time dependent changes of several properties of the sample. This is denoted as “physical aging” given that no chemical reactions occur in such a process. Understanding aging behavior is also an important point in the context of the physics of the amorphous solid state.

Room temperature ionic liquids (RTIL´s) formed by large unsymmetrical ions, show a low value of the lattice energy when compared with ionic crystals and, like other inorganic and organic substances, exhibit a strong tendency for supercooling. Despite the very strong increase of the research activity on RTIL’s in the last decade, the published studies on the molecular mobility in the amorphous solid state, and in the supercooled liquid region are scarce. Some of the exceptions are studies by ^{13}C-NMR and ^{1}H-NMR[1], and more recently by dielectric relaxation spectroscopy (DRS)[2-5]. In addition, since it is believed that the charge transport in these materials is assisted by the glassy dynamics, a deeper insight on the slow molecular mobility in the glassy state of those materials should be desirable.

In this work the relaxations on some imidazolium ionic liquids derivatives (figure 1) in the glassy state have been studied by the Thermally Stimulated Depolarisation Currents (TSDC) technique, and the obtained results will be reported. Some DSC results on the same systems will also be presented.

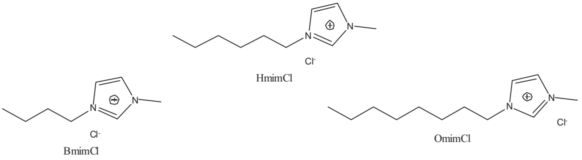


Fig.1. Molecular structures of BmimCl, HmimCl and OmimCl.

References
[1] M. Imanari, M. Nakakoshi, H. Seki, K. Nishikawa, Chem. Phys. Lett. 459, 89 (2008).
[2] A. Rivera, E.A. Rossler, Phys. Rev. B 73, 212201 (2006).
[3] A. Rivera, A. Brodin, A. Pugachev, E.A. Rossler, J. Chem. Phys. 126, 114503 (2007).
[4] A. Stoppa, J. Hunger, R. Buchner, G. Hefter, A. Thoman, H. Helm, J. Phys. Chem. B 112, 4854 (2008).
[5] J. Hunger, A. Stoppa, S. Schrodle, G. Hefter, R. Buchner, ChemPhysChem 10, 723 (2009)

Dielectric Spectroscopy of the $C0_2Y$, Y-type hexaferrite $Ba_2Co_2Fe_{12}O_{22}$ added with Bi_2O_3

M.M. Costa[1], G.F.M. Pires Júnior[2], A.M.Walterley[3], C.C Silva[2], A.S.B. Sombra[2].
[1]Physics Department, Federal University of Mato Grosso - UFMT, 78060-900 – Cuiabá – MT – Brazil
URL: http://www.fisica.ufmt.br – maurocosta@pq.cnpq.br
[2] Laboratório de Telecomunicações e Ciências e Engenharia de Materiais (LOCEM), Departamento de Física, Universidade Federal do Ceará (UFC), Caixa Postal 6030, CEP 60455-760, Fortaleza, Ceará, Brasil
URL: http://www.locem.ufc.br – sombra@ufc.br
[3]Departamento Eletro-Eletrônica, Instituto Federal de Educação, Ciência e Tecnologia de Mato Grosso - Campus Cuiabá, 78.005-200, Cuiabá, MT, Brasil

***Email address:** maurocosta@pq.cnpq.br

In a recent article[1] M. M. Costa at all repor about the same material added with PbO (0, 3, 5 and 10 wt.%). In the present work, the preparation of a layered magnetic ceramic oxide $Ba_2Co_2Fe_{12}O_{22}$ (Co_2Y) added with Bi_2O_3 is described by the solid state reaction method in the frequency range 10Hz to 1MHz were measured at several temperaturas in the range 0f 313 to 493K. X-ray diffraction (XRD) technique was used to study the structural properties. The complex-plane impedance spectra indicate that the material can be represented by a two-layer leaky capacitor which corresponds to the bulk and the grain boundary phenomena at high and low frequecies respectively. The dependence of impedance and conductictivy on temperature and frequency are discussed using the complex impedance spectroscopy (CIS) technique.. The study of the dielectric property of ferrite materials, as a function of temperature, are important for microwave absorption applications. The protection of sensitive circuits from the interference of external microwave radiation, is an important technological application of these materials.

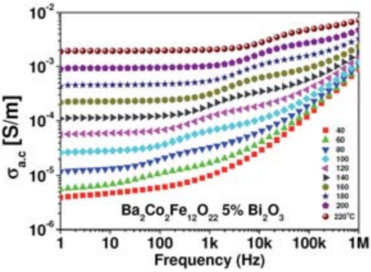


Fig. 1 The ac conductivity at different temperatures for $Ba_2Co_2Fe_{12}O_{22}$ 5% Bi_2O_3

[1] M. M. Costa, G. F. M. Pires Júnior, A.S.B. Sombra. Dielectric and Impedance Properties Studies of the of lead doped (PbO)- Co_2Y Type Hexaferrite ($Ba_2Co_2Fe_{12}O_{22}$ (Co_2Y)). accepted for publication in Materials Chemistry and Physics 2010

Nb_2O_5 nanopowders - structural, morphology and dielectric properties

M.P.F Graça *, A. Meireles, C. Nico and M.A. Valente

I3N, Physics Department, University of Aveiro, 3810-193 Aveiro, Portugal
*Email address: mpfg@ua.pt

Niobium oxide has found important technological applications, due to its physical characteristics, such as: stable electrical parameters, high dielectric constant, reduce ignition and due to their wide availability, lower cost is a present advantage [1]. It is known that the properties of Nb_2O_5 strongly depend on the synthesis procedure. In the present work, sol-gel technique was used to develop Nb_2O_5 amorphous powders. These powders were them heat-treated at several temperatures between 400 and 1200ºC. The XRD patterns of the treated powders reveal the formation of Nb2O5 in different crystalline structures. For treatments temperatures below 900ºC the Nb_2O_5 orthorhombic phase was detected and for treatments above 1000ºC the phase detected was monoclinic. For heat-treatments at intermediate temperatures the two crystal phases were observed. The Raman and FTIR spectroscopy results confirm the XRD patterns.

The electric measurements showed that the sample with monoclinic structure presents the lowest dc and ac activation energy. The sample treated at 900ºC, presenting the both crystal structures, show the highest dielectric constant (ε=94 at 1kHz and 300K) and the 800ºC orthorhombic sample shows the lowest dielectric loss. The dielectric spectroscopy analysis reveals, using the modulus formalism, the presence of a relaxation mechanism at low frequencies whose relaxation time decreases with the increase of the treatment temperature. These results were related with the morphology characteristics obtained by SEM microscopy.

References

[1] H.Störmer, J. Eur. Ceram. Soc. 29 (2009), 1743-1753.

Dielectric properties of the glasses and related crystalline phases issued from the $BaNb_2O_6$-$NaNbO_3$-WO_3-P_2O_5 system

M.A. Valente[1], M.P.F. Graça[1] and L. Bih[2]

[1] I3N – Physics Department, University of Aveiro, 3810 – 193, Aveiro – Portugal

[2] Equipe Sciences de Matériaux, FST-Errachidia, Maroc

*Email address: mav@ua.pt

It is well know that alkaline and/or earth-alkaline niobates such as NaNbO3 and BaNb2O6 exhibit interesting physical properties and several applications of them were proposed in the literature

While the $NaNbO_3$ is a material that shows a very good combination of electrical, mechanical and chemical properties required for technological materials [1] the $BaNb_{2O6}$-based compounds are receiving great attention as a new ferroelectric tungsten bronze niobate material [2]. On the other hand, phosphate glasses have unique properties and especially they have low thermal melting, softening temperatures and high thermal expansion coefficient. Tungsten based materials are well known by their optical properties.To our knowledge there is no work in the literature reporting on the glasses containing the above components. According to the chemical compositions, these glasses and/or their glass-ceramics are expected to have high permittivity and could be used as the dielectric energy-storage materials to fabricate high energy density devices. This work deals with the elaboration, thermal analysis, density measurements, X-ray diffraction (DRX), Raman and infrared (FTIR) spectroscopies, scanning electron microscopy (SEM) and dielectric properties of the $(1\text{-}y)[Ba_{(2.15\text{-}x)}Na_{(0.7+x)}Nb_{(5\text{-}x)}W_xO_{15}]\text{-}yP_2O_5$ glasses. Controlled crystallization of them under different heat-treatment temperature was carried out based on their thermograms DTA. X-Ray diffraction analysis has permitted to identify the phases. The correlation between the structure and the physical properties such as dielectric parameters shows that the thermal history of the glasses is an important influence task for controlling these properties.

References

[1] M.P.F. Graça et al. / Physica B 396 (2007) 62–69

[2}. W. Sakamoto, M. Mizuno, J. Alloys Comp. 408–412, 538 (2006)

Explaining the dielectric behavior of poly- and single-crystalline CCTO using a polaronic stacking fault defect model

F. Amaral[1-2], M. Valente[1*], L. Costa[1], F. Costa[1], A. Fernandes[1]

[1]I3N and Physics Department, University of Aveiro, 3810-193- Aveiro, Portugal
[2]College of Technology and Management of Oliveira do Hospital, 3400-124 Oliveira do Hospital, Portugal

* Email address: Filipe.amaral@estgoh.ipc.pt

The $CaCu_3Ti_4O_{12}$ (CCTO) is a material, with a perovskite structure, that has a very high dielectric constant (ε_r) and good temperature stability over a wide range, from 100 to 600 K[1,2] and frequency up to 10^6 Hz. Because of its impressive dielectric constant, reaching values higher than 10^4 at 1 MHz, CCTO has a high potential for technological applications, in particular memory devices, capacitive components and microwave devices, due to the decrease of dimensions needed in microelectronic equipment[3].

Huge ε_r values have been measured in both single crystals and ceramics[4], and, in spite of the intense debate, it is not clear if this effect is an intrinsic property of the material or if it can be related to extrinsic effects. Even though it is clear that the preparation method and doping has a great influence on the microstructure and dielectric properties of this material.

In this work we describe the preparation of CCTO fibres by laser floating zone technique (LFZ). Using gradually lower pulling rates we could observe the evolution from poly- to single-crystalline fibres.

The samples have been studied by X-ray diffraction, scanning electronic microscopy, energy dispersive X-ray spectroscopy and AC impedance spectroscopy. Microstructure of poly- and single-crystalline CCTO has been analysed and correlated with the dielectric relaxation parameters calculated using the Cole-Cole model[5]. The polaronic stacking fault defect model, proposed by Bueno et al.[6], which reconciles the opposing views of researchers on both sides of the intrinsic versus extrinsic, was also used to explain the dielectric behavior of poly- and single-crystalline samples.

References

[1] A.P. Ramirez, M.A. Subramanian, M. Gardel, G. Blumberg, D. Li, T. Vogt and S.M. Shapiro, Solid State Comm. 217, 115, (2000).
[2] M.A. Subramanian and A.W. Sleight, Solid State Sci. 347, 4 (2002).
[3] A.F.L. Almeida, P.B.A. Fevhine, J.C. Goes, M.A. Valente, M.A.R. Miranda and A.S.B. Sombra, Mat. Sci. and Eng. B 113, 111 (2004).
[4] F. Amaral, C.P.L. Rubinger, M.A. Valente, L.C. Costa and R. L. Moreira, J. Appl. Phys. 105,034109 (2009).
[5] K.S. Cole and R.H. Cole, J. Chem. Phys. 341, 9 (1961).
[6] P.R. Bueno, R. Tararan, R. Parra, E. Joanni, M.A. Ramírez, W.C. Ribeiro, E. Longo and J.A. Varela, J. Phys. D: Appl. Phys. 42, 055404 (2009).

AC conductivity of zirconia doped with rare earth oxides

Benali Z. , Ziane B. , Belarbi H. (*) ,Haouzi A.

Laboratoire synthèse et catalyse, Université IBN KHALDOUN Tiaret 14000, Algeria

(*) corresponding author , belarbi@mail.univ-tiaret.dz

In this work we elaborated a ceramic with zirconia doped with rare earth oxides (neodyme, samarium, ytterbium, gadolinium and thulium). Samples were pressureless-sintered at 1200°C for 24 h, from powders finely ground in a mortar. The electrical conductivity of the samples was investigated by dielectric spectroscopy over the range of 0.01 Hz to 1MHz by means of NOVOCONTROL spectrometer from 453K to 473K. The activation energies of the charge carriers , determined from an Arrhenius law vary 0.72 eV to 0.82 eV for the doped samples while it is 0.93 eV for the not doped sample. The conduction in this type of materials is assigned, at high-temperatures, to oxygen vacancies. The doping that not exceed 5%, allowed to lower the barrier of energy until 29 % of its initial value. We attempt to correlate the decrease of activation energies to the disorder introduced in the samples of zirconia.

Electric and dielectric response of nanosize zinc-ferrites crystallites incorporated in a glass network

M.G. Ferreira da Silva a)*, **M.P.F. Graça** b)

a) Department of Glass and Ceramic Engineering, CICECO, University of Aveiro, 3800-193 Aveiro, Portugal

b) I3N - Department of Physics, University of Aveiro, 3800-193 Aveiro, Portugal

correspond author: gsilva@ua.pt

Abstract

Ferrites are used for components to make electrical and electronic circuits including transformers nductors, switching elements, microwave circuits, and other high-frequency apparatus. Such materials are conventionally formed by sintering. This technique is complex, time-consuming and normally difficulties are encountered in producing ferrites to meet performance specification due to the variability inherent to the sintering technique. Recently, interest in the study the properties of crystallites inserted in a glass network has been shown. In the present work (100-2x) SiO_2-xFe_2O_3-$xZnO$ (mole %) glasses, with x=2.5, 5 and 10, where prepared by the sol-gel method. These glasses were heat-treated, in air, at 500 and 800ºC. In the 500ºC treated samples was confirmed, by X-ray diffraction (XRD), the presence of nanosize crystals of hematite and ferrite. However, in the 800ºC treated samples seems to be only present ferrite nanosize crystals. The morphology of these samples was studied by scanning electron microscopy (SEM). The dielectric analysis of theses samples, at room temperature, show different behaviours at 500 and 800ºC. The sample with 10 mole % of $ZnO+Fe_2O_3$ presents an anomalous behaviour. The dc conductivity measurements show that the ionic conduction in these glass-ceramics depends on the number of Zn^{2+} ions structurally inserted in the glass matrix.

Effect of adding TeO_2 in $CaCu_3Ti_4O_{12}$ on the dielectric losses

F. Amaral, B. Ferreira, M.A. Valente, M.P.F. Graça* and L.C. Costa

I3N, Physics Department, University of Aveiro, 3810-193 Aveiro, Portugal
*Email address: mpfg@ua.pt

High dielectric permittivity has been found on the oxide $CaCu_3Ti_4O_{12}$ (CCTO), in the order of 10^5 at 1 kHz and room temperature, being nearly constant to temperatures until 300 ºC [1]. These characteristics lead this material to be useful in a high number of technological applications, including the miniaturization. However, the high dielectric constant (ε') is also accompanied by a relative high dielectric loss (tan δ). The physical explanation for the high dielectric permittivity behaviour is actually an open question. Some researchers suggest that this behaviour is intrinsic [2-3], while others attribute to extrinsic effects [4-6]. Among the last ones, the barrier layer capacitor model (BLC) is commonly accepted. It is believed that insulating surfaces are formed on semiconducting grains during the sintering process. This kind of microstructure causes the electric charge accumulation at the grain boundaries, and consequently, a large number of these boundary barrier layer capacitors can explain the colossal permittivity observed for CCTO.

In this work, the change of the dielectric behaviour of the CCTO samples due to the introduction of a material with low dielectric permittivity (TeO_2) is the main goal. Thus, the composites (x)CCTO:(1-x)TeO_2, with x=0, 5, 10, 25 and 50% (%wt) were prepared by solid state reaction and then submitted to controlled heat-treatments at temperatures between 800 ºC and 1050 ºC. The samples structure was analyzed by X-Ray Powder Diffraction (XRD), the morphology by Scanning Electronic Microscopy (SEM), and Energy Dispersive Spectroscopy (EDS) was used to differentiate the chemical distribution of the grains and of the grain-boundaries. Dielectric spectroscopy measurements were performed in the frequency range between 40 Hz and 110 MHz as a function of the temperature (100 to 500 K). Dielectric measurements, at room temperature, in the microwave range were also performed.

References

[1] A. F. L. Almeida, P. B. A. Fechine, M. P. F. Graça, M. A. Valente, A. S. B. Sombra, J Mater Sci: Mater Electron 20 (2009) 163
[2] M. A. Subramanian, D. Li, N. Duran, B. A. Reisner and A. W. Sleight, J. Sol. State Chem. 151 (2000), 323.
[3] A. P. Ramirez, M. A. Subramanian, M. Gardel, G. Blumberg, D. Li, T. Vogt, S.M. Shapiro, Sol. State Commun. 115 (2000), 217.
[4] M. A Subramanian, A. W. Sleight, Sol. State Sci. 4 (2002), 347.
[5] D. C. Sinclair, T. B. Adams, F. D. Morrison, A. R. West, Appl. Phys. Lett. 80 (2002), 2153.
[6] M. H. Cohen, J. B. Neaton, L. He, D. Vanderbilt, J. Appl. Phys. 94 (2003), 3299.

Dielectric studies on antimony tellurite glasses doped with titanium

T. Satyanarayana[1*], M.A. Valente[1], M.P.F. Graça[1] and N. Veeraiah[2]

[1]Department of Physics, University of Aveiro, 3810-193 Aveiro, Portugal
[2]Department of Physics, Acharya Nagarjuna University – Nuzvid Campus, 521201, A.P., India
[*]Email: satyamphysics@rediffmail.com

Abstract

Sb_2O_3-TeO_2-B_2O_3 glasses mixed with different concentrations of TiO_2 (from 0 to 2.0 mol %) were prepared. These glasses were characterized by XRD and scanning SEM. The dielectric constant (ε'), dielectric loss ($\tan \delta$) and a.c. conductivity σ_{ac} over a wide range of frequency and temperature have been investigated. The XRD studies and SEM pictures have clearly indicated that the samples prepared were amorphous. The variation of dielectric loss with temperature exhibited dielectric relaxation effects. The observed relaxation have been analyzed by a pseudo Cole–Cole plot method and the spreading of relaxation times has been established. With the help of the optical absorption and ESR spectra, it has been identified that titanium ions co-exist in Ti^{3+} state in addition to Ti^{4+} state in these glass matrices. Tellurium ions and Ti^{3+} are assumed to be responsible for the relaxation character of dielectric loss. The dielectric parameters (ε' & ε'', and σ_{ac}) are found to increase with the rise in the concentration of TiO_2 up to 2.0 mol %, indicating an enhancement in the concentration of Ti^{3+} that take part as modifying ions. These studies have indicated that as the concentration of TiO_2 is increased up to 2.0 mol%, the insulating strength of the glasses decreases. The low-temperature part of the a.c. conductivity which is observed to be nearly temperature independent has been explained on the basis of QMT model.

Dynamics of ionic liquids based on different cations

A. Rivera-Calzada[1], K. Kaminski[2], C. Leon[1], M. Paluch[2]

[1]*GFMC, Dpto. Física Aplicada 3, Universidad Complutense de Madrid, Spain.*

[2]*Institute of Physics, Silesian University, Katowice, Poland.*

ABSTRACT

We present a study of the dynamics of molten salts, so called (room temperature) Ionic Liquids (IL), which are usually a combination of an anion and an asymmetric organic cation that are liquid even below room temperature. The IL studied can be supercooled and eventually reach the glass transition when cooling or applying pressure [1,2]. Their dynamics are nicely probed by means of dielectric spectroscopy, being the electric response dominated by the ionic conductivity, showing a VFT dependence of the dc ionic conductivity, and secondary relaxations below T_g [3]. When the alkyl chain of the cation is long we find the same qualitative and quantitative dynamic behaviour as molecular glass formers, as supercooling the samples either by reducing temperature or under high pressure, apparently unaffected by Coulomb interactions [4,5]. Dielectric measurements performed on a short alkyl chain cation, the EMIM TF_2N, will be analyzed in the search of any Coulomb fingerprint.

REFERENCES

1. P. Wasserscheid, T. Welton, *Ionic Liquids in Synthesis*, Wiley-VCH (2003)
2. Angell et al., J. Phys. Chem. B **107**, 6170 (2003)
3. A. Rivera and E. A. Rössler, PRB **73**, 212201 (2006)
4. A. Rivera, A. Brodin, A. Pugachev, E. A. Rössler, JCP **126**, 114503 (2007)
5. A. Rivera-Calzada, K. Kamisnki, C. Leon, M. Paluch, J. Phys. Chem. B **112**, 3110 (2008)

Dielectric properties of aqueous $Ca(NO_3)_2.4H_2O$ Solution

D B Suryawanshi*, A C Kumbharkhane[1]

*Department of Physics, Shri Havagiswami College, Udgir – 413 517 (India)
[1]School of Physical Sciences, Swami Ramanand Teerth Marathwada University,
Nanded - 431 606 (India)
E-mail: sdbs_123@rediffmail.com, akumbharkhane@yahoo.co.in

A time domain reflectometry (TDR) is used to determine complex dielectric permittivity spectra, in the frequency range 10 MHz to 20 GHz for aqueous Electrolyte solutions. The static dielectric constant, relaxation time and conductivity were determined using nonlinear least squares fit method. Further from static dielectric constant, hydration numbers were determined by using measured solutions density at different temperatures and concentration.

Keywords: Dielectric permittivity, TDR spectroscopy and mixed solvent,

The Evaluating of the activation parameters in the transition region of parylene C by thermally stimulated techniques.

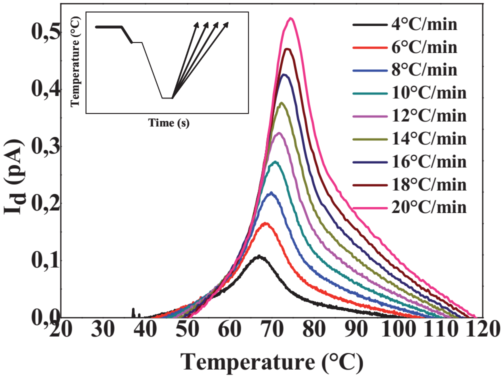
A. Kahouli[1,2*], **A.Sylvestre**[1], **J. Legrand**[3], **F. Jomni**[2], **B. Yangui**[2]

[1] Grenoble Electrical Engineering Lab. (G2Elab), CNRS, 25 Rue des Martyrs, BP166, 38042 Grenoble, Cedex 9, France

[2] Laboratory for Materials, Organization and Properties (LabMOP), Campus Universitaire-El Manar, 2092 Tunis, Tunisia

[3] Varioptic SA, Bâtiment Tony Garnier, 8B, Rue Hermann Frenkel, 69007 Lyon, France
* Corresponding author: abdelkader.kahouli@grenoble.cnrs.fr

The molecular mobility's of α-relaxation is studied by thermally stimulated depolarisation currents (TSDC) in the semi-crystalline parylene C. The activation energy of a motional process is calculated from two different procedures require a single partial polarisation (PP) experiment. The two procedures are based on the influence of the heating rate on the temperature location T_m and on the intensity of the maximum $I(T_m)$ of the PP peak. Moreover, from the maximum intensity peak (T_M) at the glass transition region, the cooperatively rearranging region (CRR) size ($V_{CRR,\ a}$) proposed by Adam and Gibbs as well as the characteristic length ($\zeta_{CRR,\ a}$)[1] of the cooperatively region could be estimated. To provide a reliable means of correlating dynamic (m and T_g) and thermodynamic (ΔC_P and ΔH_m) variable on parylene C, the fragility index m (Angell's scale)[2, 3] is calculated from TSDC data and the obtained value is compared with that obtained by differential scanning calorimetry (DSC).



