http://BDS2008.univ-lyon1.fr

LYON, TUESDAY 26 TO FRIDAY 29 AUGUST 2008

BDS 2008

5TH INTERNATIONAL CONFERENCE ON "BROADBAND DIELECTRIC SPECTROSCOPY AND ITS APPLICATIONS"

ONLYLYON For WORK and RELAX !

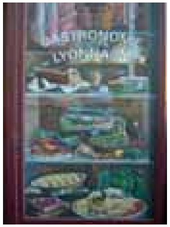
Since 1998, LYON
UNESCO World Heritage City

Organized by : IMP/LMPB, UMR CNRS 5223 - "Ingénierie des Matériaux Polymères"
Chairpersons : Gisèle BOITEUX, Gérard SEYTRE, Isabelle STEVENSON

PROGRAM

/// Welcome //////////////////////

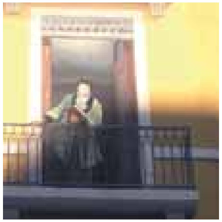
The chairpersons and the local organizing committee of (the 5th International Conference) BDS 2008 have the great pleasure to welcome you in Lyon. This joined conference of 5th IDS & 10th DRP conferences is « your conference » as you will be the main actors to present about 23 invited lectures, 52 oral contributions and 137 posters, the quality of which was notified by a very serious reviewing of more than 40 members of the International Advisory Board who are also thanks a lot !!
So, Science and Exhibition of State of Art Equipments will be the major purpose of BDS 2008 !!!



Please discover Lyon, UNESCO World Heritage City since 10 years: its 2000 years of history, from the hill of Fourvière and Old Lyon to the Presqu'île and the slopes of *La Croix-Rousse* and « French Capital of the Silk and of the Gastronomy » in second biggest academic and economic Rhône-Alpes Region.

Famous « Lyonnais » are Emperor Claude, Jean-Marie Ampère, Claude Bernard, Joseph Marie Jacquard, Hector Berlioz, Auguste and Louis Lumière and Antoine de St-Exupery, Jean-Michel Jarre, Paul Bocuse, Merieux family... and some players of Olympic Lyonnais Football team...

To the success of BDS 2008 all together in Lyon with Ampère !!!!!!!!



/// History of BDS Conferences /////

The DRP conferences 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. The successful development of the Broadband Dielectric Spectroscopy and the Time Domain Dielectric Spectroscopy inspired Yuri Feldman, John Barberian and Friedrich Kremer to organise the IDS conferences: the first one was held in 2001 in Jerusalem. Three last conferences of these series were organised together: 2nd IDS & 7th DRP in 2002 in Leipzig by Friedrich Kremer and 3rd IDS & 8th DRP in 2004 in Delft by Michael Wübbenhorst under the name BDS and 4rd IDS & 9th DRP in 2006 in Poznan by Bozena Hilczer & Jacek Ulanski.

/// Presentation of BDS Lyon Host /

« *Ingénierie des Matériaux Polymères* » composed of three laboratories (LMPB-UCBL, LMM-INSA and LRMP-University St Etienne) is affiliated to CNRS and joins about 175 persons (75 staff members, 80 PhDs, and 20 post-docs). The IMP research group activities offer a unique combination of expertise in the whole chain of knowledge for designing polymer-based materials, i.e. from polymer chemistry to physical properties of polymers (surface-interfaces, permeability, rheological, mechanical, optical and **electrical** properties, biomedical engineering) including processing methods. The final goal is to establish relationships between microstructure, morphology, and properties of polymer-based materials:
Research at IMP thrives on multi-disciplinary partnerships set up with the business world.
IMP is involved in many European projects especially as vice-coordinator of the FP6 Network of Excellence « Nanostructured and Multifunctional Polymer-Based Materials and Nanocomposites » NANOFUN POLY (2004-2008) which leds to the creation of the European Center for Nanostructured Polymers, « ECNP ».

/// Committees ///////////////////

CONFERENCE CHAIRS

Chairwoman: Gisèle Boiteux
Co-Chairs: Gérard Seytre, Isabelle Stevenson

LOCAL ORGANIZING COMMITTEE

IMP/LMPB: Andrzej Rybak, Joël Davenas, Flavien Melis,
Olivier Gain, Jean-Michel Lucas, Sylvie Novat, Nadia Yacoub,

WITH THE TEAM OF PHD STUDENTS

Erisela Nikaj, Ahmed Meskini, Lyubov Bardash,
Maksym Iurchenko, Volodymyr Levchenko.

INTERNATIONAL ADVISORY BOARD

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K. Weron (Poland)
G. Williams (UK)
M. Wübbenhorst (Belgium)
S. Yagihara (Japan)

Exhibitors in the conference

Compagnies: Novocontrol Technologies and SETARAM Instrumentation

PLACE OF CONFERENCE

Université Lumière Lyon 2, Berges du Rhône Campus
18, Quai Claude Bernard - 69007 LYON

Conferences are in ***Grand Amphitheatre*** and ***Laprade Amphitheatre***.