Partial polarisation component of α-relaxation of parylene C obtained with different heating rates. The insert schematically shows the experimental procedure used in the PP experiment. The thicker lines correspond to the experimental steps where the electric field is applied.

References

[1] P.-D. Hong , W.-T. Chuang, W.-J. Yeh, T.-L. Lin, Polymer. 43, 6879 (2002)
[2] L-M. Wang, A. Angel, and R. Richert, J. Chem. Phys. 074505 (2006)
[3] ANGELL C. A., J. Phys., Cehm. Solids, 49, 863 (1988)

Dielectric properties and hydration of DNA complexes with some intercalators

D.A. Pesina[1]*, **V.A. Kashpur**[2], **O.V. Khorunzhaya**[2] **and V.Ya. Maleev**[2]
[1]V. N. Karazin Kharkiv National University. Svoboda Sq. 4, 61077 Kharkov, Ukraine
[2]Institute for Radiophysics and Electronics NAS of Ukraine. Akad. Proskura str. 12, 61085 Kharkov, Ukraine
*Email address: dashapesina@gmail.com

Since the therapeutic effect of many anticancer, antiviral and antimicrobial drugs is caused by their interaction with DNA, finding out the molecular mechanisms of this interaction is necessary to improve their therapeutic effect. At present it is known that water plays an important role both in maintaining the DNA structure and in the process of the DNA-ligand complex formation. Although the study of water surroundings of nucleic acid-ligand complexes has been carried out using various methods including the x-ray crystallography, osmotic stress, volumetry and molecular modeling methods[1-4], there is still no reliable information on total number of water molecules in the complex hydration shell and on its hydration sites. Therefore we suggest to use the differential dielectric method in the range of millimeter wavelengths to quantitatively estimate the DNA hydration changes during the formation of DNA-ligand complexes. We have studied dielectric characteristics of aqueous solutions of some known intercalators (proflavine hydrochloride, ethidium bromide, propidium bromide) and their complexes with DNA. We also present based on the model concepts calculations of the hydration numbers of the ligands and their complexes with DNA. It has been found that the extent of hydration for all complexes is larger than the sum of hydration of their components taking into consideration P/D ratio. We compare our results with those in the literature, obtained with other methods.

References

[1] X. Qu, J.B. Chaires, J. Am. Chem. Soc., 123, 1 (2001).
[2] L.A. Marky, D.W. Kupke, B.I. Kankia, Methods Enzymol., 340, 149 (2001).
[3] X. Shi, R.B. Macgregor, Biophys. Chem., 125, 471 (2007).
[4] H. Resat, M. Mezei, Biophys. J., 71, 1179 (1996).

Finite-difference calculations for effects of T-tubules on dielectric spectra of skeletal muscle

K. Sekine[1*], A. Yamada[1], H. Kageyama[1], T. Igarashi[1], K. Asami[2]
[1]Faculty of Health Sciences, Institute of Medical, Pharmaceutical and Health Sciences,
Kanazawa University, 5-11-80 Kodatsuno, Kanazawa, Ishikawa, 920-0942, Japan
[2]Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan
*Email address: sekine@kenroku.kanazawa-u.ac.jp

Skeletal muscle cells have planar tubular networks (T-tubules) perpendicular to the long axis of the cells, and their dielectric spectra are characterized by two-step relaxation [1]. Although the high-frequency relaxation (β-relaxation) is attributed to interfacial polarization at sarcolemma, the mechanism of the low-frequency relaxation (α-relaxation) has not yet been fully understood. Interfacial polarization at T-tubules succeeded in explaining the α-relaxation observed for a single cell by the internal electrode (IE) method. However, the intensity of the α-relaxation observed for skeletal muscle tissues by the external electrode (EE) method was much larger than that predicted from the interfacial polarization. In the present study, finite-difference (FD) calculations [2] were carried out to examine whether the α-relaxation due to the interfacial polarization was amplified by interactions between adjacent cells in the measurements of skeletal muscle tissues by the EE method.

The cell was represented by a cuboid (rectangular parallelepiped) 40 μm in height and 10 μm in length and depth. The T-tubules were represented by grids perpendicular to the long axis and were placed at 2 μm intervals. The cell model was placed at the center of the outer cuboid subjected to FD calculations. The height of the outer cuboid was fixed to be 50 μm and its length and depth were changed in a range from 10.4 to 20 μm to mimic the change in the distance between adjacent cells in lateral directions. FD calculations were carried out under three types of boundary conditions that mimic the measurements of a bundle of the cells by the EE method in which the field was parallel (EE-00) and perpendicular (EE-90) to the long axis of the cells, and the measurements of a single cell with IE method. To make clear the effects of T-tubules, similar calculations were carried out for the models without T-tubules.

The models with T-tubules showed two-step relaxation. The high-frequency relaxation coincided with the one-step relaxation shown by the models without T-tubules. Hence the high- and low-frequency relaxation processes were assigned to the α- and β-relaxation, respectively. The ratio $R_{\alpha/\beta}$ of the intensity of the α-relaxation to that of the β-relaxation was almost independent of the lateral distance between the cells in all cases examined in the present study. In addition, $R_{\alpha/\beta}$-values under EE-00 and EE-90 conditions were lower than that under IE condition. These results mean that the interaction between the cells does not amplify the α-relaxation due to the interfacial polarization at T-tubules, and that other mechanisms such as counterion polarization are required to explain the large intensity of the α-relaxation observed by the EE method.

References

[1] K.R. Foster, H.P. Schwan, in: C. Polk, E.Postow (Eds.), Handbook of Biological Effects of Electromagnetic Fields, 2nd ed., CRC Press, Boca Raton, 1996, pp. 25–102.
[2] K. Asami, J. Phys. D: Appl. Phys. 39 (2006) 492–499.

Dielectric modeling of biological cells using three-dimensional finite-element method

K. Asami
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan
Email address: asami@e.kuicr.kyoto-u.ac.jp

Dielectric dispersion of a biological cell suspension in the radio-frequency range is mainly due to interfacial polarization in the heterogeneous structure of cells. Since the surface and internal cell membranes are much less conductive than the cytosol and the external medium, the membrane topology plays an important role in polarization of cells. Analysis of the dielectric dispersion requires modeling of cells. For simple cells modeled as spherical and ellipsoidal shell models, we can use analytical equations that relate the electric parameters of cell components to the dielectric dispersion [1]. In reality, however, cells possess complex structures, for which analytical equations do not suffice, and therefore numerical simulation techniques are of significant importance. There are a few concerns for dielectric modeling of cells by the finite-element method. Cells possess thin membranes, requiring extra fine meshes and considerable computational tasks. To solve the problem, the 'thin-layer' approximation (TLA) that deals with the membrane as an interface of the specific membrane impedance was adopted. It was proved that TLA was useful in greatly reducing computational tasks while accurately coinciding with analytical solutions [2].

The presence of intracellular organelles within a cell increases the numbers of subdomains and boundaries, which makes the modeling of the cell complicated. To simplify the modeling, the 'effective medium' approximation (EMA) was adopted, which regards the composite cytoplasm as an effective homogeneous phase whose dielectric properties are calculated separately. EMA was successfuly applicable to the composite cell model shown in Fig.1 [2]

Many cells have microvilli that are membrane-bound projections on the cell surface, which significantly influence the dielectric properties of the cells. To understand the influences, simulation was made with a cell model that is a sphere with cylindrical projections (see Fig.1). The simulated dielectric dispersion consisted of two relaxation processes, which corresponded to the projections and the spherical body. Conventional analysis based on the spherical shell model was applied to the simulated spectra to estimate the apparent membrane capacitance C_m. When the total surface area of a cell is constant, the apparent C_m was inversely proportional to the square of the effective cell radius and the total membrane capacitance of the cell remained constant irrespective of changing the cell volume.

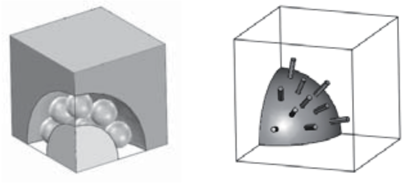


Fig.1. Cell models aligned in a cubic lattice, subjected to FEM calculation. Left: a spherical cell containing intracellular organelles. Right: a microvillous cell. One eighth of each model is shown.

References
[1] K. Asami, Prog. Polym. Sci. 27, 1617 (2002).
[2] K. Asami, submitted (2010).

Time Domain Dielectric Study of Mouse spleen B and T cell suspensions

Andrey Shendrik[1*], Gregory Elikin[2], Igor Resnick[2] and Yuri Feldman[1]

[1]Department of Applied Physics, The Hebrew University of Jerusalem, Givat Ram, Jerusalem 91904, Israel
[2] Department of Bone Marrow Transplantation & Cancer Immunotherapy, Hadassah-Hebrew University Medical Center, P.O. Box 12000, Jerusalem 91120, Israel.

*Email address: shendrik@yahoo.com

The mouse spleen single cell suspension in phosphate buffered saline (PBS) supplemented with 10% bovine serum were studied with the help of the Time Domain Dielectric Spectroscopy (TDDS). The measurements were performed using the coaxial sample cell with effective empty capacitance 0.065 pF. Data was collected at uniform time scale up to 10 ns (frequency range from 100 MHz up to 12 GHz). These measurements were performed at 25-37°C in a thermo stabilized controlled sample cell (± 0.2°C).

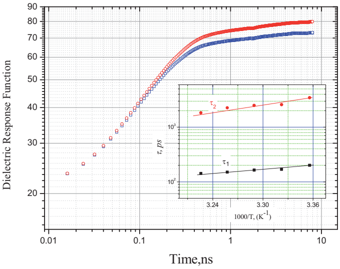


Figure 1. Dielectric response function for $8*10^6$ cell/ml B-mice lymphocytes (blue) and spleen B-lymphocytes leukemia activated (red.) at 25°C; Insert presents the Arrhenius plot for the two fast relaxation rimes for leukemia activated lymphocytes with the activation energy of the processes ~ 27 kJ/Mol (red) and ~ 10 kJ/Mol (black).

It was shown that in this particular frequency range the differences between T and B mouse lymphocytes and the differences between normal B and spleen leukemia activated B-lymphocytes are well pronounced. Figure 1 presents such a difference directly in the time domain in terms of the dielectric response function $\Phi(t)=i\omega L^{-1}[\varepsilon^*(\omega)]$. It is clear that the main diversity is in the interval 100 ps -10 ns, where the anisotropic mobility of the polar fragments of TCR or Ig molecule groups can be observed. A simple analysis of the temperature dependencies allows one to separate the two processes and evaluate their activation energies. These were found to be around 10 kJ/Mol for the fast (~ hundreds of picoseconds) and ~ 27 kJ/Mol for nanosecond process (See insert in Figure 1). This presents us with enough confidence to confirm that TDDS signals have the sensitivity to distinguish the difference in the fast mobility of polar groups on the membrane surface of the studied cells.

Dielectric Influence of the Glutaraldehyde in the Galactomannan Films

Macêdo, A.A.M. [1]*, C.C.Silva [2], Costa, M. M. [3], A.S.B. Sombra [2] and Mazzetto, S.E. [1]*****
[1] Northeast Network on Biotechnology (RENORBIO), Laboratory Products Technology (LPT), Federal University of Ceará, Fortaleza – CE, Brazil
* anaangellica@yahoo.com.br and *** selma@ufc.br
[2] Physics Department - Federal University of Mato Grosso - UFMT
[3] Telecommunications and Materials Science and Engineering Laboratory (LOCEM), Department of Physics, UFC, Campus do Pici, Fortaleza – CE, Brazil
** ccsilva@fisica.ufc.br

Natural polymers have wide availability in nature, wide variety of structures, low cost, stabilizing agents, biodegradable, atoxicity and easy chemical modification. Polymeric materials, generally, have low electrical conductivity and are known as dielectric or insulation[1, 2]. The term dielectric is used when the material is applied to capacitors and, insulating when the material has the function of electrically isolating components of an electrical circuit. The efficient use requires knowledge of their properties. Natural polymers are replacing synthetic polymers due to the increasing interest in the production of novel materials and prepared from polysaccharides represent a new category of environmentally safe materials[3]. Galactomannans, natural polymers, are polysaccharides that occur in the endosperm of the seeds of leguminous plants as cell wall storage components and energy reserves.Galactomannan was obtained from seeds of *Adenanthera Pavonina* L. family Leguminosae (Fabaceae) and subfamily Mimosoideae. To improve the properties of galactomannan is require chemical treatment with crosslinking agents glutaraldehyde treated with three different concentrations 0.01, 0.05 and 0.1 %, GG1, GG2 and GG3, respectively. The influence of the glutaraldehyde in the galactomannan films was characterized using Infrared Spectroscopy (IR), the properties, such as, dielectric loss, loss tangent; real and imaginary modulus was showed using Dielectric Relaxation and thermally characterized using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), under nitrogen atmosphere.

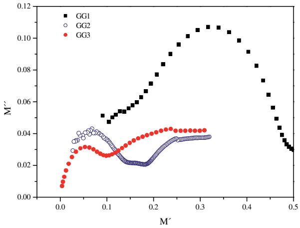


Figure 1 – Imaginary versus Real modulos of samples GG1, GG2 and GG3

References
[1] E.G. Azero and C.T. Andrade, Polym. Test 21, 551-556 (2002).
[2] Y. Cheng, K.M. Brown and R.K. Prud'homme, International Journal of Biological Macromolecules 31, 29-35 (2002).
[3] Šimkovic, I., Carbohydrate Polymers. 74(4), 759-762 (2008)

Thermally stimulated currents study on the amorphous state of two disaccharides: cellobiose and gentiobiose

H. P. Diogo[1*], J. J. Moura-Ramos[2], S. S. Pinto[1,2], T. G. Nunes[1]
[1]Centro de Química Estrutural, Complexo Interdisciplinar,
Instituto Superior Técnico, 1049-001 Lisboa, Portugal
[2]Centro de Química-Física Molecular, Complexo Interdisciplinar,
Instituto Superior Técnico, 1049-001 Lisboa, Portugal
*Email address: hdiogo@ist.utl.pt

It is well recognized that some saccharides such as gentiobiose, cellobiose, raffinose, and trehalose, which are found in desiccation-resistant organisms, act as lyoprotectants of proteins, liposomes and related pharmaceutical materials. The mechanism by which these carbohydrates assist to protect the integrity of such materials is only partially understood, but this ability seems to be a consequence of their hydrogen-bonding features and of their significant tendency for supercooling.

Cellobiose and gentiobiose are structurally related to trehalose, also a disaccharide with a linkage between two D-glucose units. The strong ability of trehalose for biopreservation[1,2] is well recognized. The nature of the residual mobility below the glass transition temperature is believed to represent a crucial issue from the point of view of biopreservation. The study of the slow molecular mobility in structurally related molecules, and the characterization of the glass transition in those substances, will surely help us to understand the origin of this important ability exhibited by some sugars.

This communication reports the comparative study on the slow molecular mobility in the amorphous phase of cellobiose and gentiobiose, carried out by the dielectric technique of the Thermally Stimulated Depolarisation Current (TSDC). The investigation on the effect of aging, in the amorphous gentiobiose, was performed on the sub-Tg region during annealing at T =343 K. The features of different motional components of the secondary relaxation have been monitored as a function of time as the glass structurally relaxes on aging. Finally the steepness index or fragility, m, of cellobiose and gentiobiose was determined by DSC based on of the scanning rate dependency of Tg, indicating that these disaccharides are moderately fragile liquids.

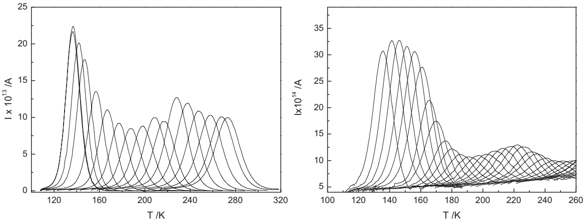


Fig.1. Partial polarisation components of the slow mobility of amorphous gentiobiose (left) and cellobiose (right).

References

[1] (*a*) K.C. Fox, Science 267, 1922 (1995); (*b*) J.L. Green, C.A. Angell, J. Phys. Chem. 93, 2880 (1989).

Dielectric properties of the Collagen_Chitosan membrane in the temperature range

M.M. Costa[1], J.C. Góes[2], S. D. Figueirô[2], A.S.B. Sombra[2].
[1]Physics Department, Federal University of Mato Grosso - UFMT, 78060-900 – Cuiabá – MT – Brazil
URL: http://www.fisica.ufmt.br – maurocosta@pq.cnpq.br
[2] Laboratório de Telecomunicações e Ciências e Engenharia de Materiais (LOCEM), Departamento de Física, Universidade Federal do Ceará (UFC), Caixa Postal 6030, CEP 60455-760, Fortaleza, Ceará, Brasil
URL: http://www.locem.ufc.br – sombra@ufc.br

***Email address:** maurocosta@pq.cnpq.br

In the present work, samples of pure chitosan and membrane Chitosana_Collagen be analyzed for investigate dielectric and electrical modulus properties in the frequency range 1Hz to 1MHz were measured at several temperaturas in the range of 313 to 513K using complex impedance spectroscopy technique to investigate the relaxation processes involved. Dielectric results suggest dielectric relaxation in the material. Electric modulus representation (**M***) is proved to be the most suitable for the analysis of the dielectric data. Fig.1 exhibits the variation of M'' with frequency for Chitosan_Collagen at different temperatures. Two well-defined relaxation mechanism is observed in the temperature range of 313 – 513K. The relaxation peaks shift towards higher frequencies with increasing on temperature. The presence of such relaxation peaks in the M'' plots indicates that the samples are ionic conductors. The activation energy calculated from electric modulus spectra is 2.67 and 2.76 eV.

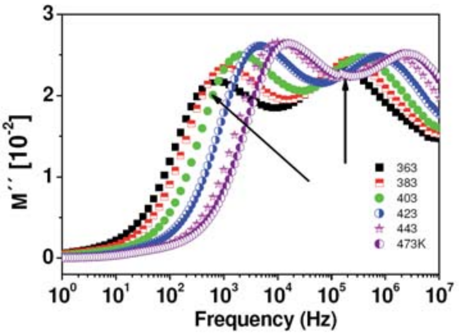


Fig.1 Modulus variation with frequency for Chitosan_Collagen at various temperatures (K)

[1] J. Einfeldt, D. Meiβner, A. Kwasniewski. Polymerdynamics of cellulose and other polysaccharides in solid state-secondary dielectric relaxation processes. Prog. Polym. Sci 26 (2001) 1419-1472

Glass transitions in aqueous solution of protein (hen egg lysozyme)

A.Panagopoulou[1*], **M.Aravantinou**[1], **D.Nanopoulos**[1], **A.Kyritsis**[1], **P.Pissis**[1]
[1] Department of Physics, National Technical University of Athens. Zografou Campus,
15780 Athens, Greece
*Email address: panagann@central.ntua.gr

In this work we employ broadband relaxation spectroscopy (DRS) and thermally stimulated polarization currents (TSDC)[1] techniques to investigate water and protein dynamics in mixtures of water and lysozyme over wide ranges of composition, from dilute solutions (18.5% protein) to practically dry protein pellets.

In a recent article[2] N.Shynyashiki et al. presents results of DRS measurements performed on the 20 wt % aqueous solution of bovine serum albumin (BSA). In this work[5] three main dielectric relaxation processes are detected. The fastest relaxation process having relaxation time of 100 or 1000 s at ca. 110K is due to the secondary relaxation of un-crystallized water (UCW) hydrogen bonded to the hydrated BSA. The intermediate relaxation process with 100 s relaxation time at ca. 135K is due to ice. The slowest relaxation process having relaxation time of 100 s at ca. 200K is interpreted to originate from local chain conformation fluctuations of protein slaved by water[3].

Experimental data of our studies reveal, for the lysozyme aqueous solutions, similar molecular behavior to that of the BSA aqueous solution[2]. Additionally, thermally stimulated polarization currents technique (TSDC), due to its resolving power, gives an insight into the dependence of the α relaxation process of lysozyme chains on the water content in the mixtures.

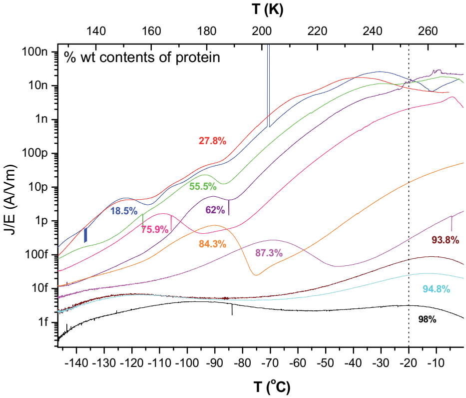


Fig.1. TSDC thermograms of lysozyme water mixtures. The dashed vertical line highlights the polarization temperature T=-20°C.

References

[1] P.Pissis, J.Mol. Liq., 41, 271-279 (1989).

[2] N.Shinyashiki, W.Yamamoto, A.Yokoyama, T.Yoshinari, S.Yagihara, R.Kita, K.L.Ngai, S.Capaccioli, J.Phys. Chem. B., 113, 14448-14456 (2009).

[3] K.Kawai, T.Suzuki and M.Uguni, Biophys.J., 90, 3272-3738 (2006).

Design and performance test of a Coaxial waveguide for measurement of dielectric constant in a broad microwave region (1GHz to 6GHz)

J. Monteiro[1], S.K. Mendiratta[1*] and J. C. Pedro[2]

[1]I3N – Aveiro, Physics Department, Aveiro University, Campus Universitário, 3810 – 193 Aveiro, Portugal
[2] IT/Aveiro University, Campus Universitário, 3810 – 193 Aveiro, Portugal
[*]Corresponding author, skm@ua.pt

Perturbation of the Q-factor of a resonant waveguide cavity has been extensively used to measure the dielectric and permeability parameters of materials. In this method the small frequency shift and the changes in the damping response are correlated with the complex dielectric constant of the material at the resonant frequency of the cavity. The method has the adequate accuracy and resolution when the calibration is carried out with the help of a standard material; the major shortcoming, however, of the method lies in the fact that a single waveguide cavity gives the dielectric constant at only one frequency. In order to overcome this difficulty we have designed a coaxial waveguide with air as a dielectric of adequate size such that small samples can be placed in a hole in the centre and the variations in the complex network parameters like s_{11} with the guide terminated with a short can be measured and correlated with the complex dielectric constant of the material. The frequency of measurement can be tuned by employing a variable length shorted waveguide at one end. The measurement set-up without the additional variable length waveguide but with the network analyzer and the specimen holder is shown in the figure below.

In this paper we give the design details of the wave-guide, the measurements we have used and the procedure to determine the complex dielectric constant at several frequencies in the region of 1GHz to 6GHz. Our results show that the method and the associated specimen holder can indeed be used to measure the complex dielectric constant of small samples of solids and liquids at several frequencies.

Analysis of dielectric spectra of human subjects during glucose excursions

F. Dewarrat[1], M. Talary[1], Y. Feldman[2], A. Caduff[1*]
[1] Solianis Monitoring AG, Leutchenbachstrasse 46, 8050 Zürich, Switzerland
[2]Applied Physics Dept., The Hebrew University of Jerusalem, 91904, Israel

*Email address: andreas.caduff@solianis.com

It has been shown[1,2] that blood glucose concentration changes can be tracked in human subjects by evaluating impedance measurements of the skin and the underlying tissue. To date, the most efficient models we have for estimating the glucose level have been derived via multiple regression analysis of the complex dielectric spectra as well as of the other quantities measured with the multisensor glucose monitoring system (MGMS). Although the information obtained by this multivariate approach is able to reflect clinically interesting physiological conditions[3], for an improved physical understanding of the underlying phenomena it is also necessary to apply other fitting methods.

The choice of the appropriate function to fit dielectric spectra depends on several parameters, such as the frequency range, the number of measured frequency points available and the expected complexity of the model system. In our case the standalone MGMS measures the impedance magnitude and phase at 16 frequency points between 0.1 and 100 MHz, so it is not advisable to use functions with too many free parameters where a robust and prospectively applicable fitting procedure is required.

As an initial approach, we have concentrated on the MHz frequency region and used the same Cole-Cole function as implemented by Gabriel[4], with the restriction of one dispersion. Since the MGMS is measuring the impedances with three separate electrodes of different characteristic sizes (and so penetration depths in the skin), the fit is calculated for the three measurement sets. The time series of these fitted quantities are compared with the change in the reference blood glucose.

Whilst the quantities obtained with the measurement of the electrode with the shortest penetration depth shows no or weak correlation to the reference glucose, the quantities obtained with the measurement of the electrode with the longest penetration depth shows stronger correlation. Among these, the exponent responsible for the stretching of the dispersion and the amplitude of the dispersion show the largest correlation to the reference glucose values. Note that the importance of the dispersion width as a parameter to monitor living tissues has been emphasised recently by other workers such as Ivorra[5]. Other quantities such as the center of the dispersion are shown to be sensitive to the changes that occur over the day (daily trend).

References

[1] M. Talary, L. Falco, F. Dewarrat, A. Caduff, hal-00268253, BDS Lyon, 2008
[2] A. Caduff et al., Biosensors and Bioelectronics 24, 2009
[3] S. Grimnes, O. Martinsen, Bioimpedance and Bioelectricity Basics, 2008.
[4] S. Gabriel, R. W. Lau, C. Gabriel, Phys. Med. Biol. 41, 1996
[5] A. Ivorra et al, Physiol. Meas. 26, 2005

Segmental dynamics of semicrystalline poly(vinylidene fluoride) nanorods

J. Martín[1], C. Mijangos[1], A. Sanz[2], T. A. Ezquerra[2], A. Nogales[2]*
[1]Instituto de Ciencia y tecnología de Polímeros (CSIC). Juan de la Cierva 3, 28006 Madrid, Spain
[2]Instituto de Estructura de la Materia (CSIC). Serrano 121, 28006 Madrid, Spain
*Email address: emnogales@iem.cfmac.csic.es

The dynamics of a semicrystalline poly(vinylidene fluoride) (PVDF) confined within self-ordered alumina templates[1] is studied by means of dielectric spectroscopy. The PVDF is confined within with higly homogeneous cylindrical nanopores with diameters ranging from 20 to 60 nm. In particular, for pore sizes of the order of 20 nm, the existence of a highly constrained relaxation is associated with the polymer-alumina interfacial layer[2] (Figure 1). When the PVDF is confined to this level in alumina templates, most of the chains are located in the interfacial region, where the mobility is severely restricted, and because of that, crystallization is highly inhibited. The counterbalance between spatial confinement and interfacial interactions controls at the nanometer level the dynamic and semicrystalline structure of the polymer.

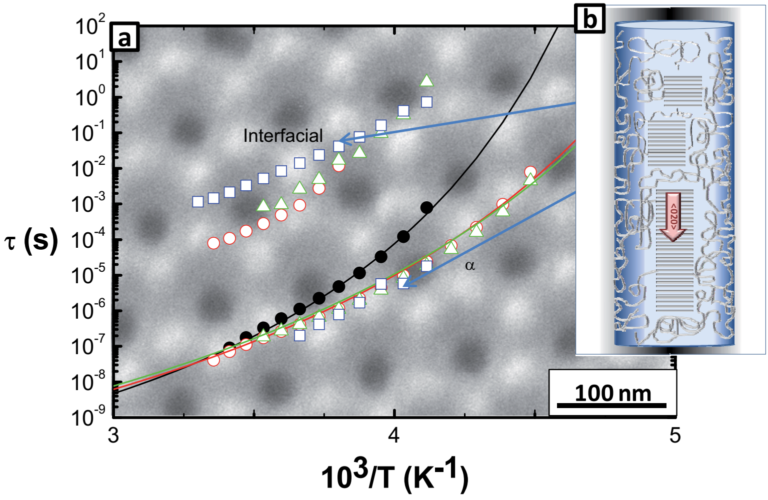


Fig.1. (a) Dependence of the relaxation time (τ) of the observed relaxations, with the reciprocal temperature for the relaxations for the studied samples: (●) B, (O) P60, (Δ) P35, and (□) P20. Continuous lines are the best fittings to the VFT equation. (b) Escheme of proposed model for polymer regions withdifferent mobility in 20 nm in diameter pores.

References
[1] H. Masuda, K. Fukuda. Science 268, 1466 (1995).
[2] J. Martín, C. Mijangos, A. Sanz, T.A. Ezquerra. Macromolecules 42, 1466 (2009)

Impact of surface interactions on the glassy dynamics of thin layers of PMMA

M. Tress[1*], M. Erber[2], E.U. Mapesa[1], K.-J. Eichhorn[2], A. Serghei[3], B. Voit[2] and F. Kremer[1]
[1]Institute for Experimental Physics I, University of Leipzig, Linnéstr. 5, 04103 Leipzig, Germany
[2]Leibniz Institute for Polymer Research Dresden, Hohe Str. 6, 01069 Dresden, Germany
3Department of Polymer Science and Engineering, University of Massachusetts Amherst, 120 Governor’s Drive, Amherst, MA 01003-9263, USA
*Email address: martintress@gmx.de

The glassy dynamics of thin (≥ 6 nm) layers of PMMA is studied by means of Broadband Dielectric Spectroscopy (BDS) in 2 different sample arrangements: on the one hand in a conventional approach using evaporated aluminum electrodes and on the other hand prepared with highly conductive silicon electrodes which are covered with nanostructures as spacers. The latter preparation method is demonstrated to be more robust against artefacts occurring especially in thin layers and thus used in the further experiments. The supporting surface is systematically changed from strongly hydrophilic to strongly hydrophobic. The measured glassy dynamics of the investigated layers is neither affected by the decreasing layer thickness nor by the particular type of the substrate. These results are confirmed by ellipsometric measurements carried out at the identical material prepared under the same conditions.

Charge transport in confined ionic liquids

C. Iacob[*], *J. R. Sangoro, P. Papadopoulos, J. Kärger and F. Kremer*
Institute of Experimental Physics I, University of Leipzig, Linnéstr. 5, 04103, Leipzig, Germany
*Email address: iacob@rz.uni-leipzig.de

Broadband Dielectric Spectroscopy is employed to study charge transport in ionic liquids (ILs) in oxidized silicon nanoporous membranes[1-6]. The dielectric spectra are interpreted in terms of hopping of charge carriers in spatially randomly varying energy barriers. By applying the Einstein-Smoluchowski relation to the dielectric spectra, diffusion coefficient is obtained. At higher temperatures, the diffusion coefficients of the confined and bulk ionic liquids are identical for all pores sizes while ILs are observed to diffuse faster in comparison to their bulk value at lower temperatures. The results are discussed with respect to the interplay between the dynamic glass transition and charge transport in ILs.

References

[1] F. Kremer, A. Schönhals. Broadband Dielectric Spectroscopy*,* Springer (2003).
[2] M. Arndt, R. Stannarius, W. Gorbatschow and F. Kremer. Phys. Rev .E, 54, (1996)
[3] C. Iacob, J.R. Sangoro, A. Serghei, S. Naumov, Y. Korth, J. Kärger, C. Friedrich and F. Kremer. J.Chem.Phys. 129, 234511 (2008)
[4] J.R. Sangoro, C. Iacob, A. Serghei, C. Friedrich and F. Kremer. Phys. Chem. Chem. Phys. 11, 913-916 (2009)
[5] J.R. Sangoro, A. Serghei, S. Naumov, P. Galvosas, J. Kärger, C. Wespe, F. Bordusa and F. Kremer Phys. Rev. E, 77, 051202 (2008)
[6] C. Iacob, J.R. Sangoro, P. Papadopoulos, R. Valiullin, S. Naumov, J. Kärger and F. Kremer *Submitted.*

Restricted Segmental Relaxation in Oriented Semicrystalline Poly(vinilydene fluoride) as Revealed by Broad Band Dielectric Spectroscopy

A. Linares[1*], A. Nogales[1], A. Sanz[1], T.A. Ezquerra[1], M. Pieruccini[2]
[1]Instituto de Estructura de la Materia (CSIC), C/ Serrano, 121 28006 Madrid (Spain)
[2]Istituto per i Processi Chimico-Fisici (CNR), Viale Ferdinando Stagno d'Alcontres, 37 98158, Messina, Italia
[*]E-mail address: alinares@iem.cfmac.csic.es

The effect of confinement by crystals on the α-relaxation, observed by dielectric broadband spectroscopy, in isotropic as well as in oriented semicrystalline poly(vinilydene fluoride), is analysed on the basis of a new thermodynamic model[1]. In both samples, it has been found that the average free-energy barrier, ΔF, for conformational rearrangements is of the same order of the dispersion barrier heights, $\delta(\Delta F)$, around ΔF, i.e. the increase of the barrier height in conformational rearrangement is accompanied by an increase in the heterogeneity of constraining conditions. At a given temperature T, the readjustment free energy is larger in the oriented sample. In addition, it is worth noting that in oriented poly(vinilydene fluoride) the regions of cooperative rearrangement are significantly larger and, moreover, their size increase upon decreasing T. This feature, which underlies the Adam-Gibbs approach for liquids, is pointed out for the first time from direct data analysis in the case of confinement enhanced cooperativity. In addition to the above analysis, the samples have been characterized by DSC, WAXS and SAXS experiments.

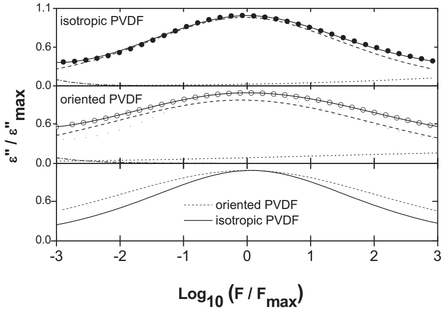


Fig. 1. Normalized ε''/ε''max ratio vs. Log (F/Fmax) at -30 ºC. Continuous lines are Havriliak-Negami fits and dashed, dotted, dash-dotted lines are α, β and conductivity contributions, respectively. Lower panel shows the Havriliak-Negami fits corresponding to the α relaxation of both isotropic and oriented PVDF for the sake of comparison

References

[1] M. Pieruccini and T.A. Ezquerra, Eur. Phys. J. E 29, 163 (2009)

DYNAMICS IN ULTRATHIN LIQUID FILMS STUDIED BY SIMULTANEOUS DIELECTRIC SPECTROSCOPY (DRS) AND ORGANIC MOLECULAR BEAM DEPOSITION (OMBD)

S. Capponi*, S. Napolitano, M.Wübbenhorst

Department of Physics and Astronomy, Katholieke Universiteit Leuven, Celestijnenlaan 200D, Leuven, 3001, Belgium.

*Email address: simona.capponi@fys.kuleuven.be

Glass forming liquids show deviations from their cooperative bulk-dynamics when they are geometrically confined to nanometer dimensions. In this context, ultrathin films of (H-bonding) glass forming liquids are of particular interest, since both the dimension (thickness) and the surface interactions can be controlled in an independent way.

This work focuses on the glass transition dynamics of ultrathin films of glycerol as studied by dielectric spectroscopy (DRS). Ultrathin films are produced by molecular beam deposition onto a glass substrate patterned with an interdigitated comb electrode (IDE), an open configuration that allows the real-time study of the relaxation dynamics of the glycerol films upon continuous variation of the film thickness by deposition or desorption.

DRS measurements on thin, equilibrated, glycerol films were prepared by slow desorption, and revealed a remarkable broadening of the relaxation time distribution below 9nm. In particular, for films below 1.6nm (corresponding roughly to 3 glycerol mono-layers) a slowing down of the dynamics (increase in the mean relaxation time) was observed already at 30°K above the bulk glass transition temperature T_g.

Alternatively, we have also investigated films of glycerol that were deposited on a target at a temperature significantly below T_g to form an “ultrastable” glass [1], i.e. a glassy state with an extremely low fictive temperature. These film revealed a dramatically slowed-down of the dielectric relaxation dynamic that goes along with an unusually high dielectric relaxation strength, which persisted up to 10K above the bulk-T_g.

The experimental results will be discussed in terms of the concurrent presence of finite size effects and surface induced perturbations on the structural dynamics.

Their respective contributions have been determined by specifically designed experiments focused on the study of the interaction with the substrate and of the spatial extent of its influence on the dynamics.

[1] *S.F. Swallen, M.D.Ediger et al, SCIENCE VOL 315 , 353, (2007).*

Behavior of dielectric properties of thin conductive polymers film

M. Olariu[1*], R. Ciobanu[1], S. Aradoaei[1]
[1]Gheorghe Asachi Technical University of Iasi, Faculty of Electrical Engineering, Bld. Prof. D. Mangeron, no. 53-55, 700050, Iasi, Romania
*Email address: molariu”ee.tuiasi.ro

In the last period of time, for overcoming the disadvantages of classic metallic electromagnetic panels (e.g. high weight, possibility of being a subject of oxidation) a new class of polymers attracted the interest of the international scientific society. The new materials called nanoconductive polymers are expected to exhibit very high dielectric constant and dielectric losses and consequently good electric conductivity (at least around 10^{-2}S/cm). The hereby paper is presenting the dependence of dielectric properties of Polybacrylonitrile(PAN) /polypyrrole (PPy) composite in terms of dielectric constant, conductivity and dielectric losses in a frequency domain between 0.01Hz and 10^6Hz and at different temperatures starting from 25°C up to 200°C. The composite films having of different pyrrole concentrations up to 150 µl show a non-polar or a very weak polar character. Their dielectric constant is not varying too much and is constant in a big domain of frequencies. By introducing 200 µl pyrrole the character of composite film is transformed in a polar one. The dielectric constant increased too much that can be observed better at frequencies below 10^5 Hz. The similar attitudes can be observed about the losses, in the case of the composite films having 50, 100 and 150 µl pyrrole concentrations the quantity of pyrrole did not bring to much changes of conductivity. An increase of losses in the case of PAN-PPy200 which is due to the increased conductivity of the composite film is noticed.

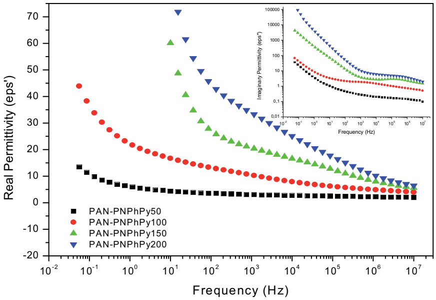


Fig.1. The dielectric constant and losses of PAN-PNPhPy composite thin films at 25 °C

References

[1] Youngs, et. al, Broadband Dielectric Spectroscopy of Conducting Polyaniline, IEE Proc-Sei. Meas Technol., Vol. 145, No. 4, July 1998, pg. 166-170.
[2] Williams, G., Dielectric and Electrical Properties of Materials, Dielectric Newsletter, Issue March 1994, pg. 1-3.
[3] Dakin, T.W., Conduction and Polarization Mechanisms and Trends in Dielectrics, IEEE Electrical Insulation Magazine, September-October 2006 — Vol. 22, No. 5, pg. 11-28.

Glassy dynamics in nanometer thin layers of polystyrene

<u>E.U. Mapesa</u>[1*], M.Erber[2], M.Tress[1], , K.-J. Eichhorn[2], A. Serghei[2], B. Voit[2] and F. Kremer[1]
[1]Institute for Experimental Physics I, University of Leipzig. Linnestrasse-5, 04103 Leipzig, Germany.
[2]Leibniz Institute for Polymer Research. Hohe Strasse-6, D-01069 Dresden, Germany.
*Email address: urandu@rz.uni-leipzig.de

Broadband Dielectric Spectroscopy (BDS) and Ellipsometry are combined to study the glassy dynamics of nanometric layers (≥ 5nm) of polystyrene. For the former, two types of sample arrangement are applied, that is, the conventional method[1,2,3] where evaporated metal electrodes are used and a novel arrangement[4] in which insulating silica nanostructures serve as spacers between highly conducting doped-silicon counter electrodes. Within the limits of the experimental accuracy (+/- 2K) both approaches, BDS and Ellipsometry, deliver the coinciding result that – compared to the bulk - the dynamic glass transition is *not* shifted. Furthermore the dielectric measurements as carried out in both sample geometries prove, that the relaxation time distribution function is *not* broadened.

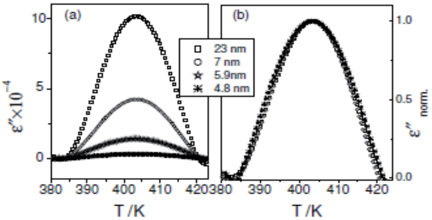


Fig.1(a). Thickness dependence of dielectric loss against temperature for polystyrene (M_W = 319 kg/mol) measured in the novel geometry at 1.0 kHz. The same data is shown normalised in (b).

References

[1] L. Hartmann, K.Fukao and F. Kremer, in *Broadband Dielectric Spectroscopy*, edited by F.Kremer and A. Schönhals, Springer, New York (2002).
[2] K. Fukao and Y. Miyamoto, Phys. Rev. E 64, 011803 (2001).
[3] A. Serghei and F. Kremer, Progr. Colloid Polym. Sci. 132, 33, (2006).
[4] A. Serghei and F. Kremer, Rev. Sci. Instrum. 77, 116108 (2006).

Dielectric spectrum and water activity of swine skin gelatin-gel

R. Shirakashi[1*], R. Sakane[2], J. Yamada
[1]I.I.S., The University of Tokyo, 4-6-1 Komba, Meguro-ku, Tokyo, Japan
[2]Dep. of Mech. Eng., Shibaura Inst. of Tech., 3-7-5 Toyosu, Koutou-ku, Tokyo, Japan
*Email address: aa21150@iis.u-tokyo.ac.jp

Bound water in biomaterial or biosis has different thermophysical properties from bulk water[1] because of strong interaction with biomolecules. This bound water plays an essential role to keep the living system, e.g. stabilization of proteins, phosphate lipids, with regard to the phenomena, the desiccation tolerance of mammalian skin, yeast, insect and plant. Depression of phase change[2], water activity[3], relaxation dielectric property[4] or T1, T2 relaxation of NMR[5] are the common effects of bound water. In this article, we measured the dielectric spectra (frequency-domain reflectometry(FDR): 100MHz~6GHz) of swine skin gelatin-gel containing 40 to 90wt% water using network analyzer. In addition, water activity,a_w, and frozen water ratio were measured by a water activity meter and Differential Scanning Calorimetry(DSC). Two types of dielectric relaxation were found whose relaxation times are 10 and 100 times longer than pure water (Fig.1). Water in gelatin-gel of 40~70wt% moisture content shows endotherm at temperature below 0 degree, and water in gelatin-gel less than 30wt% moisture content shows no endo- or exotherm. The first threshold of moisture contents 70wt% corresponds to the moisture content below which the water activity of gelatin-gel is less than 1, and the second threshold of moisture contents 30wt% corresponds to the moisture content below which the water activity of gelatin-gel drastically decrease as moisture content decreases (Fig.2). Considering relaxation of water kinetic measured by FDR, we suspect that 2 types of water with different relaxation time may correspond to bound water existing in gelatin-gel of 30~70wt% and 0~30wt%.

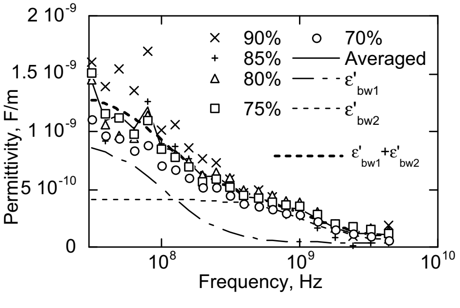


Fig.1. Dielectric spectrum of bound water in gelatine-gel

References

[1] W. Drost-Hansen, “Chemistry of the Cell Interface”, PartB, Chap.6, Academic Press (1971)
[2] G.M. Mrevlishvili, Biofizika, 22, pp.180-191 (1977)
[3] H.B. Bull and K. Breese, Arch. Biochem. Biophys., 137, pp.299-305 (1970)
[4] J.P. Grigera, et.al., Biopolymers, 18, pp.35-45 (1971)
[5] G.N. Ling, “In Search of the Physical Basis of Life”, Plenum Press (1984)

Destabilizing hydrogen-bonded structures in monohydroxy alcohols

C. Gainaru,[1] M. Preuß,[1] A. Reiser,[2] R. Böhmer[1]
[1] Fakultät für Physik, Technische Universität Dortmund, 44221 Dortmund, Germany
[2] Kirchhoff-Institut für Physik, Universität Heidelberg, 69120 Heidelberg, Germany

The slow Debye process that shows up on the low-frequency side of the structural relaxation peak in monohydroxy alcohols is only poorly understood. It seems clear that the hydrogen bonds present in these substances are involved in this still elusive relaxation phenomenon. Therefore it is interesting to find out which factors stabilize or destabilize the formation of hydrogen bonded supramolecular structures in monohydroxy alcohols. One experimental option to weaken an H-bond network is to mix monohydroxy alcohols with substances that modify their bonding characteristics.[1,2] In the present contribution we discuss new broad-band dielectric results on an alcohol system for which we diluted the density of H bonds. Other means to destabilize supramolecular structures, which we will discuss, are the application of sufficiently large external pressures and the consequences of soft spatial confinement.

[1] e.g., L.-M. Wang, S. Shahriari, and R. Richert, J. Phys. Chem. B 109, 23255 (2005).
[2] T. El Goresy, R. Böhmer, J. Chem. Phys. 128, 154520 (2008)

Changing the dielectric properties of insulating oil under the influence of water content.

M. Jaroszewski[*], **J. Pospieszna**
Wrocław University of Technology, Dept. of Electrical Engineering, 50-370 Wrocław, Poland
*Email address: maciej.jaroszewski@pwr.wroc.pl

There are many methods for characterization of dielectric materials. As far as typical power transformer oil insulation is concerned, examples of such methods are DGA (dissolved gas in oil) or HPLC (high performance liquid chromatography) for identifying decomposition products due to high temperatures or partial discharges, or Karl Fischer tests for detecting moisture.

Water in oil may originate from air moisture in the case of breathing transformer, or as the thermal decomposition of cellulose-based solid insulating materials. Water can be present at oil under a number of physical and physico-chemical states that can be simplified as dissolved water (molecular distributed and associated), dispersed water (colloids and emulsions), free water. Water is particularly detrimental to oil insulation systems dielectric properties and its resistance to ageing. Breakdown voltage of the insulating oil is reduced with increasing moisture content in the oil.

Classical methods of measuring dielectric response include (power frequency) capacitance, tg δ and insulation resistance. More recently extensions such as measurements of dielectric frequency response have found increasing popularity. Dielectric spectroscopy is a powerful method for quality characterization of dielectrics materials, including transformer oils[1,2,3], provide information on properties of insulating oil depending on moisture content, obtained from distribution of relaxation times in broad range of frequencies[4,5,6].

In this paper the discussion is based on dielectric frequency response.

References

[1] E. Tuncer, Y.V. Serdyuk, S.M. Gubanski, Dielectric mixtures: Electrical properties and modelling, IEEE DEI, Vol.9 No.5, October 2002.

[2] W.S. Zaengl, Dielectric spectroscopy in time and frequency domain for HV power equipment, Part I: Theoretical considerations, IEEE Electrical Insulation Magazine, Vol.19, No.5 October 2003

[3] O. Hassan et al., Detection of oil-pressboard insulation aging with dielectric spectroscopy in time and frequency domain measurements, International Conference on Solid Dielectrics, Toulouse, France, 2004

[4] W.S. Zaengl, Dielectric spectroscopy in time and frequency domain for HV power equipment (transformers, cables, etc.), 12th Symposium on High Voltage Engineering, 2001

[5] O. Hassan et al., Detection of oil-pressboard insulation aging with dielectric spectroscopy in time and frequency domain measurements, International Conference on Solid Dielectrics, Toulouse, France, 2004

[6] B.-M. Sax et al., Dielectric spectroscopy-a method of investigating the stability of water-oil emulsions, Progress in Colloid & Polymer Science Vol. 77, 1988.

Study of the Molecular Dynamics under crystallization of Triton X-100

Esther G. Merino, João Sotomayor, Madalena Dionísio, Natália Correia*
REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa, 2829-516 Caparica, Portugal.
*Email address: n.correia@dq.fct.unl.pt

The work is focused on the molecular mobility of Triton X-100 with molecular formula,$C_{14}H_{22}O(C_2H_4O)_n$ where the average number of ethylene oxide units per molecule is n=10. This nonionic surfactant was selected due to its wide use in industrial and pharmaceutical formulations and in biochemical research[1,2].

As main technique, dielectric relaxation spectroscopy was used, in a frequency range from 10^{-1} to 1×10^{6} Hz and over the temperature range from 153 to 298K. The study was complemented by Differential Scanning Calorimetry analysis.

For dielectric measurements, the Triton X-100 sample was previously heated to 373 K to eliminate water (initial water content 0.28% w/w). The sample was cooled down at a cooling rate of 15 $K\cdot min^{-1}$ while measuring the complex permittivity. The real part of the complex permittivity, ε', shows no discontinuity in the cooling run until ~ 249 K (for the frequency of 10^4 Hz), temperature at which presents the characteristic step of the glass transition. In the plot of the imaginary part, ε'' *vs* temperature, the glass transition emerges as a well defined peak centered at 233 K. From the agreement of the rise observed in ε' and in the dielectric strength with the increase predicted by the Fröhlich-Kirkwood equation it was concluded that no dipolar moment is lost due to immobilization if crystallization occurred during cooling. Therefore, Triton-X 100 is a glass former.

Upon further heating carried at 10 $K\cdot min^{-1}$ this fully amorphous sample undergoes cold-crystallization as denoted by an abrupt decrease in both ε' and ε''.

These results are in good agreement with DSC data where the glass transition is detected at 212 K (203 K in ref 3) and further cold- crystallization occurs at 232 K.

A detailed dynamical study concerning the time evolution of intensity, position and shape of the α-relaxation of Triton X-100 upon isothermal cold-crystallization carried at different temperatures will be presented.

Besides the α relaxation process associated with the dynamic glass transition, secondary processes were also detected. A detailed relaxation map is provided.

Acknowledgements
The authors acknowledge the financial support to Fundação para a Ciência e Tecnologia (FCT, Portugal) through the projects PTDC/CTM/64288/2006 and PTDC/CTM/69145/2006.

References

[1] H.Z. Yuan, G.Z. Cheng, S. Zhao, X.J. Miao, J.Y. Yu, L.F. Shen, Y.R. Du. Langmuir, 16, 3030-3035 (2000)
[2] K. Asami. J. Phys.: Condens. Matter 19, 376102 (2007)
[3] E. Larraz, C. Elvira, J.L.Román. J Polym Sci Part A: Polym Chem,41, 1641–1649 (2003).

Dynamics of Orientationally Disordered Mixed Crystals composed of CN-cyclohexane and Cyclohexane

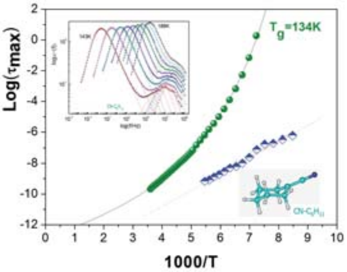
J. C. Martinez-Garcia[1], J. Ll. Tamarit[1*], M. Barrio[1], L. C. Pardo[1], N. Veglio[1], P. Lunkenheimer[2] and A. Loidl[2]

[1] Grup de Caracterització de Materials, Dept. Física I Enginyeria Nuclear, Universitat Politècnica de Catalunya, 08028, Barcelona,Catalonia (Spain)

[2] Experimental Physics V, Center for Electronic Correlations and Magnetism, University of Augsburg, 86135 Augsburg, Germany

*Email address: jose.luis.tamarit@upc.edu

Orientationally disordered (OD) phases, known also as plastic phases, can be considered as one of the most important experimental model systems for the glass transition studies.[1] OD phases, in which the centers of mass of the molecules form a translational long-range ordered lattice while the orientational degrees of freedom are thermally activated, often can be driven into an orientational glass (OG). Despite the fact that in OD phases the dynamics on approaching the glass temperature *Tg* is governed solely by orientational degrees of freedom, in many aspects it resembles the "canonical pattern" of supercooled liquids and polymers.[2]



In supercooled OD phases the main α-relaxation process can be accompanied by a secondary β-relaxation as in structural glasses.[3-5] One of the most representative compounds showing such processes is CN-cyclohexane (CN-Ch). The aim of this work is to analyze the behavior of the α- and β-relaxation processes of the dipolar CN-Ch compound (μ=3.79 D) in the mixed crystals formed with the non-polar cyclohexane (Ch). Both compounds are known to crystallize in the same OD lattice, thus giving rise to mixed crystals $(Ch)_{1-X}(CN\text{-}Ch)_X$ for the whole composition range as probed by calorimetric and X-ray diffraction measurements.

Despite dilution of CN-Ch molecules on Ch lattice are expected to strongly modify the dynamics of the relaxation map, it will be shown that starting from a critical composition, the α-relaxation time appears almost constant as a function of the mole fraction. On the contrary, the homogeneous/heterogeneous scenario seems to be strongly modified as a function of composition.

References:

[1] J. Ll. Tamarit, S. Pawlus, A. Drozd-Rzoska, and S. J. Rzoska, in "*Soft Matter under Exogenic Impacts*", pp. 161-187. Eds. S. J. Rzoska and V. A. Mazur, Springer, 2007. ISBN: 978-1-4020-5870-7

[2] R. Fayos, F. J. Bermejo, J. Dawidowski, H. E. Fischer, and M. A. González, Phys. Rev. Lett. **77**, 3823 (1996); A. Drozd-Rzoska, S. J. Rzoska, S. Pawlus, J. Ll. Tamarit, Phys. Rev. B **74**, 064201 (2006).

[3] L. C.Pardo, P. Lunkenheimer, and A. Loidl, J. Chem. Phys. **124**, 124911 (2006)

[4] N. V. Surovtsev, S. V. Adichtchev, J. Wiedersich, V. N. Novikov, and E. A. Rössler, J. Chem. Phys. **119**, 12399 (2003)

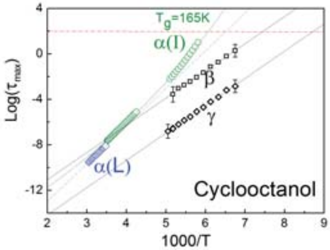
[5] C. Tschirwitz, S. Benkhof, T. Blochowicz, and E. Rössler, J. Chem. Phys. **117**, 6281 (2002)

Dynamics of Orientationally Disordered Mixed Crystals composed of Cycloheptanol and Cyclooctanol

J. C. Martinez-Garcia[1*], **J. Ll. Tamarit**[1], **L. C. Pardo**[1], **M. Barrio**[1], **N. Veglio**[1], **A. Drozd-Rzoska**[2] **and S.J. Rzoska**[2]
[1] Grup de Caracterització de Materials, Dept. Física I Enginyeria Nuclear, Universitat Politècnica de Catalunya, 08028, Barcelona,Catalonia (Spain)
[2] Experimental Physics V, Center for Electronic Correlations and Magnetism, University of Augsburg, 86135 Augsburg, Germany
*Email address: julio.cesar.martinez@upc.edu

Orientationally Disordered (OD) phases, formed by pseudoglobular shaped molecules, are characterized by the existence of a regular lattice formed by the centre of mass of the molecules which are disordered with respect to the orientational degrees of freedom. These materials give rise to an orientational glass (OG) on cooling in which only the orientational degrees of freedom are frozen in.[1,2] This is a unique situation, since supercooled liquids giving rise to structural glasses (SG), which can be considered as canonical glassy systems regarding the number of experimental studies carried out so far, are influenced by both the translational and orientational degrees of freedom. Pure compounds cycloheptanol (cC7-ol) and cyclooctanol (cC8-ol) belong to this kind of systems and are known to display at least one OD phase of simple cubic symmetry and, within this phase, a continuous formation of mixed crystals between them was demonstrated in the past.[3]

The orientational dynamics of these compounds and their OD mixed crystals have been studied by means of broadband dielectric spectroscopy at temperatures near and above the OG transition temperature. The dielectric loss spectra of cC7-ol and cC8-ol show, in addition to the well-pronounced α-relaxation peaks with a continuous temperature shift (characteristic of the freezing of the molecular dynamics), secondary relaxations (β and γ for cC8-ol and γ for cC7-ol) which are intramolecular in nature.



The dynamics of several OD mixed crystals was recently studied[4] and surprisingly enough one of the secondary relaxations was not evidenced. We show here by means of a careful set of measurements for several mixed crystals and of a detailed analysis procedure the existence of the secondary relaxations for the mixed crystals. The results, moreover, doubtless reinforce the physical origin of each of the secondary relaxations.

References:

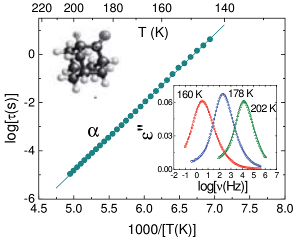
[1] R. Fayos, F. J. Bermejo, J. Dawidowski, H. E. Fischer, and M. A. González, *Phys. Rev. Lett. 77*, 3823 (1996); A. Drozd-Rzoska, S. J. Rzoska, S. Pawlus, J. Ll. Tamarit, *Phys. Rev. B*, *74*, 064201 (2006).
[2] R. Brand, P. Lunkenheimer, A. Loidl, *J. Chem. Phys. 116*, 10386 (2002).
[3] M. A.Rute, J. Salud, P. Negrier, D.O. López, J.Ll.Tamarit, R. Puertas, M. Barrio, D. Mondieig, *J. Phys. Chem. B*, *107*, 5914 (2003)
[4] L. P. Singh, S. S. N. Murthy, *J. Phys. Chem. B*, *112,* 2606 (2008)

Statistical Disorder Effects on the Dynamics of 2-Adamantanone

M. Romanini[1*], **J. C. Martinez-Garcia**[1], **J. Ll. Tamarit**[1], **M. Barrio**[1], **L. C. Pardo**[1], **Ph. Negrier**[2], **D. Mondieig**[2]
[1] Grup de Caracterització de Materials, Dept. Física I Enginyeria Nuclear, Universitat Politècnica de Catalunya, 08028, Barcelona,Catalonia (Spain)
[2] Experimental Physics V, Center for Electronic Correlations and Magnetism, University of Augsburg, 86135 Augsburg, Germany
*Email address: michela.romanini@upc.edu

2-Adamantanone ($C_{10}H_{14}O$, 2O-ada) is a cage-like polar molecule in which a double bound of the oxygen atom to the adamantine cage provides a rigid molecular structure with C_{2v} point group symmetry. As for many 1- or 2-adamantane derivatives, this compound displays several solid phases and, in particular an orientationally disordered (OD) one.[1,2]

Cooling from the liquid phase 2O-ada crystallizes into an OD cubic phase I at ca. 530K. On further cooling at around 208 K phase I transforms to a more ordered low-temperature phase (II).[1,2] It was assumed originally that such phase II exhibited a complete orientational order, but dielectric measurements[3] clearly revealed the existence of two relaxation processes, related to the existence of some kind of disorder involving irrefutably dipolar reorientation.



A Rietveld refinement procedure has enable us to solve the structure of phase II for which it appears the existence of a statistical disorder in such a way that three sites are possible for the oxygen atom with occupation factors of 0.25 (O1), 0.25 (O2) and 0.50 (O3). Such a statistical disorder of the oxygen atom (and thus, of the dipole orientation) gives rise to dielectric spectra with the characteristic features of the disordered phases. Figure shows the relaxation time as a function of the reciprocal temperature obtained from the α-relaxation process (see inset) within the "ordered" phase II. This system is another example of a very simple type of glass former where strongly restricted reorientational motions in a long-range ordered crystalline lattice becomes frozen.[4]

References:

[1] J. P. Amoureux, M. Castelein, M. Bée, B. Arnaud, and M. L. Shouteeten, *J. Phys. C* **15** (1982) 1319.
[2] R. Decressain, J. P. Amoureux, and E. Cochon, *Phys.Status Solidi B* **190** (1995) 295.
[3] R. Brand, P. Lunkenheimer, and A. Loidl, *J. Chem. Phys.* **116** (2002) 10386.
[4] M. Zuriaga, L.C. Pardo, P. Lunkenheimer, J.Ll. Tamarit, N. Veglio, M. Barrio, F.J. Bermejo, A. Loidl., *Phys. Rev. Lett.* **103** (2009) 075701.

Dominant Parameter for Dielectric α-relaxation Time of Polyhydric Alcohols

M. Nakanishi[*], **R. Nozaki**
Department of Physics, Faculty of Science, Hokkaido University, Sapporo 060-0810, Japan
*Email address: nakanishi@dielectrics.sci.hokudai.ac.jp

Polyhydric alcohols consist of several OH groups and carbon backbone chain, where the number of OH and C in a molecule are defined as N_{OH} and N_C, respectively. Sugar alcohols are one of the polyhydric alcohols. Most of the sugar alcohols consist of equal number of OH and C ($N_{OH}=N_C$) and linear backbone chain. On the glass transition of sugar alcohols such as glycerol ($N_{OH}=N_C$=3), threitol ($N_{OH}=N_C$=4), xylitol ($N_{OH}=N_C$=5) and sorbitol ($N_{OH}=N_C$=6), a systematic N_C dependence of fragility and glass transition temperature (T_g) has been previously reported [1-4]. The systematic dependence implies that a common mechanism dominates the glass transition behavior of sugar alcohols. However, the dominant parameter mostly affecting the systematic behavior has not been investigated yet because within the sugar alcohols system $N_{OH}=N_C$. To distinguish the parameter, we examined several trihydric alcohols with $N_{OH}\neq N_C$, such as glycerol (N_{OH}=3, N_C=3), 1,2,4-butanetriol (N_{OH}=3, N_C=4), 1,2,6-hexanetriol (N_{OH}=3, N_C=6), 3-methyl-1,3,5-pentanetriol (3MPT) (N_{OH}=3, N_C=6) and 1,2,7-heptanetriol (N_{OH}=3, N_C=7), by broadband dielectric spectroscopy.

The Arrhenius diagram for α-relaxation of all the samples are shown in Fig. 1. It is apparent that the temperature dependence of all the tryhidric alcohols follow a similar Vogel-Fulcher-Tamman manner. Furthermore, the fragility and T_g both obtained from the data exhibit systematic N_{OH} dependences. Since N_{OH} is identical among trihydric alcohols, this result strongly suggests that the dominant parameter is N_{OH} rather than N_C.

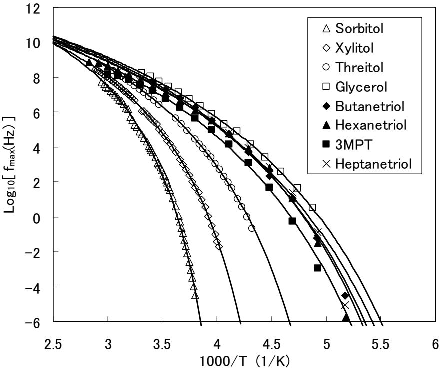


Fig. 1. Arrhenius diagram for peak frequency of α-relaxation. Solid curves show the VFT equations obtained by least square fitting.

References

[1] A. Döß, M. Paluch, H. Sillescu, G. Hinze, *Phys. Rev. Lett.* **88**, 095701 (2002).
[2] A. Döß, M. Paluch, H. Sillescu, G. Hinze, *J. Chem. Phys.* **117**, 6582 (2002).
[3] A. Minoguchi, K. Kitai, R. Nozaki, *Phys. Rev. E* **68**, 031501 (2003).
[4] A. Minoguchi, T. Kaneko, H. Sotokawa, R. Nozaki, *J. Non-Cryst. Solid.* **352**, 4742 (2006).

Microwave dielectric properties and relaxation in alkali metals and ammonium fluoride aqueous solutions

A.Lileev, **A.Lyashchenko,**
Institute of General and Inorganic Chemistry RAS, 119991 Leninsky pr. 31
Moscow, Russia,
*Email address: lilaser@mail.ru

The complex dielectric permittivity for the series of aqueous alkali metals (Na, K, Cs) and ammonium fluoride solutions was investigated in microwave range (7.5-25 GHz) in a wide area of salt concentrations. Such frequency interval was chosen because it corresponds to the maximum of the dispersion of dielectric permittivity of water and aqueous electrolyte solutions. Thus we are able to find the molecular-kinetic changes of water under the action of the solutes. The measurements were made at 288- 308K temperature interval. Because these solutions are high conductive liquids, the low-frequency specific electrical conductivity (σ) was investigated for calculation of ionic losses. The ionic losses (ε''_i) were estimated by relation $\varepsilon''_i=\sigma/\varepsilon_0\omega$, where ω – the circular frequency, ε_0 – the dielectric permittivity of vacuum.

Complex dielectric permittivity is described by the Cole-Cole relaxation model for all studied solutions in the investigated frequency range. Static dielectric constant (ε_s) was determined from the Cole-Cole diagrams by means of circular extrapolation to the zero frequency. The reduction of dielectric constant is observed when the salt concentration is increased. It depends from ionic radiuses of cations: when ionic the radius increase from Li to Cs, values of ε_s decrease in same order. The temperature coefficient of ε_s decreases with the increase of salt concentration and equal to zero at high concentrations.

The values of dielectric relaxation time (τ) were found by means of the graphical decision of Cole-Cole equation. The frequency dependence of function $[(\varepsilon_s-\varepsilon')^2+(\varepsilon'')^2]/[(\varepsilon'- \varepsilon_\infty)^2+(\varepsilon'')^2]$ in logarithmic coordinates becomes a straight line, which crosses the x-axis at a point corresponding to $\omega_0=1/\tau$. The activation characteristics ($\Delta G_\varepsilon^{++}$, $\Delta H_\varepsilon^{++}$, $\Delta S_\varepsilon^{++}$) were found from temperature dependences of τ. The Eyring's theory of absolute speeds of reactions was used for these calculations.

The changes of τ values characterize the water molecule mobility in the hydration shells of ions. The values of dielectric relaxation time decrease in comparison with pure water for alkali metals fluoride solutions at all investigated temperatures. It proves the increase of mobility of H_2O molecules in solutions under action of the dissolved ions. The decreases of τ are more pronounced at low temperatures when the structure of water in solutions is destroyed by thermal motion of molecules in lesser degree. The values of $\Delta H_\varepsilon^{++}$ reflect the structuredness of H-bond water net in solutions. The decrease of $\Delta H_\varepsilon^{++}$ in alkali metals fluoride solutions shows that the structure-breaking effect exists in these solutions. The appositive changes of τ and $\Delta H_\varepsilon^{++}$ values are observed for NH_4F solutions. It related with features of structure of NH_4^+ and F^- ions. They can form four tetrahedral H-bonds with H_2O molecules without disorder of initial structure. Note that NH_4F is unique salt that form solid solutions in ice. For NH_4F solutions the values of $\Delta H_\varepsilon^{++}$ increase in comparison with pure water as well as τ. It means that in NH_4F solutions is observed stabilization of water H-bond set. For the first time this effect established in the case of hydrophilic hydration of ions. The mechanism of this stabilization effect considerably differs from ones of hydrophobic hydration of ions with nonpolar groups (alkyl substituted ammonium salts for example).

This work was supported by the grants of Presidium RAS and RFBR № 08-03-00095

Dielectric Relaxation in ATP and AMP aqueous solutions

Evgeniya Levy[1*], Alexander Puzenko[1], Andrey Shendrik[1], Ido Segev[1], Mark Talary[2], Andreas Caduff[2] and Yuri Feldman[1]

[1]Department of Applied Physics, The Hebrew University of Jerusalem, Givat Ram, Jerusalem 91904, Israel
[2]Solianis Monitoring AG, Leutchenbachstrasse 46, 8050 Zürich, Switzerland
*Email address: genja.levy@mail.huji.ac.il

It has been traditional to divide the dielectric properties of water present in biological tissues into the response characterised as bound or free depending upon its proximity or otherwise to neighboring macromolecules, membranes or other kinds of interface.

The dielectric dispersion in most of biological systems follows the Cole-Cole (CC) dispersion[1]. This is typical for various aqueous systems[2], including ionic solutions, aqueous solutions of physiologically active non-ionic molecules, such as nucleotides, amino acids and sugars, etc[3]. Phenomenologically, the CC law can be represented by a frequency dependent complex dielectric permittivity $\varepsilon^*(\omega)$, given by: $\varepsilon^*(\omega) = \varepsilon_\infty + \Delta\varepsilon/[1 + (i \cdot \omega \cdot \tau)^\alpha]$, where ω is the cyclic frequency, i is the imaginary unit, ε_∞ is the high frequency limit of the complex dielectric permittivity, $\Delta\varepsilon$ is the dielectric strength of the relaxation process, τ is a characteristic time scale and the exponent α is referred to as a measure of symmetrical broadening in the dielectric losses associated with the relaxation peak ($0<\alpha\leq1$). It has been found experimentally that α is strictly dependent on temperature, structure, composition, pressure and other controllable physical parameters[4].

The main goal of this research is to study the hydration of the Adenosine-5'-triphosphate (ATP) in aqueous solution and to compare this with Adenosine monophosphate (AMP) molecule. The dielectric measurements of ATP and AMP solutions as the functions of temperature and concentrations were provided in the broad frequency range (1 MHz – 50 GHz) with the help of a Time Domain Dielectric Spectroscopy (TDDS) and Millimetre Vector Network Analyser (MVNA).

As a result of the analyses we discuss the response of the γ-dispersion observed in the ATP and AMP aqueous solutions in terms of CC $\alpha(\ln\tau)$ dependencies.

References

---

[1] K.S. Cole, R.H. Cole J. Chem. Phys. 9, 341 (1941).
[2] Y. Hayashi, N. Shinyashiki, S. Yagihara. J. Non-Cryst. Solids. 305, 328 (2002).
[3] K. Fuchs, U. Kaatze. J. Phys. Chem. B. 105, 2036 (2001).
[4] Y. Feldman, A. Puzenko, Ya. Ryabov. in S.A. Rice, Y.P. Kalmykov, W.T. Coffey, Eds., Fractals, *Diffusion and Relaxation in Disordered Complex Systems, Adv. Chem. Phys*. 133 A, 1 (2006).

Monitoring changes during network formation by dielectric measurements

M.T. Viciosa[1*], M. Dionísio[2], J.L. Gómez Ribelles[3,4,5]
[1] CQFM, Instituto Superior Técnico, Universidade Técnica de Lisboa, Avda Rovisco Pais, 1049-001 Lisboa, Portugal.
[2] REQUIMTE, Dpto de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal.
[3]Centro de Biomateriales e Ingeniería Tisular, Universida Politécnica de Valencia, Camino de Vera s/n E-46022 Valencia, Spain.
[4] Centro de Investigación Príncipe Felipe, Avda. Autopista del Saler 16, 46013 Valencia, Spain.
[5] CIBER en Bioingeniería, Biomateriales y Nanomedicina, Valencia, Spain.

Email address: teresaviciosa@ist.utl.pt

Tetra-ethylene glycol dimethacrylate, TeEGDMA, is a glass former material whose glass transition temperature, T_g, detected by DSC is –83 ºC[1]. This monomer is being widely used in the networks production for dental materials, information storage systems, etc. To monitor free radical polymerization of this compound fast data acquisition is required and Dielectric Relaxation Spectroscopy, DRS, easily can be employed with this aim since measurements can be done at relatively high frequencies.

In this work, isothermal polymerization of TeEGDMA with 0.1 % w.t. of 2,2-azobis- isobutyronitrile (AIBN) has been studied analyzing time dependence of the electric modulus spectrum, M''(*f*). The selection of M'' instead of permittivity is due to the high conductivity that this mixture TeEGDMA/AIBN presents at the polymerization temperatures studied (around 70 ºC). A clear peak revealing space charge motions has been detected in M'' during all the polymerization process (see Figure 1). The principal feature detected is a decrease in intensity and a shift to lower frequencies observed at a critical polymerization time that can be identified with the vitrification time (the T_g of the final polymer is expected around 200 ºC[2]).

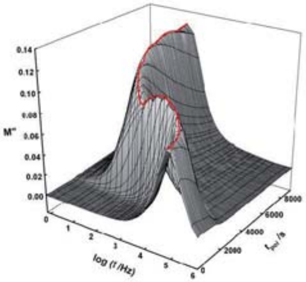


Figure 1. 3D electric modulus corresponding to TeEGDMA/AIBN during isothermal polymerization at 64 ºC.

Post-polymerization studies reveal that under these experimental conditions, almost all the monomer has been consumed, oppositely to that happened to DEGDMA, other member of the same family of monomers[3].

Acknowledgements: Fundação para a Ciência e Tecnologia by finantial support, SFRH/BPD/3961/2007.

References

[1] M.T. Viciosa, M. Dionísio, J. Non-Cryst. Solids 341, 60 (2004).
[2] M.T. Viciosa, N. Rouzé, M. Dionísio,J.L. Gómez Ribelles, Eur. Pol. J. 44, 155 (2008).
[3] M.T. Viciosa, A.R. Brás, J.L. Gómez Ribelles, M. Dionísio, Eur. Pol. J. 43, 1516 (2007).

Dynamics of water in poly(propylene glycol) studied by BDS and low temperature ATR-FTIR

Lokendra P. Singh*[3], **Silvina Cerveny**[1], **Angel Alegría**[1,2], **Juan Colmenero**[1,2,3]

1. Centro de Fisica de Materiales (CSIC, UPV/EHU)-Materials Physics Center, Paseo Manuel de Lardizabal 4, 20018, San Sebastián, Spain
2. Depto. de Física de Materiales, UPV/EHU, Facultad de Química, San Sebastián
3. Donostia International Physics Center, San Sebastián, Spain

*Email address: lokendrapratap_singh@ehu.es, lps.jnu@gmail.com

By mixing of water with other substances it is possible to avoid crystallization and entering the “no man´s land” region. In this work we used this strategy to study the water dynamics in the low temperature range (110-250K) of solutions of poly(propylene glycol) (PPG) with two different molecular weights (M_n = 425 and 725 g/mol). We combined broadband dielectric spectroscopy (10^{-2}-10^{8}Hz) and Fourier transform infrared spectroscopy (FTIR) using the attenuated total reflectance method (ATR) in the same temperature interval.

As in other hydrophilic water solutions [1], the dielectric spectra show two relaxations: the slower one related to the cooperative rearrangements of the solute plasticized by water [in well agreement with the calorimetric glass transition (T_g)] and the faster one usually attributed to the reorientation of the water dipoles in the system. This process dominates the dielectric properties of aqueous solutions (it is symmetric with an Arrhenius--like temperature dependence below T_g) whereas the main relaxation process is seen as a weak process.

In this work, we will discuss the changes in the ATR-FTIR signals (with both the hydration level and the molecular weight) of the distinct groups of PPG and we will relate them with the results observed by the dielectric measurements. In particular, we will discuss the effects on the -OH stretching bands of water in the region of 3500 to 4000 cm^{-1}.

References

[1]. S. Cerveny, A. Alegria, J. Colmenero Phys. Rev. E 77, 031803 (2008)

Dielectric relaxation and ac conductivity of poly(N-vinylcaprolactam)-water systems

I. Malyshkina*, N. Gavrilova, E. Makhaeva, G. Markin
Moscow State University, Physics Dept., Leninskie Gory, 119991 Moscow, Russia
*Email address: malysh@polly.phys.msu.ru

Water plays an essential role in many chemical and biological processes. The role of water is often played by a limited number of water molecules in a strongly restricted molecular environment, where the water displays properties which are not characteristic of the free state. Many papers have been dedicated to the investigation of new physical properties of water in different polymer matrices at negative temperatures [1–3]. Unusual properties of water for some polymer systems appear at certain concentrations of water in the case of a certain balance of interactions between water molecules and polymer molecules [4]. This balance, in its turn, is defined by the quantity of water molecules present in the polymer matrix.

In this work films of poly(*N*-vinylcaprolactam) (PVCL) with variable contents of water have been studied. The interaction of water molecules and the polymer matrix of PVCL was investigated with the use of dielectric spectroscopy (at $10^{-1}\div10^{7}$ Hz) as a function of temperature (–100÷50°C) and water concentration (at less than 1, 5 and 24 wt. %). The data have been analyzed within permittivity, conductivity and dielectric modulus formalisms. For all samples no water crystallization was observed during DSC scans.

At lower water content (1 and 5 wt. %) two dielectric relaxations can be seen. In the same time for the film with hither water content (24 wt. %) only one relaxation was observed. The relaxation process typical for all films is accompanied by anomalies in temperature dependence of conductivity. The activation energy values derived from the temperature dependencies of this dielectric relaxation and peaks of conductivity are the same that testify to the conducting nature of this relaxation. Additional relaxation process related to the dc-conductivity was observed for the sample with 24wt. % water content, which is accompanied by the peak of dielectric modulus.

References

[1] S. Cerveny, J. Colmenero, A. Alegria, Eur. Phys. J. 141, 49 (2007).
[2] G. Johari, A. Hallbrucker, E. Mayer, Nature. 330, 552 (1987).
[3] J. Swenson, R. Bergman, J. Howells, Chem. Phys. 113, 2873 (2003)
[4] S. Cerveny, G. Schwartz, G. Bergman, et al, Phys. Rev. Lett. 93, 245 702 (2004).

Dielectric permittivity and electrical conductivity of ionic mixtures soil/rainwater

A.Soualmia[*], **M.Abdelguerfi***
[*] Faculté de Physique Equipe Spectroscopie Diélectrique USTHB
BP 32 El Alia Alger, Algerie

*Email address :meriemsoualmia@yahoo.fr
a_soualmia@yahoo.fr

The characterization of dielectric materials can be reduced to the measurement of its complex permittivity and its electrical conductivity, which can first of all inform about its more or less polar aspect and its more or less conducting character. It is generally acted in fact of the response of device under test studied when it is subjected to an external excitation, for instance the electric field of an electromagnetic waveform

Accordingly the ordinary ground which is an ionic compound containing water can thus be regarded as a dielectric medium containing the electric charges which present a behaviour related to the application of the electric field; precisely water that the ground contains is the object of this study

Indeed the water content of the grounds is an essential parameter which represents a key variable in many fields like agronomy, geology, civil engineering.

The knowledge of this parameters, results, as it will be shown, from measurement of the permittivity; measurement results carried out by using the principle of the reflected waveforms obeying the propagation equation s of Maxwell. The method we proposed is well connected with several others, TDR probe method, capacitive probe, neutrons method.

The ordinary soil is an ionic compound in which ions can be released when its mixed water We could carry out on samples to various mass and volume proportions of measurements of permittivity and conductivity using a technique based on frequency domain reflectometry. The ionic solutions thus obtained go from the soil only dries until the ultimate measurement considered correct for a solution at winter rainwater 68%.We took again the series of measurements 14 months later while having taken the care to preserve under good conditions the dry soil and winter rainwater. The comparative results seem to be interesting for agronomy for example where the soils are classified according to their electric conductivity and dielectric permittivity

Key words : conductivity,permittivity,rainwater,soils

Multiple phase diagram in supercooled ethanol studied by Simultaneous Dielectric Spectroscopy and Neutron Diffraction

A. Sanz[1]*, I. Puente-Orench[2], M. Jiménez-Ruiz[2], A. Nogales[1] and T. A. Ezquerra[1]
[1]Instituto de Estructura de la Materia, CSIC, C/ Serrano 121, 28006, Madrid, Spain
[2]Institut Laue-Langevin (ILL), BP 156-38042 Grenoble Cedex 9, France
*Email address: asanz@iem.cfmac.csic.es

Ethanol, one the simplest alcohols, has a strong dipole moment and can be easily quenched into the glassy state by fast cooling from room temperature. In addition to that, ethanol presents a non trivial phase diagram where, below the melting temperature and depending on the thermal history, exists either as a supercooled liquid SCL (translational and rotational disorder), crystalline solid C (translational and rotational order) or plastic crystal PC (translational order but rotational disorder)[1]. We have previously proven the feasibility of performing simultaneous neutron diffraction ND and dielectric spectroscopy DS experiments with a special cell[2]. The access to simultaneous information of both amorphous and crystalline phase foresees an improvement in the understanding of crystallization processes in condensed matter. This simultaneity is especially attractive for investigating the phase diagram of ethanol, where, apart from the crystallization phenomena, two more phase transitions can be observed. These two phase transitions referred as SCL to PC and PC to C respectively. Some of these phase transitions have already been studied by means of neutron and dielectric techniques but a complete picture of the isothermal structural changes in supercooled ethanol is still missing. We have studied, for the first time, the phase diagram of deuterated ethanol by simultaneous measurements of ND and DS in order to correlate structural and dynamic aspects during isothermal phase transitions. This work allows checking if the model proposed for the crystallization of isopropanol, which indicates that a breakage of the hydrogen bonding network takes place before the crystallization process, can be extended to other low molecular weight alcohols[2].

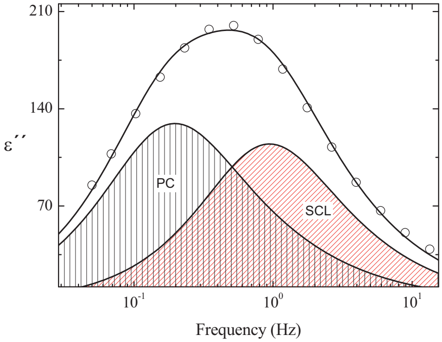


Fig.1. Dielectric curve during isothermal phase transition of ethanol-d6 from supercooled liquid to plastic crystal at 105 K.

References

---

[1] M.A. Ramos et al. Phys. Rev. Lett. vol. 78, 1, 82 (1997)
[2] A. Sanz et al. Phys. Rev. Lett. vol. 93, 1, 015503 (2004)

Dielectric studies of sodium carboxymethylcellulose

V. Holcman[*], **T. Palai-Dany, K. Liedermann**
Department of Physics, Faculty of Electrical Engineering and Communications,
Brno University of Technology, Technicka 8, 616 00 Brno, Czech Republic
*Email address: holcman@feec.vutbr.cz

Dielectric studies of a sodium salt of carboxymethylcellulose (NaCMC) with molecular weight 0.55 x 10^6 in a broad temperature and frequency range, 215 – 385 K, 20 Hz – 1 GHz, are presented. The observed dielectric spectrum of this polyelectrolyte is interpreted as a sum of a conduction process and two relaxation processes with different activation energies. Microscopic origin of the observed spectra at the molecular level is examined. It is proposed that the low-frequency relaxation is due to correlated reorientations of carboxymethyl groups and that the high-frequency relaxation is brought about by interaction between the NaCMC sample itself and the electrode material. This relaxation is of interfacial character and seems to be correlated with the degree of electrode aging, i.e. with the state of electrodes applied on the NaCMC foil. This interpretation is supported by the results of measurements on NaCMC with different electrode materials and on other cellulose derivatives.

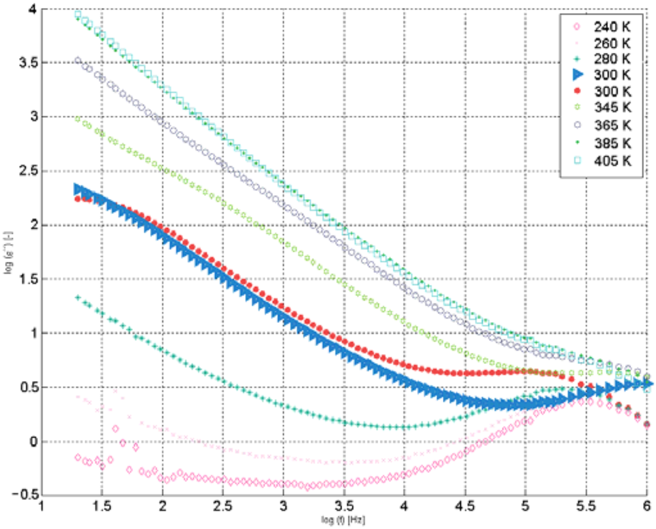


Fig.1. Dielectric loss in NaCMC as a function of frequency and temperature; all colour symbols – graphite electrodes, large blue triangles – brass electrodes, 300 K.

References
[1] E. El Shafee. Carbohydrate Polymers, 31 (1996) 93-98.
[2] H. Montes, J.Y. Cavaillé. Polymer, 40(1992), 2649-2657.
[3] K. Liedermann, L. Lapčík, Jr. Carbohydrate Polymers, 42 (2000), 369-374.

Infrared dispersion of dipropyl ethers

J.P. Hawranek*, W. Wrzeszcz, M. Pajdowska and H.A. Kołodziej

Faculty of Chemistry, University of Wrocław
F. Joliot-Curie 14, 50-383 Wrocław, Poland
* HJP@wchuwr.pl

The spectra of the real and imaginary components of the complex electric permittivity and complex polarizability of liquid di–*n*-propylether and di-*iso*-propylether were determined in the Visible, Near Infrared, Mid Infrared and Far Infrared spectral regions (25000 - 100 cm^{-1}). Also the total molar polarization was determined from low frequency dielectric measurements and the molar electronic polarizatiom from refractive index measurements.

The molar vibrational polarization related to various spectral ranges has been determined. and compared for both liquids. It has been found to be extremely small for overtone bands. The main contribution stems from the region of deformation modes of the molecules. The total molar vibrational polarization originating from internal vibrational modes in the 15000 - 160 cm^{-1} region amounts to 2.62 cm^3 $mole^{-1}$ for di–*n*-propylether and 1.79 cm^3 $mole^{-1}$ for di-*iso*-propylether. The difference is mainly due to the contribution of distortion modes for di–*n*-propylether in the Far Infrared, since in the Mid Infrared region the values for both molecules are comparable.

The results enable the discussion ot the vibrational polarization due to hydrogen bond formation in liquid *n*-propanol [1].

[1] Hawranek J.P., Michniewicz N., Wrzeszcz W. and Pajdowska M.,
J. Non-Cryst. Solids, 353 (2007) 4555.

Infrared dispersion of intramolecularly H-Bonded *o*-Hydroxybenzylidenemethylimine

J.P. Hawranek*, W. Wrzeszcz, M. Matusiak-Kucharska, M. Pajdowska

Faculty of Chemistry, University of Wrocław, 50-383 Wrocław, F. Joliot-Curie 14, Poland
* HJP@wchuwr.pl

The spectra of the real and imaginary components of the complex electric permittivity and complex polarizability for neat liquid o-Hydroksybezylidenemethylimine (HBzMI) and Benzylidenemethylimine (BzMI) were determined in the Visible, Near Infrared, Mid Infrared and Far Infrared spectral regions (25000 - 100 cm^{-1}). The low frequency electric permittivities of both liquids have been also determined.

Molar vibrational polarization values related to various spectral ranges have been determined. They have been found to be extremely small for overtones. Contributions stemming from internal vibrations [1] down to 100 cm^{-1} were determined for both molecules. The largest contribution stems from the deformation vibrations range. The total molar vibrational polarization originating from internal modes absorbing from 12500 down to 600 cm^{-1} amounts to 1.40 $cm^3 \cdot mole^{-1}$ for BzMI and 3.12 $cm^3 \cdot mole^{-1}$ for intramolecularly H-bonded HBzMI.

The considerable contribution due to the formed intramolecular H-bonding has been evaluated and discussed. A 12.8 – fold increase of the molar vibrational polarization of the OH group due to intramolecular H – bond formation was shown. The increase due to charge redistribution is approximately 2.2 - fold. Only a slight increase in the molar electronic polarization with H-bond formation was observed in the studied system.

[1] M. Matusiak, W. Wrzeszcz, T. Dziembowska and J.P. Hawranek, J. Mol. Struct., 704 (2004) 223.

Molecular dynamics in PVME hydrogels at sub-zero temperatures

R. Kisiel[1*], **M. Kozanecki**[1], **A. Schoanhals**[2], **M. Pastorczak**[1], **K. Koynov**[3], **L. Okrasa**[1], **H.J. Butt**[3], **K. Krysiak**[1], **J. Ulanski**[1]

[1] Department of Molecular Physics, Technical University of Lodz, Zeromskiego 116, 90-924 Lodz, Poland
[2] Federal Institute for Materials Research and Testing, Unter den Eichen 87, 12205 Berlin, Germany
[3] Max-Planck Institute for Polymer Research, Ackermannweg 10, 55-128 Mainz, Germany
*Email address: renata.pstrokonska@p.lodz.pl

From applicative point of view the most promising group of hydrogels are stimuli-responsive (particularly: thermo-responsive) materials [1]. Their main advantage is abrupt change in the properties in response to even small modification in environmental conditions. These materials are mostly synthesized from polymers exhibiting lower critical solution temperature (LCST) in water, and poly(vinylmethylether) PVME is an example of such polymer. In a case of crosslinked macromolecules LCST is manifested in a volume phase transition [2].

Systematic studies of hydrogels are commonly conducted in the range of temperature between 0-100°C, nevertheless, investigations of these materials at temperatures below freezing point of water seems to be also important. They should help to understand better phenomena involved in synthesis and applications of cryogels as well as lyophilization processes. From this point of view, molecular dynamics is especially interesting, because it may give valuable information helpful to design hydrogels with precisely define diffusive and/or mechanical properties.

An influence of temperature, crosslinking and swelling degrees on molecular dynamics in thermo-responsible PVME hydrogels was an object of performed investigations. BDS (including high frequency region 1MHz - 3GHz) and DMA were used to study hydrogels synthesized by electron beam irradiation of PVME (to obtain networks with different density of crosslinks various irradiation doses were applied). Investigations were performed at sub-zero temperatures.

Whereas, changes in mechanical modulus of the systems below 0°C relate to freezing and melting (also “pre-melting”) of ice, the high frequency BDS results revealed molecular relaxation process of unfrozen water. Shapes of temperature dependencies of mechanical modulus of the system and dielectric strength of water process, suggests that the water freezes in PVME gels rapidly, while the water melting is strongly influenced by the polymer network. The melting process extends from c.a. -20°C (glass transition of linear PVME) up to 0°C. It means that the molecular dynamics of polymer network and water molecules is interdependent in hydrogels (mobility of the network is stimulated by water molecules, and simultaneously structure and dynamics of water are dependent on polymer concentration). DMA results showed also that the molecular dynamics in PVME gels strongly depends on water content only for weakly swollen samples (below swelling degree 5).

References

[1] Chaterji S., Kwon I.K., Park K., *Smart Polymeric Gels: Redefining the Limits of Biomedical Devices,* Prog. Polym. Sci. 2007 (32) 1083–1122

[2] Gil E.S., Hudson S.M., *Stimuli-responsive polymers and their bioconjugates*, Prog. Polym. Sci. 2004 (29) 1173–1222

Influence of Gemini surfactant on phase behaviour of phosphocholine DMPC water suspension

K. Szpotkowski, A. Wypych, M. Kozak and S. Jurga*
Department of Macromolecular Physics, Faculty of Physics, A. Mickiewicz University,
Umultowska 85, 61-614 Poznań, Poland
*Email address: zfmak@amu.edu.pl

Binary systems phospholipid/Gemini surfactants can create bicelles in water solution[1]. Structure of bicelle has an intermediate shape between two dimensional bilayer and spherical micelles, and is regarded as a powerful medium for studying physics of membranes and membrane - associated biomolecules[2].

We have studied the phase behaviour of a mixture of DMPC (1,2-dimyristoyl-sn-glycero-3-phosphocholine) and Gemini surfactant GEM-IK1 (1,1'-(1,4-butane)bis 3-decyloxymethylimidazolium chloride) by means of Small Angle X-ray Scattering (SAXS), Fourier Transform Infrared Spectroscopy (FTIR) and Broadband Dielectric Spectroscopy (BDS). SAXS measurements revealed a formation of bicelles, in DMPC/GEM-IK1 water suspension, of diameter size 26 ÷34 nm at 282K (Fig. 1).

It was found that the small step in the dielectric constant ε' is related with the transition from gel to liquid crystalline phase (Fig 2), which is supported by the temperature dependence of the symmetric and antisymmetric CH_2 vibration modes as well as antysymetric stretching PO_2 band frequencies, as revealed by FTIR measurements. The presence of the surfactant in DMPC water suspension causes a decrease of the phase transition temperature, as found by means of FTIR and BDS techniques.

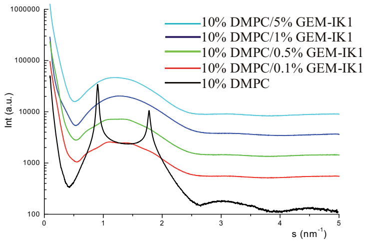


Fig. 1. SAXS curves recorded for DMPC and DMPC/GEM-IK1 systems at temperature 282 K.

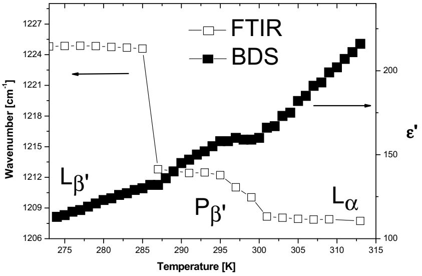


Fig.2. The real part of dielectric permittivity ε' (at 1.5 MHz) and the asymmetric stretching vibrations of PO_2 of DMPC suspension in the temperature range from 273 to 315 K. Phase transitions are visible as steps in presented curves. $L_{\beta'}$, $P_{\beta'}$, L_{α} denote planar gel, rippled gel and liquid–crystalline phases, respectively.

References:
[1] J. Katsaras, T.A. Harroun, J. Pencer, M.P. Nieh, Naturwissenschaften 92 (2005) 355.
[2] M. Kozak, M. Kempka, K. Szpotkowski, S. Jurga, Journal of Non-Crystalline Solids 353. (2007) 4226.

Acknowledgements: This work is supported by 6th Framework Programme under SoftComp Grant No 502235-2 and research grant No N N202 285338 (Poland).

Dielectric and electric properties of nanodiamonds water suspensions

A.V. Adeljanov[1*], O.A. Gorobchenko[1], E.M. Mamotyuk[2], O.T. Nikolov[1], V.N. Ivaschenko[3], S.V. Gatash[1]
[1]V.N.Karazin Kharkov National University, Svobody Sq. 4, 61077 Kharkov, Ukraine
[2]S.P. Grigor'ev Kharkov Institute of Oncology and Medical Radiology, Pushkinskaya Street 82, 61000 Kharkov, Ukraine
[3]Scientific Production Enterprise "SINTA" Ltd., Gvardeyskoy Armiy Street 143, Kulinychi, 62404 Kharkov, Ukraine
*Email address: adel_vil@mail.ru

At the present time, the nanodiamonds (NDs) find application in various technologies. The use of NDs in biology and medicine offers the greatest promise [1]. It was revealed that NDs could be the new class of medical nanomaterials for delivering anti-cancer chemicals to cells [2]. NDs could also be employed against tuberculosis or viruses. The instability of NDs water suspensions is a serious obstacle to their use in medicine. The investigation of the water state in the NDs suspensions is of obvious interest in connection with the problem of the stability of NDs suspensions and revealing the mechanisms of the NDs influence on biological objects.

In the present work the NDs water suspensions produced by Scientific Production Enterprise "SINTA" Ltd (Kharkov, Ukraine) were studied. The concentrations of NDs in the suspensions were 0,1 wt % - 3,5 wt %. The real (ε') and imaginary (ε'') parts of the complex permittivity ($\varepsilon^*=\varepsilon'-j\varepsilon''$) of the suspensions were measured by the microwave dielectric method described [3]. A resonator type ultra high frequency (UHF) dielectrometer at the frequency of 9.2 GHz has been used. The low-frequency conductivity was measured by the alternating current bridge at 1 kHz. The static dielectric permittivity and the frequency of water molecules dielectric relaxation were found from the Debye equations.

It was found that the real part of the complex permittivity decreases and the imaginary part increases with the increase of the NDs concentration. It was also found the reduction in the static dielectric permittivity and in the frequency of water molecules dielectric relaxation with the increase of the concentration of NDs. These observations can result from decreasing of the amount of bulk water in the system and from the ordering of its structure. The values of ε_s were compared with the theoretically obtained values of the effective permittivity of NDs suspensions. The hydration of NDs was taken into account. The two types of the structured water in the suspensions of NDs were found.

References

[1] Nanodiamonds: Applications in Biology and Nanoscale Medicine. / Dean Ho (Ed.) Springer, 288 (2010).
[2] Houjin Huang, Erik Pierstorff, Eiji Osawa, Dean Ho. Nano Letters 7(11), 3305 (2007).
[3] E.V. Hackl, S.V. Gatash, O.T. Nikolov. J. Biochem. Biophys. Meth. 63(2), 137 (2005).

Role of counterions on thermal behavior of aqueous phospholipid-surfactant systems

M. Kozak[*], **A. Wypych, K. Szpotkowski and S. Jurga**

Department of Macromolecular Physics, Faculty of Physics, A. Mickiewicz University,
Umultowska 85, 61-614 Poznań, Poland
*Email address: mkozak@amu.edu.pl

Phosphocholine derivatives make the most abundant class of lipids in mammalian membranes and are also major membrane components in eukaryotic organisms. In water solution they create several types of structural phases, which depend on the concentration of lipids, temperature and type of additives [1-3]. The organisation of phospholipids molecules in water solution and formation of their new structural phases depend also on the presence of surfactants. Most of surfactants are salts, which dissociate in water solution, causing an increase of ion (counterion) species in system studied.

The aim of the work was to determine the presence of various surfactant (comprising different counter ions, like for instance: NO_3 and CH_2COOH) on phase transition of two phospholipids. Aqueous suspension of 1,2-dimyristoyl-sn-glycero-3-phosphocholine (DMPC) or 1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC) were used as a model systems reflecting the membrane behaviour. The mixtures of phospholipid-surfactant have been investigated by means of dielectric (impedance) spectroscopy (DS) and Fourier Transform Infrared Spectroscopy (FTIR). The special attention was devoted to the role of different groups of counterions in phospholipid-surfactant system and their ability to change organization within hydration layer of phospholipid.

Acknowledgements
This work is supported by the research grant No N N202 248935 (from Ministry of Science and Higher Education, Poland).

References

1. R. Koynova, M. Caffrey, Biochim. Biophys. Acta-Rev. Biomembranes 1376 (1998) 91.
2. R. Winter, Biochim. Biophys. Acta-Prot. Struct. Mol. Enzymol. 1595 (2002) 160.
3. M. Kozak, A.Wypych, K. Szpotkowski, S. Jurga, A. Skrzypczak, Journal of Non-Crystalline Solids, 356 (2010) 747–753.

Influence of selected technological parameters on the dielectric properties of carbon-unwoven fabric composite systems.

M. Jaroszewski[*], **J. Pospieszna**
Wrocław University of Technology, Dept. of Electrical Engineering, 50-370 Wrocław, Poland

*Email address: maciej.jaroszewski@pwr.wroc.pl

Carbon – unwoven fabric composite is a promising material for use as a electromagnetic screens [1-4]. Appropriate materials are chosen mainly on the basis of their mechanical properties, such, as low weight and elasticity. Deposition of thin plasma layer on the rough fabric surface should also increase the active surface of the shield, which strongly influences the effectiveness of reflection at interfacial layers [5]. Efficiency of reflection at the interfacial surfaces depends, among the others, on the surface area. In the case of fabric such developed surface can be made of surfaces of fibers with plasma carbon layer. Distribution of internal field is determined mainly by the fibers orientation and polarization of incident field.

In the process of putting thin carbon layer coatings onto the fabric the method of low temperature glow discharges plasma - PAPVD (Plasma Assisted Physical Vapour Deposition) was used. Low temperature plasma method has been previously successfully applied for deposition of thin metallic (Zn, In, Ti) and oxide (ZnO, In_2O_3) layers onto pressboards and polypropylene fabrics [6]. Obtained layers exhibited good adhesion to the substrate.

For the assessment of the unique buffering properties of the deposited layers dielectric spectroscopy method has been chosen. Our earlier research showed that plasma carbon layer deposited on more rough fabric surface strongly influences its electrical properties [7]. In the present paper, we report that their dielectrics properties could be changed depending on the morphology of substrate surface and on parameters of the plasma generating process. Measurements of the complex admittance were performed in the frequency range of 40 Hz – 10 MHz.

This publication was prepared with the key project – POIG no. 01.03.01-00-006/08 co-financed from the founds of European Regional Development Found within the framework of the Operational Programme Innovative Economy.

References

[1] J. Avloni, L. Florio, A.R. Henn, R. Lau, M. Ouyang, A. Sparavigna, Cornell University Library, arXiv.org
[2] V. Bogush; Journal of Optoelectronics and Advanced Materials Vol. 7, No. 3, June 2005, 1635 - 1642
[3]Curtis, M. D.; Shiu, K.; Butler, W. M.; Huffmann, J. C. J. Am. Chem. Soc. 1986, 108, 3335.
[4] Li-Li Wanga,b, Beng-Kang Tayb, Kye-Yak Seeb, Zhuo Suna, Lin-Kin Tanb, Darren Luab, Carbon 47 (2009),1905 –1910
[5] Pospieszna J., Electrical Review, Conferences, No 1, (2006).
[6] Ziaja J.; Koprowska J.; Janukiewicz J., Fibres & Textiles in Eastern Europe, No 5 (70), (2008)
[7] Jaroszewski M.; Pospieszna J.; Ziaja J. Journal of Non-Crystalline Solids 356 (2010) 625–628

Dielectric properties and structures of melt compounded poly(ethylene oxide)-montmorillonite nanocomposites

Shobhna Choudhary, **R.J. Sengwa***
Dielectric Research Laboratory, Department of Physics, J N V University.
Jodhpur – 342 005 India
*Email address: rjsengwa@rediffmail.com

The organic-inorganic nanocomposites comprising polymer and montmorillonite (MMT) clay synthesized by solution intercalation and melt compounding techniques is the new challenging area for their structural characterization by dielectric spectroscopy[1-9]. Dielectric studies reveal that a large exfoliated MMT structures in polymer matrix decreases the real part of dielectric function[1,4,9]. In present work the relative complex dielectric function, electric modulus, and alternating current (ac) electrical conductivity of melt-compounded poly(ethylene oxide) (PEO)-montmorillonite (MMT) clay nanocomposites upto 20 wt% MMT loading were investigated over the frequency range 20 Hz to 1 MHz. The MMT concentration dependent intercalated and exfoliated structures of the dispersed MMT in PEO matrix were recognized by the variation in real part of dielectric function. Relaxation times for PEO local chain motion were determined from the loss peak frequency of dielectric function (Fig. 1) and electric modulus spectra. A correlation is explored between relaxation times and the interactions compatibility of PEO molecules with dispersed MMT clay nano platelets, and their effect on PEO chain dynamics. AC conductivity spectra of the PEO-MMT nanocomposite over five decades of frequency obey almost straight line fit of two different slopes, which changes significantly with clay concentration (Fig. 2).

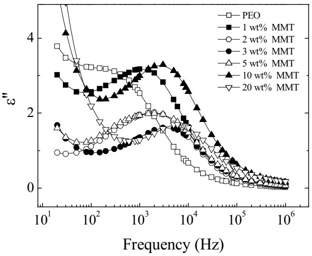


Fig. 1 Dielectric loss spectra of the PEO-MMT clay nanocomposites

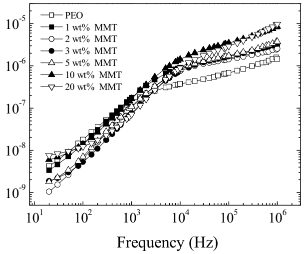


Fig. 2 AC conductivity spectra of the PEO-MMT clay nanocomposites

References

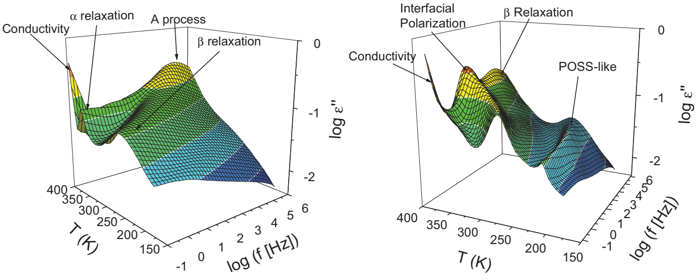
[1] N. Noda, Y.H. Lee, A.J. Bur et al, Polymer 46, 7201 (2005).
[2] M. Pluta, J.K. Jeszka, G. Boiteux, Eur. Polym. J. 43, 2819 (2007).
[3] J. Mijović, H. Lee, J. Kenny, J. Mays, Macromolecules 39, 2172 (2006).
[4] M. Böhning, H. Goering, A. Fritz et al, Macromolecules 38, 2764 (2005).
[5] R.J. Sengwa, S. Choudhary, S. Sankhla, Colloids Surf. A 336, 79 (2009).
[6] C. Pandis, E. Logakis, V. Peoglos et al, J. Polym. Sci.: Part B: Polym. Phys. 47, 407 (2009).
[7] R.J. Sengwa, S. Sankhla, S. Choudhary, Colloids Polym. Sci. 287, 1013 (2009).
[8] R.J. Sengwa, S. Choudhary, S. Sankhla, Polym. Int. 58, 781 (2009).
[9] R.J. Sengwa, S. Sankhla, S. Choudhary, Indian J. Pure Appl. Phys. 48, 196 (2010).

Structural investigation of nanocomposites based on Poly(methyl methacrylate) and Methacryl Polyhedral Oligomeric Silesquioxanes

Purv J. Purohit*, Andreas Schönhals

BAM Federal Institute of Materials Research and Testing, Unter den Eichen 87, 12200 Berlin, Germany
*Email address: purv.purohit@bam.de

Enhancement of polymer properties by use of different types of nano-sized fillers is explored continuously from nearly past two decades. Polymer based nanocomposites have shown remarkable improvement in properties as compared to conventional scaled composites because of the length scale of interaction of the nanofillers with the polymer segments. Perseverant efforts are made to fully understand the structure-property relationship of such polymer based nanocomposites. Nanocomposites of Poly(methyl methacrylate) as matrix and MethacrylPOSS (MPOSS) as the nanofiller were prepared. The structure-property relationships of the nanocomposites were analyzed using dielectric spectroscopy, FTIR and DSC. FTIR results show that the composition of nanocomposites might not be the same as expected from the formulation. Dielectric spectrum of PMMA shows a β relaxation process at lower temperatures (higher frequencies) and a dynamic glass transition (α relaxation) at higher temperatures (lower frequencies). MPOSS can be molecularly dispersed in PMMA upto 10 vol% of the nominal formulation, which can be concluded as no additional dielectric process is observed for nanocomposites as compared to pure PMMA. At concentrations above this, an additional process in the region of the dynamic glass transition of MPOSS (Fig. POSS like) is observed along with an additional narrow peak (interfacial polarization). The latter can be well described by Maxwell-Wagner-Sillars polarization indicating phase separated morphology. The glass transition temperature reduces with increasing concentration of MPOSS in the nanocomposites indicating plasticization of PMMA.



PMMA5 **PMMA30**

Figure: 3D representation of dielectric spectra of PMMA5 (5vol% MPOSS) and PMMA30 (30vol% MPOSS)

Molecular mobility at the interfaces of nanostructured polymers filled by functional nanofillers

H. Rekik[1,2], M. Arous[1], A. Kallel[1] I. Stevenson-Royaud[2], G. Boiteux[2] and G. Seytre[2]

[1]Laboratoire des Matériaux Composites Céramiques et Polymères, Faculté des Sciences de Sfax, 3018 Sfax, Tunisie
[2]Université Lyon 1, UMR CNRS 5223, IMP, Laboratoire des Matériaux Polymères et des Biomatéroiaux, Bât. ISTIL, 15, Bld Latarjet, F-69622 Villeurbanne Cedex France
*Email address: isabelle.royaud@univ-lyon1.fr

Abstract

Polyvinylidene fluoride (PVDF) and polypropylene (PP) films have been filled with different volumic fraction of titanate dioxide TiO_2 by two ways: dispersion in the melt or in-situ generation. The objective of this work is to probe by DRS the different molecular mobility induced by the processes and the space charges repartition by scanning electron microscopy mirror effect. It was shown that the behaviour of PVDF in these nanocomposites is close to that of PVDF matrix. The main changes being the slowing down of the dynamics of the β and the α_c relaxations as a function of TiO_2 volumic fraction and the existence of charge carriers trapping at the interfaces. The MWS polarisation in the different nanocomposites will be also analysed.

Keywords

Composite material; polyvinylidene difluoride polymer; Composite; titanate dioxide; Dielectric properties

Dielectric studies of segmental and global chain dynamics in intercalated poly (propylene oxide) amines/layered silicate nanocomposites

S. Kripotou[1*], A, Kyritsis[1], K. S. Triantafyllidis[2], P. I. Xidas[2], P. Pissis[1]
[1] Department of Physics, National Technical University of Athens, Zografou Campus, 15780, Athens, Greece
[2] Department of Chemistry, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece
*Email address: roulak@central.ntua.gr

The molecular mobility of poly (propylene oxide) amines intercalated in montmorillonite clays, was studied by dielectric relaxation spectroscopy (DRS, 10^{-2} – 10^{6} Hz, 120K – 350K) and thermally stimulated depolarization current techniques (TSDC, 120K – 350K). Differential scanning calorimetry (DSC) was used as a supplementary technique. The inorganic clay used for the preparation of the organoclay studied in this work was an industrially purified Na+ - montmorillonite (PGW, Nanocor Inc.) with a cation exchange capacity (CEC) of 120 meq/100 g. The organic clays were prepared by ion-exchanging the inorganic clay with the diprotonated forms of the commercially available α, ω-diamines (polypropylene oxides with amines as terminal groups) known as Jeffamine D-series, D4000, D2000, D400.

Depending on the chain length of the diamine, different orientations of the PPO chains were adopted in the clay galleries: Low molecular weight Jeffamines (MW ~ 400) intercalate as lateral bilayer to inclined monolayer and the gallery heights are restricted to d_{001} basal spacing values of approximately 17 Å. For Jeffamines with MW values of 2000 and 4000 the PPO chains adopted a folded configuration within the galleries resulting in d_{001} values of approximately 46 Å[1]. The polymeric chains are restricted between successive clay nanolayers which define a 3D gallery system where the chains are actually confined in one dimension related to the gallery height and effectively anchored to the clay internal surfaces.

Jeffamines exhibit, in addition to the transverse dipole moment component that gives rise to the segmental α process, a persistent cumulative dipole moment along the chain contour. This part of dipole moment of the PPO chains can be relaxed via the normal mode (nm process). Dielectric Spectroscopy was used to provide information on the chain dynamics by monitoring all the possible motions of the macromolecules, from local chain motions up to global chain translational and rotational motions.

Our results reveal striking differences in the long range polymer dynamics for all the intercalated systems studied. For low MW (MW ~ 400) intercalated PPO chains, the segmental and global chain motions was found to be strongly suppressed.

References

[1] C.S. Triantafillidis, P.C. LeBaron, T.J. Pinnavaia, Journal of Solid State Chemistry 167, 354 (2002).

Activation energy of conductivity at glass transitions of hybrid organic-inorganic polymer systems

M. Iurzhenko[1, 2*], G. Boiteux[2], Ye. Mamunya[1], E. Nikaj[2], E. Lebedev[1]
[1]Institute of Macromolecular Chemistry of NAS of Ukraine, Kharkivske shossee, 48, 02160, Kyiv, Ukraine.
[2] Laboratoire des Matériaux Polymères et des Biomatériaux (LMPB) - UMR CNRS 5223 "Ingénierie des Matériaux Polymères" Université Claude Bernard Lyon1, Bâtiment ISTIL, 15 Boulevard A. Latarjet, 69622, Villeurbanne Cedex, France
*Email address: 4ewip@ukr.net

Hybrid organic-inorganic polymer systems (HOIS) were synthesized *in situ* by joint polymerization of urethane and inorganic oligomers[1]. Mixture of two isocyanate-containing products (macrodiisocyanate MDI and poly(isocyanate) PIC) with different molecular weights and numbers of reactive groups as the organic component was used. Inorganic component was metal silicate that exists in oligomeric form in water solution[2]. Previously it was shown the presence of two glass transitions in HOIS synthesized[3]. Both isocyanate-containing products separately react with metal silicate due to reactions between NCO-groups of organic component and Si-OH of inorganic component. That produces two interpenetrating hybrid organic-inorganic networks (HIPN) in bulk OIS, which differ by cross-linking rate, molecular mobility, degree of freedom of macromolecular chains etc. Each hybrid IPN is characterized by its own glass transition temperature dominates in OIS depending on content of organic component and, accordingly, restricts the mobility of another HIPN. Thus, three temperature regions of structural order of HOIS present on temperature dependencies of physical characteristics: glass (first HIPN)/glass (second HIPN), viscous-elastic/glass and viscous-elastic/viscous-elastic. The impact of structural order of HOIS on their electrophysical and dielectric properties were studied. The activation energies and changes of conductivity and permittivity at structural transitions of both hybrid IPN were investigated (Fig. 1).

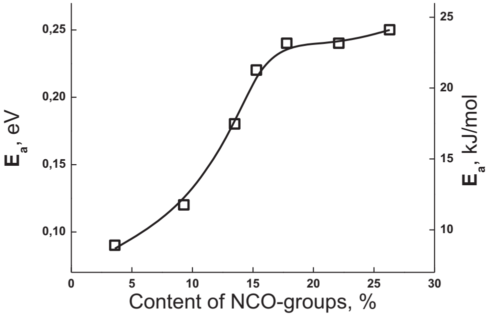


Fig.1. Activation energy of HIPN based on urethane oligomer at glass transition region (-50 °C)

References
[1] Ye.P. Mamunya, V.V. Myshak, E.V. Lebedev. Polym. J. 26, 40 (2004).
[2] Ye.P. Mamunya, V.I. Shtompel, E.V. Lebedev, P. Pissis, A. Kanapitsas, G. Boiteux. Europ. Polym. J. 40, 2323 (2004).
[3] Ye.P. Mamunya, M.V. Iurzhenko, E.V. Lebedev, S.S. Ischenko, G. Boiteux, G.Seytre. J. Non-Cryst. Sol. 353, 4288 (2007).

Dielectric spectroscopy of a new metal-containing polymer structure.

V. T. Avanesyan*, **E. G. Vodkailo**
Herzen State Pedagogical University, Saint-Petersburg, Moika R. 48, 191186, Russia.
*Email address: avanesyan@mail.ru

Metal containing polymers are a new and interesting class of materials for designing nano- and optoelectronic devices. The conducting redox polymers based on complexes of transition metals with Schiff's bases satisfy the requirements of the stability and photo- and electrosensitivity[1, 2]. In this paper, we are concerned with the electrophysical properties of metal-containing polymer films based on the Cu(II) complex with tetradentate ligand [CumSalpn] in an alternating-current electric field. The polymer samples were synthesized by the anode polarization of an electrode in the solution of the initial monomer complex [CumSalpn], the polymer films thus prepared had a thickness of the order of 1 μ. The frequency dependences of the capacitance and dielectric loss were measured at the temperature T=293 K with the use of an E7-20 broadband immitance meter in the frequency range 10^2–10^6 Hz. Figures 1 demonstrate the frequency dependences of dielectric permittivity ε' and factor of the losses ε'' for samples of the polymer complex [CumSalpn] and H_2mSalpn-1.3 ligand of the metal center. The values of dielectric parameters for the structure under study decrease with an increase in the frequency of the measuring field. The dielectric response at low frequencies may be related to the dynamics of the orientation of the structural units (relaxators) of the [CumSalpn] polymer. The occurrence of these relaxators is associated, in particular with the rupture of chemical bonds in the polymer accompanied by base electrolyte ions. With increasing frequency, separate elements of the polymer chain begin to participate in the relaxation process. These are presumably phenyl rings, including hydrocarbon CH groups. Thus, the frequency dispersion of dielectric parameters in an alternating electric field is clearly defined. The obtained data can be useful for the choice of the monomer architecture in order to obtain a supramolecular metal-containing polymer with the optimum electrical properties.

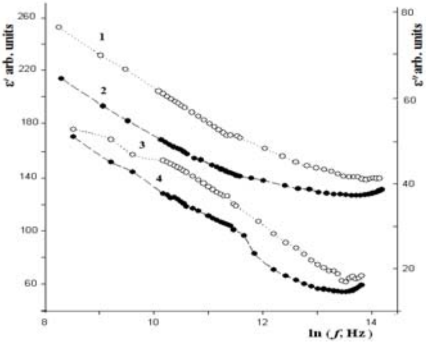


Fig.1. Frequency dependences of the ε'(1, 2) and ε''(3, 4) for polymer complex [CumSalpn] and H_2mSalpn-1.3 ligand respectively.

References

[1] B. de Castro, R. Ferreira, C. Freire, H. Garci'a. New J. Chem., 26, 405 (2002).
[2] V. T. Avanesyan, G. V. Vovk, M. Yu. Puchkov, G. A. Shagisultanova. Polymer Science, 50, 262 (2008).

Dynamic dielectric study of carbon nanotubes dispersion in polyamide 11

D. Carponcin[1], **E. Dantras**[1,*], **C. Lacabanne**[1]
[1]Laboratoire de Physique des Polymères, Institut Carnot CIRIMAT,
31062 Toulouse Cedex 9, France
*Email address: dantras@cict.fr

Introduction of carbon nanotubes (CNTs) in an insulator polymer matrix allows observing an electrical percolation phenomenon [1]. Even if other particles (like carbon black or metallic nanowires [2]) can make the composite conductor for a given concentration, carbon nanotubes, thanks to their large aspect ratio, can reach very low percolation thresholds [3]. The aim of this work is to ensure a good CNTs dispersion to preserve a large apparent aspect ratio. The novelty in this kind of study is the choice of the host matrix: polyamide 11 (PA11), a semi-crystalline polymer, has been chosen due to its good mechanical properties. Two methods of CNTs dispersion will be compared through composites DC conductivity study (value extracted from dynamic conductivity at low frequency); i.e. solvent way and melt mixing process [4]. Concerning the second one, twin screw extruder parameters should be investigated to optimize CNTs dispersion in PA11. The dielectric studies have been found to be particularly well suited for characterizing CNTs dispersion.

Below the percolation threshold, the influence of CNTs on the dielectric relaxations associated with the glass transition has been followed. Two components are observed independently from the CNT content: the lower temperature one is dependent upon CNTs indicating that CNTs are localized in the soft amorphous phase; contrarily, the higher temperature one is unmodified since the rigid amorphous phase is too cohesive to be penetrated by fillers. The evolution of the corresponding average relaxation times versus reciprocal temperature is shown in Figure 1 for a composite at 0.3 wt %, as example. The influence of CNTs content will be discussed.

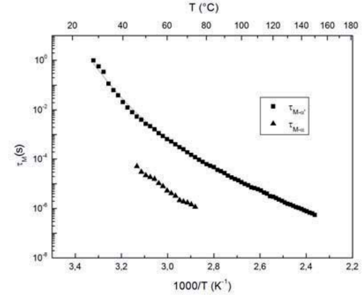


Fig.1. Arrhenius diagram for a CNTs /PA 11 composite at 0.3 wt %

References

[1] D. Stauffer. Taylor & Francis, London and Philadelphia (1985).
[2] A. Lonjon, L. Laffont, P. Demont, E. Dantras, C. Lacabanne J. Phys. Chem. C 113, 12002 (2009)
[3] S. Barrau, P. Demont, C. Maraval, A. Bernes, C. Lacabanne Macromol. Rapid. Commun. 26, 390 (2005)
[4] B. Krause, P. Pötschke, L. Häubler. Compos. Sci. Technol. 69, 1505 (2009).

Domain size and internal dynamics of poly(butylene terephthalate)/decylamine/fullerene nanocomposite

A. Woźniak-Braszak[1*], M. Baranowski[1], W. Grzesiak[2], B. Brycki[2], K. Jurga[1], J. Jurga[3], K. Hołderna-Natkaniec[1]
[1]Faculty of Physics, Adam Mickiewicz University. Umultowska 85, 61-606 Poznan, Poland
[2]Faculty of Chemistry, Adam Mickiewicz University. Grunwaldzka 6, 60-780 Poznan, Poland
[3]Institute of Materials Technology, Poznan University of Technology. Piotrowo 3, 61-138 Poznan, Poland
*Email address: abraszak@amu.edu.pl

The solid-state ^{1}H NMR on-resonance and off-resonance techniques have been performed to study molecular dynamics and domain size in heterogenous nanocomposites based on poly(butylene terephthalate) and nanoparticles C_{60} modyfied by *n*-decylamine (DA). The spin–lattice off-resonance relaxation times in the rotating frame $T_{1\rho}^{off}$ as well as the second moment M_2 of absorption line were analysed as a function of temperature. To determine the size of heterogeneities and characterize the morphology of the nanocomposites, the ^{1}H NMR spin-diffusion experiments designed by Goldman-Shen were performed[1,2,3,4]. The results from the measurements give us new insight into the spin-diffusion phenomenon and relaxation behavior of these new polymeric materials[5].

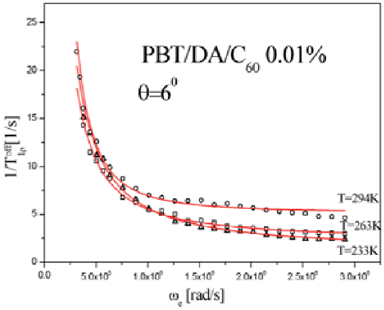


Fig.1. The relaxation rate $1/T_{1\rho}^{off}$ of PBT/decylamine/C_{60} 0,01% and as a function of effective frequency ω_e, with $\Theta=6^0$ which is the angle between the off resonance filed and the effective field[6] at 233K, 263K and 294K, respectively.

Acknowlegements
Financial support under the grant N 507 0806 33 Polish Ministry of Sciences and Education.

References

[1] M. Goldman, L. Shen, Phys. Rev. 144, 321 (1965).
[2] F. Melinger, M. Wilhelm, H. Spiess, Macromolecules 32, 4686 (1999).
[3] A. M. Kenwright, B. J. Say, Solid State NMR 7, 85 (1996).
[4] F. Mellinger, M. Wilhelm, K. Landfester, H. W. Spiess, A. Haunschild, J. Packusch, Acta Polym., 49, 108 (1998).
[5] A. Woźniak-Braszak, J. Jurga K. Jurga, B. Brycki, K. Hołderna-Natkaniec, J. Non - Cryst. Solids, (2010) in print.
[6] K. Jurga, Z. Fojud, A. Woźniak-Braszak, Solid State NMR 25, 119 (2004).

The influence of concentration of TCNEO/C_{60} adduct on the molecular dynamics and domain size in PBT/TCNEO/C_{60}

A. Woźniak-Braszak[1*], W. Grzesiak[2], B. Brycki[2], K. Jurga[1], J. Jurga[3],
K. Hołderna-Natkaniec[1]
[1]Faculty of Physics, Adam Mickiewicz University. Umultowska 85, 61-606 Poznan, Poland
[2]Faculty of Chemistry, Adam Mickiewicz University. Grunwaldzka 6, 60-780 Poznan, Poland
[3]Institute of Materials Technology, Poznan University of Technology. Piotrowo 3, 61-138 Poznan, Poland
*Email address: abraszak@amu.edu.pl

Molecular dynamics and domain size in poly(butylene terephthalate)/TCNEO/C_{60} nanocomposites has been studied by ^1H solid-state NMR method as a function of concentration of TCNEO/C_{60} adduct. It is suggested that modification of PBT with fullerene C_{60} would give new attractive nanocomposite material both with improved chemical and physical properties[1,2]. The molecular dynamics of the nanocomposites has been studied using solid-state pulse NMR spin-lattice relaxation and continuous wave methods. The basis of off-resonance NMR technique[3] is to measure the spin-lattice relaxation time $T_{1\rho}^{off}$ in the presence of an off-resonance rf field. The obtained rates of relaxation times as a function of angular frequency are fitted into equation $\frac{1}{T_{1\rho}^{off}} = \frac{K}{4}\sin^2\theta J(\omega_e,\tau_c,\beta) + \frac{1}{T_1}$, using the following density function given by Davidson and Cole: $J(\omega_e,\tau_c,\beta) = \frac{2\alpha}{\omega_e}\left[\frac{\sin(\beta\arctan(\omega_e\tau_c))}{(1+\omega_e^2\tau_c^2)^{\frac{\beta}{2}}}\right]$, where $K = 64\cdot10^{-50}\ m^6/s^2$ for protons, ω_e is the effective frequency, τ_c is upper cut-off correlation time, β is the width of the distribution of correlation times and T_1 is the spin-lattice relaxation time in the laboratory frame. The correlation cut-off times were found in different temperatures, below and above the glass transition temperature, respectively. The ^1H NMR spin-diffusion experiments designed by Goldman-Shen[4] were performed in order to estimate domain size of nanocomposite[5]. The results demonstrate that the molecular dynamics and domain size of PBT/TCNEO/C_{60} nanocomposites depends on the concentration of TCNEO/C_{60} adduct.

Acknowlegements
Financial support under the grant N 507 0806 33 Polish Ministry of Sciences and Education.

References

[1] A. K. Kalkar, H.W. Siesler, F. Pfeifer, S.A. Wadekar, Polymer 44, 7251 (2003).
[2] A. Woźniak-Braszak, J. Jurga K. Jurga, B. Brycki, K. Hołderna-Natkaniec, J. Non - Cryst. Solids, (2010) in print.
[3] K. Jurga, Z. Fojud, A. Woźniak-Braszak, Solid State NMR 25, 119 (2004).
[4] M. Goldman, L. Shen, Phys. Rev. 144, 321 (1965).
[5] F. Mellinger, M. Wilhelm, K. Landfester, H. W. Spiess, A. Haunschild, J. Packusch, Acta Polym., 49, 108 (1998).

Electric Characterization of poly(lactide)/MWCNT nanocomposites

A. Bello[1], M. Grimau[2], E. Laredo[1], D. Wu[3]
[1]Departamento de Física, [2] Departamento de Ciencia de los Materiales,
Universidad Simón Bolívar, Caracas, Venezuela
[3]School of Chemistry and Chemical Engineering, Yangzhou University, China
Email address: abello@usb.ve

Nanocomposites based on polylactide, an amorphous polymer, with MWCNT as a nanofiller with concentration, *p*, ranging from 0 to 7 % in weight, were studied by Dielectric Spectroscopy ($10^{-3} \leq f \leq 3x10^{6}$ Hz) in a wide temperature range. Figure 1 shows the variation of the imaginary part of the dielectric constant at 70 ºC as the CNT concentration, *p*, increases. For the pure sample, in the frequency window swept here, the segmental relaxation, α_S, is observed together with the normal mode at lower frequencies, α_N, associated to the dipolar moment parallel to the backbone. The molecular dynamics analyzed for the 0 and 2% MWCNT concentrations do not show any significant changes in the relaxation map in the presence of CNT. The data taken in the complex conductivity domain allowed the determination of the percolation parameters, scaling law, percolation threshold, critical exponents and tunneling conduction between conductive clusters.[1] The evidence provided by these results, indicates a non-universal behavior in this material, as the value obtained for t, the exponent of the scaling percolation equation above the concentration percolation threshold, p_c, is larger[2] than the expected universal value $t_u = 2$. Also, tunneling is not contributing to the conductivity of the nanocomposites with the highest CNT concentration. Finally, the master curve drawn in Figure 2 shows time-concentration superposition at room temperature; time-temperature superposition in the whole temperature range (-140 to 105 ºC) is not valid for these nanocomposites even at $T<T_g$. At T >70ºC the time superposition is discarded as the sample crystallizes during the dielectric measurements.

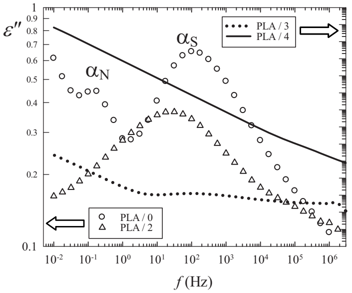


Fig.1. Dielectric losses of nanocomposites PLA / *p* MWCNT at 70 ºC; *p* = 0% and 2% (left axis); *p* = 3 and 4% (right axis).

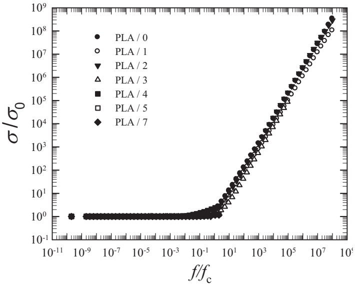


Fig. 2: Master curve showing time-concentration superposition at room temperature in the PLA/MWCNT composites

References

[1] E. Laredo, M. Grimau, A. Bello, D. Wu, Y. Zhang and D. Lin (submitted to Biomacromolecules).
[2] A. Linares, J.C. Canalda, M.E. Cagiao, M.C. García-Gutierrez, A. Nogales, I. Martín-Gullón, J. Vera, T. A. Ezquerra, Macromolecules, 41, 7090 (2008).

Dielectric dispersion and conductivity analysis in piezoelectric composite materials

H. Hammami[1, 2 *], **A. kallel**[1]
[1]Laboratoire des Matériaux Composites, Céramiques et Polymères, Faculté des Sciences de Sfax, 3018 Sfax,
Tunisie
[2]Laboratoire d'Optimisation de la Conception et d'Ingénierie de l'Environnement, (LOCIE-ESIGEC)-Université de Savoie, 73376 Le Bourget du Lac,
France
*Email address: helmi.hammami@fss.rnu.tn

A series of 1-3 connectivity PZT fibres/epoxy resin composites with different volume fraction is studied by means of dielectric spectroscopy in the wide frequency range 0.1 Hz-100 kHz and temperature varying from the ambient to 210 °C. Ac conductivity data are analysed using the "universal power law" and its scaling is studied by the Jonscher's universal power law. At low frequencies ac conductivity tends to be constant, while in the high frequency region verifies the exponential law of conductivity. In the intermediate frequencies, the examined systems exhibit strong dispersion with frequency and the produced fitting curves deviate from the experimental data by not being able to describe the recorded relaxation and pointing out that in the vicinity of the relaxation peaks the power law is not applicable. Finally, dipolar relaxation mechanisms and interfacial or Maxwell-Wagner-Sillars relaxation were revealed in the frequency range and temperature interval of the measurements. These relaxation mechanisms were analysed using the electric modulus formalism.

Dielectric study on polyaniline/polymethylmetacrylathe composite films near the percolation threshold

Z. Ben Othmen[1], **A. Fattoum**[2], **M. Arous** [1*]
[1] Laboratoire des Matériaux Composites Céramiques et Polymères, Faculté des Sciences de Sfax, 3000 Sfax Tunisia
[2] Institut Supérieur des Sciences Appliqués et de Technologie, Route de Mednine, Gabès Tunisia
*Email address: Mourad.Arous@fss.rnu.tn

Free standing and plasticized composite films of polyaniline/polymethylmetacrylathe (Pani/PMMA) were made by using co-dissolution and casting method. The polyaniline weight percentage is taken near the percolation threshold (<5%). The glass transition temperature (Tg) of the PMMA matrix is influenced by the presence of polyaniline. Dielectric measurements as a function of temperature and frequency revealed the presence of relaxation processes attributed to α and β relaxations of PMMA matrix. The ac conductivity in the high frequency side is well described by a frequency power law; the variation of the exponent s with temperature is compatible with a polaronic charge transport in the composite due to conducting polyaniline inclusion. The UV-Vis absorption spectra revealed the presence of absorption bands characteristic of polyaniline.

Influence of preparation procedure on the conductivity and transparency of SWCNT-polymer nanocomposites

J.J. Hernández[1], M.C. García-Gutiérrez[1], A. Nogales[1], D.R. Rueda[1],
M. Kwiatkowska[2], Z. Roslaniec[2], A. Szymczyk[2], T.A. Ezquerra[1]
[1]Instituto de Estructura de la Materia. Serrano 121, 28006 Madrid, Spain
[2]Szczecin University of Technology, Institute of Materials Science and Engineering.
Piastow Av. 19, 70-310 Szczecin, Poland.
*Email address: emdaniel@iem.cfmac.csic.es

Single-wall carbon nanotubes (SWCNT) have attracted much attention since their discovery. Their exceptional mechanical, electrical, thermal properties and high aspect ratio make them excellent candidates as fillers in multifunctional nanocomposites.
Because of van der Waals attraction among nanotubes and their large surface areas, SWCNT tend to form agglomerates which prevent from an efficient transfer of their superior properties to the nanocomposite. Therefore, the nanotube dispersion in the polymer matrix is a big concern. As reported by some authors [1] the existence of fractal morphology of branched agglomerates of SWCNT has significant negative impact on the mechanical properties of the nanocomposite material. However, as far as the electrical properties are concerned, the impact of aggregation on the mechanisms of percolation, the so called static and kinetic percolation and on the electrical conductivity are still under investigation [2]. It has been reported that the onset of the conductivity in CNT nanocomposites is closely related to the aggregation level of the conducting nanotubes [3]. Agglomeration of nanotubes, rather than a simple random arrangement of isolated elements, appears to improve the efficiency of the conducting network [4].

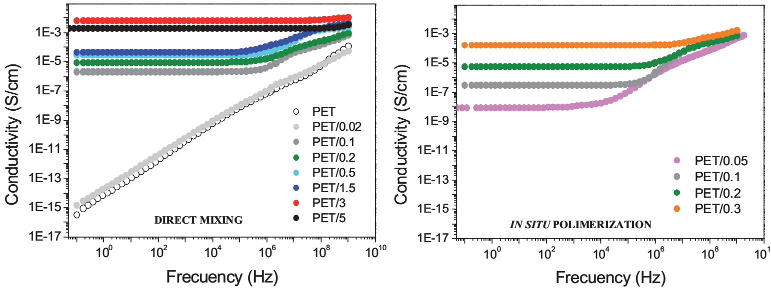


Fig.1. Conductivity as a function of frecuency for PET/SWCNT nanocomposites prepared by direct mixing and *in situ* polimerization.

References

[1] J.N. Coleman, U. Khan, Y.K. Gunko. Adv. Mater. 18, 689–706 (2006).
[2] W. Bauhofer, J.Z. Kovacs. Compos. Sci. Technol. (2009)
[3] J.K.W. J.E. Sandler Kirk, I.A. Kinloch, M.S.P. Shaffer, A.H. Windle. Polymer, 44. 5893–9 (2003).
[4] F.H. Gojny, M.H.G. Wichmann, B. Fiedler, I.A. Kinloch, W. Bauhofer, A.H. Windle, Polymer, 47. 2036–45 (2006)

Polyimide nanocomposite thin films based on a nitrile-containing polyimide and $BaTiO_3$

Lidia Okrasa[1*], **Elena Hamciuc**[2], **Corneliu Hamciuc**[2], **Irina Bacosca**[2]
[1]Department of Molecular Physics, Technical University of Lodz, Zeromskiego 116,
90-924 Lodz, Poland
[2]"Petru Poni" Institute of Macromolecular Chemistry, Aleea Gr. Ghica Voda 41A,
Iasi-700487, Romania
*Email address: lidia.okrasa@p.lodz.pl

Polyimide nanocomposite thin films were prepared by casting solutions resulting from direct mixing of a poly(amic acid) containing nitrile groups and surface modified $BaTiO_3$ nanoparticles onto glass plates, followed by thermal imidization under controlled temperature conditions. The surface of $BaTiO_3$ nanoparticles was modified by treating with 3-aminopropyltriethoxysilane coupling agent. Three samples with different content of $BaTiO_3$ nanoparticles were compared with the pure polymer sample. The nanocomposite films were investigated by atomic force microscopy, scanning electron microscopy, thermogravimetric analysis, dynamic mechanical analysis and dielectric spectroscopy. The relation between structure and properties has been investigated.

Dielectric spectroscopy measurements were done two times. At low temperature range during first scan there is seen relaxation correlated the most probably with the phenyl ring motions strongly influenced by moisture absorption content. Such relaxation is observed in all polyimide samples, which are not completely dry. This relaxation disappears in second scan because of removing even trace amount of water. What is interesting, this relaxation appears again after even short contact with air, which is not completely dry. At higher temperature range there are few relaxation phenomena, which strongly depend on content and on temperature treatment of sample.

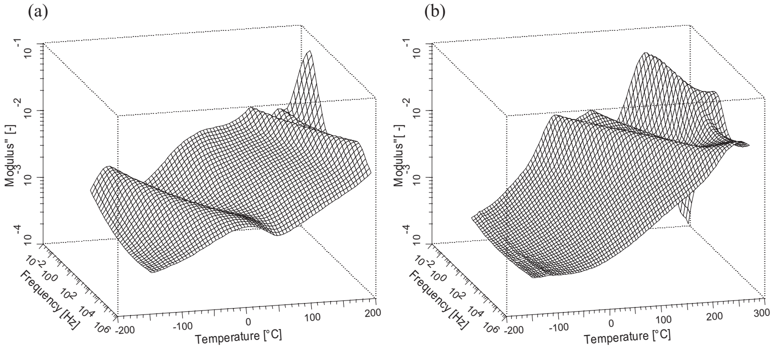


Fig.1. Frequency and temperature dependence of the imaginary electric modulus for the polyimide nanocomposite with 20% of $BaTiO_3$: (a) first scan, (b) second scan (after heating up to 200°C without opening of the measurement cell).

Acknowledgements: This work was supported by CNCSIS – UEFISCSU, project number PNII – IDEI code ID_997/2008. The dielectric investigations were financed by Department of Molecular Physics of Technical University of Lodz (Poland).

Polymer nanocomposite films based on silica and a polyimide-polydimethylsiloxane copolymer

Lidia Okrasa[1*], **Corneliu Hamciuc**[2], **Elena Hamciuc**[2]
[1]Department of Molecular Physics, Technical University of Lodz, Zeromskiego 116,
90-924 Lodz, Poland
[2]"Petru Poni" Institute of Macromolecular Chemistry, Aleea Gr. Ghica Voda 41A,
Iasi-700487, Romania
*Email address: lidia.okrasa@p.lodz.pl

Silica-containing polymer nanocomposite films were prepared via sol-gel technique and thermal cyclodehydration using a poly(amic acid), precursor of a polyimide–polydimethylsiloxane copolymer, and tetraethoxysilane. The poly(amic acid) was obtained by polycondensation reaction of 4,4'-oxydiphthalic anhydride with a mixture of 1,3-bis(4-aminophenoxy)benzene and a bis(aminopropyl)oligodimethylsiloxane of controlled molecular weight, in different ratios, followed by end-capping with an aminosilane coupling agent - 3-aminopropyltriethoxysilane. The surface morphology of the films was investigated by scanning electron microscopy and atomic force microscopy. The free surface energy was evaluated based on contact angle measurements.

The nanocomposite films were flexible. They had good mechanical properties and high thermal stability. BDS and DMA methods were used to emphasize the influence of silica content in the polymer matrix. At lower temperature the polymer films exhibited there transitions: an α_1 relaxation due to the presence of polydimethylsiloxane segments and two secondary relaxation processes, γ and β, correlated with local movements. The temperature/frequency position and activation energy of the secondary relaxations depend on the silica contents in the sample. At higher temperature an α_2 transition correlated with the upper glass transition of the polyimide segments was observed. On increasing the concentration of silica a slightly decrease of dielectric constant and an increase of thermal stability were observed.

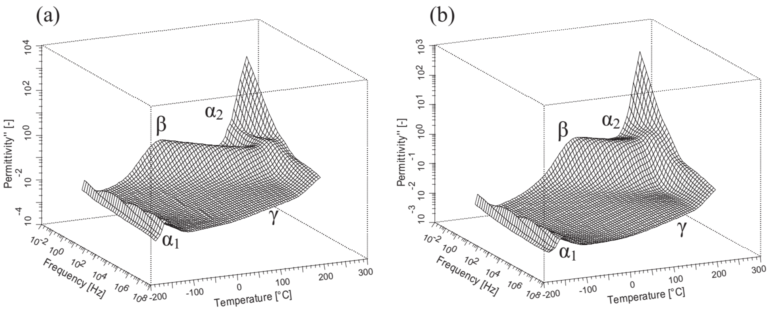


Fig.1. Frequency and temperature dependence of the permittivity for the pure polymer (a) and polymer nanocomposite with 20% of silica (b).

Acknowledgements: This work was supported by CNCSIS – UEFISCSU, project number PNII – IDEI code ID_997/2008. The dielectric investigations were financed by Department of Molecular Physics of Technical University of Lodz (Poland).

Dielectric analysis of natural nanocellulosic fibers filled polymer nanocomposites. Influence of surface treatments

M. Bouchhima[1], M. Arous [1*], S. Boufi[2], A. Kallel[1]
[1] Laboratoire des Matériaux Composites Céramiques et Polymères, Faculté des Sciences de Sfax, 3000 Sfax Tunisia
[2] Laboratoire Sciences des Matériaux et Environment, Faculté des Sciences de Sfax, 3000 Sfax, Tunisia
*Email address: Mourad.Arous@fss.rnu.tn

Dielectric analysis was performed on nanocellulosic fibers reinforced poly(acrylate-co-styrene of butyle) copolymer nanocomposites. Nanocellulosic fibers were incorporated into the matrix, with different volumic fraction, as such or after surface modification involving the silane coupling agents, namely γ-methacryloxypropyltrimethoxy (MPS). Dielectric parameters (permittivity, loss factor, tand and ionic conductivity) of pure copolymer and nanocomposites were obtained in a frequency range of 0.1 Hz–1MHz and temperature range of -100°C to 200°C. The dielectric properties of the composites showed a strong dependence on nanofiber content, testing frequency and temperature. In addition to the a relaxation associated to the glass transition of the pure copolymer and ionic relaxation caused by the mobility of dielectric charges, the presence of nanocellulosic fibers in the composite gives rise to other relaxation associated to MWS interfacial polarization. The MWS relaxation arises from the trapping of electric charges at the interfaces between the nanofibers and the copolymer. Percolation phenomenon was observed in the dielectric analysis, similar to the percolation in electrical conductivity studies.

Influence of orientation of molecules on photodielectric properties nematic of the liquid crystal with impurity fullerene and dyes.

V.E.Vovk*, A.V Koval'chuk.
Institute of Physics, National Academy of Science of Ukraine, 46, prospect Nauky, 03028 Kyiv, Ukraine
*Email address: vovk@iop.kiev.ua

In work[1] it has been shown, that for reception of the ordered photosensitive structures it is possible to use liquid crystals (LC). Thus measurements of photosensivity of such structures were carried out only at one orientation of molecules. Investigation of influence of orientation of molecules on photosensivity of structures on basis LC is the matter of big interest. It was a subject of researches of the given work.

With the help of processing by ultrasound and applications of solvents photosensitivity in a seen range of lengths of waves of a mixture nematic liquid crystal (E25M), molecules C60 (1 wt. %) and molecules LiTCNQ (3 and 4 wt. %) have been received. For better solubility C60 with chemically modified molecules of diamine (4-8 molecules of diamine to one molecule C60) were applied.

The research of such mixes were carried out by osciloscopic method[2] in the frequency range of 10^{-1}-10^{6} Hz and temperatures 293-350 in darkness and at illumination by the focused light of halogen lamps. Measurements were carried out with planar and homeotropic orientations of molecules. The effect of influence of light was determined from the analysis of the attitude relation of values of a component complex dielectric constant measured at illumination (ε'_p) up to those measured in darkness (ε'_d). It is shown, that the most distinct clearest maxima are observed on frequency dependence $\varepsilon'_p/\varepsilon'_d$. In the case of homeotropic orientations there are two such maxima - for frequencies of about 1 and 10^4 Hz. For planar orientation of molecules one maximum $\varepsilon'_p/\varepsilon'_d$ is observed only at frequency of 10^3 Hz. Prominent feature of frequency dependence $\varepsilon''_p/\varepsilon''_d$ is the sharp increase of photosensivity at the lowest frequencies only at planar orientation of molecules.

On the basis of the received data and the analysis of dielectric spectra mechanisms of observable effects are offered.

References

[1] E. Charlet, E. Grelet, P. Brettes, H. Bock, and H. Saadaoui Appl. Phys. Lett. 92, 024107 (2008)
[2] Twarowski A.J., Albrecht A.C. J. Chem. Phys.20,.2255 (1979)

Self-assembly and molecular dynamics of nanographenes

C. Grigoriadis[1*], N. Haase[2], G. Floudas[1], K. Müllen[2]
[1]University of Ioannina, Department of Physics, P.O. Box 1186, 451 10 Ioannina, Greece and Foundation for Research and Technology-Hellas (FORTH), Biomedical Research Institute (BRI)
[2] Max Planck Institute for Polymer Research, Mainz, Germany
*E-mail chgrigor@cc.uoi.gr

Discotic liquid crystals are materials where self-assembly is driven by non-covalent intermolecular interactions. The aromatic cores are responsible for the π-stacking whereas the presence of aliphatic chains ensures solubility, processability and a rich thermotropic behavior. During the self-organization process, the disk-shaped molecules organize into columns that further assemble into two-dimensional arrays whereas the alkyl chains fill the intercolumnar space. Highly ordered columnar structures of HBC were found to be very promising as active semiconductors in organic field-effect transistors and photovoltaic devices. The self assembly and molecular dynamics a series of dipole functionalized nanographenes were studied using differential scanning calorimetry (DSC), wide-angle x-ray scattering (WAXS), and dielectric spectroscopy (DS) as a function of temperature.[1-5] There is a phase transformation from the liquid crystalline (Lc) phase at high temperature to the crystilline phase (Cr) at lower temperature. The effect of dipole substitution is to destabilize the crystalline phase (Cr).[2] All compounds display a strong dipolar relaxation (α-process) reflecting in- and out- of plane disk motion with a strong temperature dependence that conforms to the Vogel-Fulcher Tammann (VFT) equation.[1] The inter- and intra-columnar thermal expansion was studied in a series of dipole functionalized hexa-*peri*-hexabenzocoronenes that undergo a transition form the high temperature liquid crystalline to a crystalline phase at lower temperatures.[4] Within the liquid crystalline phase the intra- and inter-columnar thermal expansions were different but both positive. Within the crystalline phase the inter-columnar thermal expansion is negative. Responsible for the negative thermal expansion is the increase of the tilt angle of the discotic cores with respect to the columnar axis. Similarities and differences with the thermal contraction in graphite and in graphenes are discussed.

References

[1] M.M. Elmahdy, G. Floudas, M. Mondeshki, H.W. Spiess, X. Dou, K. Müllen, Phys. Rev. Lett. 100, 107801 (2008).
[2] M.M. Elmahdy, X. Dou, M. Mondeshki, G. Floudas, H.-J. Butt, H.W. Spiess, K. Müllen J. Am. Chem. Soc. 130, 5311 (2008).
[3] M.M. Elmahdy, M. Mondeshki, X. Dou, H.-J. Butt, H.W. Spiess, K. Müllen, G. Floudas J. Chem. Phys. 42, 5709 (2009).
[4] C. Grigoriadis, N. Haase, H.-J. Butt, K. Muellen, G. Floudas Adv. Mater. in press, (2010).
[5] N. Tasios, C. Grigoriadis, M.R. Hansen, H. Wonneberger, C. Li, H.W. Spiess, K. Müllen and G. Floudas, J. Am. Chem. Soc. (submitted) (2010).

Dielectric and magnetic analysis of dispersed particles in composites of unknown microstructure

R. Pelster[*]**, B. Hallouet**
FR 7.2 Experimentalphysik, Universität des Saarlandes, D-66123 Saarbrücken, Germany
*Email address: rolf.pelster@mx.uni-saarland.de

In general, the details of the microstructure in nano-composites are unknown. Nevertheless there is a need to determine the intrinsic properties of the dispersed phase from the measured effective properties of the system. Due to the unknown microstructure a tentative analysis using simple mixture formulas can be highly erroneous. We present several methods to extract at least a partial (but exact!) information from dielectric spectra. These methods apply to composites containing conducting particles, that give rise to a polarization peak in the dielectric spectrum (MWS interfacial polarization):

(i) Using basic physical considerations, such as energy conservation, we show that measured spectra can be easily converted into strict lower bounds for the particles conductivity.
(ii) For isotropic composites, the spectra can be converted into lower and upper bounds for both the conductivity and the permittivity of the particles (using the spectral representation).
(iii) Combining dielectric and magnetic measurements, also the intrinsic magnetic permeability of particles can be evaluated.[1]

In order to illustrate and to test the procedures, we have prepared model-composites (semi-conductive Ga As particles in a epoxy resin) as well as magnetic nano-composites (nano-particles of magnetite in a polymer).

References

[1] B. Hallouet, B. Wetzel and R. Pelster , Journal of Nanomaterials, Vol. 2007, Article ID 34527, 11 pages, 2007. doi: 10.1155/2007/34527

BDS study of sols and films of silver nanoparticles capped alkyl carboxylate ligands

G.F. Novikov, P.V. Buzin, L.I. Kuzub, M.V. Gapanovich, L.M. Bogdanova, E.V. Raben

Institute of Problems of Chemical Physics, RAS.
Semenov's pr., 1, Chernogolovka, Moscow region, Russia, 142432
Email address: ngf@icp.ac.ru

In this work the results of BDS study (10^{-3}-10^{5} Hz) of sols of Ag nanoparticles (N capped by alkyl carboxylate ligands in toluene and thin films on ITO substrate obtained by evaporation of solvent are presented. Ag NPs have been synthesized by the low temperature duction of the Ag carboxylate (see fig.1) in the presence of triethyl amine which plays the r both the reducing agent and the reaction medium [1].

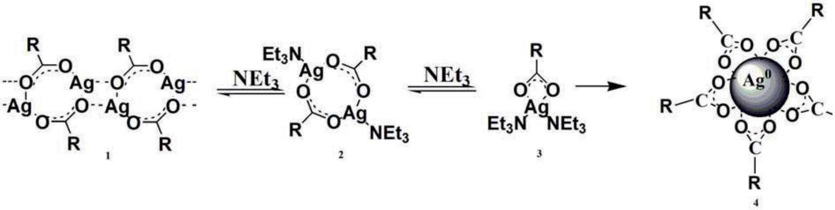


Fig.1. Scheme of the capped silver nanoparticles formation. $R=CH_3(CH_2)_{12}$, $NEt_3=N(C_2H_5)_3$

The frequency dependence of specific alternating current (*ac*) conductivity and comp electric modulus was used to estimate the temperature-frequency intervals of charge transfer long and short distances, respectively. With increasing the concentration of Ag NPs, specific conductivity increases. In low frequency region, the *ac* conductivity dependence transform into plateau, that corresponded to direct current conductivity (*dc*). In spite of the fact that, c ductivity depended on concentration of Ag NPs, the percolation threshold was unreachable ev for highest concentration 0.036 g/cm^3, and no conducting clusters or bridges are formed in th sols. Also electronic conductivity was not founded. The temperature dependence of specific conductivity show considerable deviation from Arrhenius dependence, that points to the sign cant contribution of cooperative effects in the charge carriers transport mechanism. The cons erable increase (more then 30°C) of Vogel temperature, T_0, and vitrification temperature, T_g, sols in comparison with pure solvent was found. It might be supposed that these cooperative fects reflect primary stage of superlattice formation. Although the dielectric characteristics sols generally controlled by the conductivity relaxation, the dielectric response was observed the high-frequency range (1-10^3 Hz) at low temperature (-50 - +10°C). This response was resu ing from the presence of NPs in the solution. It was supposed that the relaxation was caused motion of ion impurities on the Ag NPs surface within the carboxylate ligands shell. Dielect properties of films strongly depended both on characteristics of NPs and on preparation con tions of films. As in sols, the *dc* conductivity and dielectric response of Ag NPs in films was c to ion impurities.

The work was carried out under financial support of Russian Foundation of Basic Resear grant No. 08-03-12088_ofi.

---

[1] L.I.Kuzub, L.M.Bogdanova, T.S.Kurkin, V.I.Torbov, L.I.Gurieva, B.A.Rozenberg, P.V.Buzi // in book of papers "Structure and Dynamics of Molecular Systems" (in Russian), Vol.XVI, Is. 2, Ioshkar Ola-Moskva-Ufa-Kazan, 2009, P.134.

Study of the Electrical Conductivity of Polyamide 66 and Carbon Nanofibers Composites by Dielectric Spectroscopy

J.C. Canalda[*], **A. Linares, M.E. Cagiao, T.A. Ezquerra**
Instituto de Estructura de la Materia (CSIC), C/ Serrano, 121 28006 Madrid (Spain)
[*]E-mail address: jccanalda@iem.cfmac.csic.es

Polymer composites based on high aspect ratio nanofillers such as carbon nanotubes (CNTs) and carbon nanofibers (CNFs) are receiving considerable attention because of their unique multifunctional properties at very low filler loading[1,2]. Among the several factors that affect the properties of polymer composites, including dispersion and distribution of the filler within the polymer matrix, the filler aspect ratio is a crucial factor especially for electrical properties. The electrical percolation threshold, which is the critical filler concentration that is required to initiate a conductive network within of the insulating matrix, is known to decrease with increase in the filler aspect ratio. In this work, we focus on the study of dielectric behaviour of composites based on polyamide 6,6 (PA66) and different contents of CNFs. Experiments were performed over films of about 1 mm thickness, obtained by compression molding, using a Novocontrol system integrating an ALPHA dielectric interface, in a frequency window of $10^{-2} < F/Hz < 10^{7}$, at room temperature. The electrical conductivity σ (F) as a function of frequency for samples with different volume concentration, is depicted in Fig. 1.

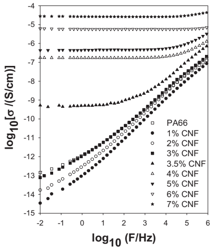


Fig. 1. Frequency dependence of σ (F) for PA66-CNF nanocomposites with different vol-% nanoadditive concentrations

As shown, for nanoadditive concentrations equal or below 3 vol-%, σ (F) follows a linear dependence with frequency with a slope close to 1, which is characteristic of insulating materials. For higher concentrations, σ (F) adopts a characteristic behavior that can be formally depicted by the so called universal dynamic response[3] described by a law of the type:

$$\sigma(F) = \sigma_{dc} + \sigma_{ac} = \sigma_{dc} + A \bullet F^{s}$$

This law introduces a critical frequency, F_c, above which $\sigma(F) = \sigma_{ac} \propto F^{s}$. From the fits of the equation, the σ_{dc} values can be extracted. For insulating samples, the conductivity at the lowest measured frequency (10^{-2} Hz) been considered as σ_{dc} for comparative purpose. From the analysis of the results, mechanism of charge transport in these systems will be discussed.

References

[1] A. Nogales, G. Broza, Z. Roslainec, K. Schulte, I. Šics, B.S. Hsiao, A. Sanz, M.C. García-Gutiérrez, D.R. Rueda, C. Domingo and T.A. Ezquerra, Macromolecules 37, 7669 (2004)
[2] A. Linares, J. C. Canalda, M. E. Cagiao, M. C. García-Gutiérrez, A. Nogales, I. Martín-Gullón, J. Vera and T. A. Ezquerra, Macromolecules 41, 7090 (2008)
[3] A.K. Jonscher, Nature 267, 673 (1977)

Development of an experimental approach to detect phase transitions in dilute solution

B. Vanroy,[1,2] S. Napolitano,[2*] I Monnaie,[3] E Nies,[1] K. Robeyns,[1] B. Goderis[1]
and M. Wübbenhorst[2]

[1]KULeuven, Dept Chemistry, Celestijnenlaan 200F, 3001 Leuven, Belgium
[2]KULeuven, Dept Physics and Astronomy,
Celestijnenlaan 200D, 3001 Leuven, Belgium
[3]Eindhoven University of Technology, Laboratory of Materials and Interface
Chemistry. Den Dolech 2, 5612 AZ Eindhoven, The Netherlands

*Email address: simone.napolitano@fys.kuleuven.be

The goal of this research is to determine the melting point of [6,6]-phenyl-C_{61}-butyric acid methyl ester, PCBM, in solution of 1,2-dichlorobenzene, ODCB. The melting point is a crucial parameter in the determination of the liquid-solid equilibrium conditions necessary to improve the morphology of PCBM, a molecule largely used in the active layer of polymer based organic solar cells.

To measure the properties of concentrations down to 10^{-2} w/w%, where many of the available experimental techniques fail due to a reduced signal to noise ratio, we developed a new experimental method that allowed us to investigate phase transitions of molecules in dilute solution.

The dielectric constant of the solutions was measured in a liquid parallel plate cell as function of temperature and frequency at different heating and cooling rates. Melting processes appeared as peaks in the temperature dependence of the dielectric constant, in the same range determined from Wide Angle X-ray Diffraction, WAXD. The results were used to construct the phase diagram of PCBM in ODCB.

Dielectric, NMR and FTIR studies of phosphorus Podand family systems

B. Orozbaev[1], Z. Fojud[1], M. Makrocka-Rydzyk[1], Aleksandra Wypych[1], G. Schroeder[2], S. Jurga[1]
[1] Faculty of Physics, A. Mickiewicz University, Poland
[2] Faculty of Chemistry, A. Mickiewicz University, Poland

In the last decade the world chemical industry is highly focused on the new technologies featuring cost cutting and carbon dioxide emission reduction, mainly by lowering thresholds of energy reaction. Many classes of natural as well as artificial substances can be used at different points of chemical reaction paths. One of such group are "supramolecular ligands" systems, which belong to supramolecular chemistry. Many unique properties like complexation, conformational minimising steric hindrance, chelating metal ions of different size and key-and-lock matching mechanism make them very attractive for modern chemistry and physics. The recognition of molecular motions in the systems studied can provide insight into their structure-property relationship.

In our work we focused on P-Podand family (Phosphorous Podands) compounds comprising different types of chains bounded to central phosphorous ion. Three types of P-Podand systems with following types of chains: alkyl ($P-[O-(CH_2)_{17}-CH_3]_3$), glycol ($P-[O-(CH_2CH_2O)_{15}-CH_3]_3$) and di-block glycol-alkyl ($P-[O-(CH_2CH_2O)_{10}-(CH_2)_{15}-CH_3]_3$)); were investigated by Differential Scanning Calorimetry (DSC), Nuclear Magnetic Resonance (NMR), Broadband Dielectric Spectroscopy (BDS) as well as Fourier Transform Infrared (FTIR) techniques [1].

The DSC studies show that the presence of alkyl groups causes stiffening of the system in comparison with P-Podand with glycol chains. Moreover, in P-Podand with glycol-alkyl chains, we observed two-stage crystallisation process interpreted as a result of independent crystallizations of the alkyl and glycol blocks. The glycol-alkyl P-Podand system shows self-assembling properties driven by amphiphilic interactions. The spectroscopic methods (NMR and BDS) permitted us to distinguish three types of motions: a) methyl groups rotation around the C_3 symmetry axis; b) segmental motions of the alkyl groups and/or glycol groups in the disordered phase (depending on the substance) and c) the overall motion (both rotational and translational). FTIR investigations allowed to associate existing relaxation processes with appropriate motions of chain's fragments.

References:

[1] Orozbaev B., Fojud Z., Makrocka-Rydzyk M., Schroeder G., Jurga S., "*Molecular dynamics of Podand studied by broadband dielectric and nuclear magnetic resonance spectroscopies*", Macromolecular Chemistry and Physics 208 (2007) 2121-2127

Author Index

IEM

INSTITUTO DE ESTRUCTURA
DE LA MATERIA

GOBIERNO
DE ESPAÑA

MINISTERIO
DE CIENCIA
E INNOVACIÓN

CSIC
Consejo Superior de Investigaciones Científicas

MODELICO
Modelización y Simulación de Sistemas Complejos (S2009ESP-1691),
Programa de Actividades I+D entre Grupos de Investigación de la Comunidad de Madrid 2010-2013

¡MADRID!
MADRID
CONVENTION
BUREAU

Con la colaboración de

La Suma de Todos
Comunidad de Madrid

MADRID
about you

SEDOPTICA
SOCIEDAD ESPAÑOLA DE ÓPTICA

novocontrol Technologies

solartron
analytical