CONTACT

bds2008@univ-lyon1.fr *(even during the conference)*

Emergency contact
T. 06 22 63 81 39 / T. 00 33 6 22 63 81 39

Emergency phone numbers
Police 17 – Hospital 15 – Fire 18

ORGANIZATION

Université Claude Bernard Lyon 1 - UMR CNRS 5223
IMP/LMPB - « Ingénierie des Matériaux Polymères / Laboratoire des Matériaux Polymères et des Biomatériaux ».
ISTIL building
43, Bd du 11 Novembre 1918
69622 Villeurbanne Cedex France

PUBLIC TRANSPORTS

(a 4 days free pass is included for all participants)
Tramway, nearest station: ***Quai Claude Bernard***, line **T1**
Bus, nearest station: ***rue de l'Université***, **line 53**
Subway, nearest station: ***Jean Macé***, **line B**
Taxis (English speaking) 04 78 28 23 23 / 00 334 78 28 23 23
You will find a map of Lyon with tramway and subway in your satchel.

ATM (Cash machine)
ask ***rue de Marseille***, 250m from BDS

Internet access
WI-FI and internet room for free (PC and Mac).

Tourism Office
Place Bellecour, **subway lines A and D**
T. 04 72 77 69 69
www.lyon-france.com
www.rhone-alpes-passions.com

/// Social events ///

All Inclusive for all participants and their registered accompanying guests

Monday, August 25 at 6 pm

Welcome reception – University Lyon 2, Atrium
Registration will start at 4.30 pm

Tuesday, August 26 at 7:30 pm

Evening reception at « *Grand Lyon* »
20, Rue du Lac – Lyon

Do not forget your badge
and map of Lyon

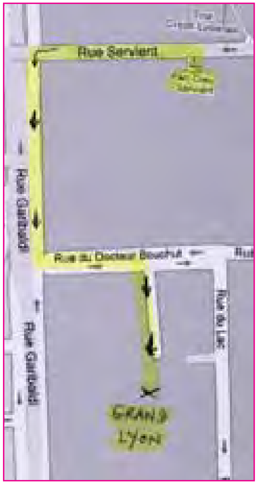
Way

From BDS, go to station
Quai Claude Bernard
(a few meters left from BDS exit)
and take the **T1 tramway**
(direction IUT Feyssine)

STOP at station
« Part-Dieu Servient »,

Walk back (100m) to
Rue Garibaldi, go down this street (100m) and turn left at
Rue Docteur Bouchut

Then turn right on the pedestrian way to Grand Lyon building



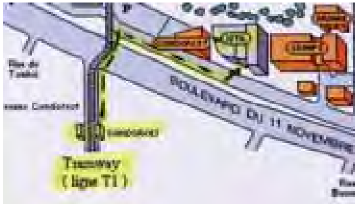
Wednesday, August 27 at 5:45 pm

Commented cruise on ***Hermès Boat*** on *Rhône* and *Saône* Rivers
*Boat starts from river side **Quai Claude Bernard** in front of University Lyon 2 and will go to:*
*« **Abbaye de Collonges** » **Paul Bocuse***
Quai de la Jonchère
69660 Collonges au Mont D'Or
www.bocuse.fr
Conference dinner start at 7:45 pm
***** All participants MUST bring their invitation card *****
If you miss the boat, only taxi can drive you to this place.

Thursday, August 28 at 6 pm

Concert by BDS scientists in **University Claude Bernard Lyon 1**
And « Wine and Cheese » Party at 7:45 pm

*Go to station **Quai Claude Bernard** (a few meters left from BDS exit) and take the **T1 tramway** (direction IUT Feyssine), the same than for « **Grand Lyon »** reception.*
*Tramway will stop at 13 stations before arriving at **Condorcet** station. From this station, walk 100m along the tramway rail, turn right when you enter in the campus, after crossing **Boulevard du 11 Novembre 1918** and go to **ISTIL building**.*



Tuesday 26th August

8:30-9:00 **OPENING**

Molecular dynamics

Chairman: **BERBERIAN JOHN**

9:00-9:30	**Ngai Kia**, Capaccioli S., Shahin Thayyil M.	*Recent progress in understanding relaxation of complex interacting systems*
9:30-9:50	Kalmykov Yuri, Coffey William, Titov Serguey	*Inertial effects in anomalous dielectric relaxation*
9:50-10:10	Capaccioli Simone, Kessairi Khadra, Lucchesi Mauro, Prevosto Daniele, Shahin Thayyil M., Rolla Pierangelo	*Mutual Dependence of Primary and Johari-Goldstein Secondary Relaxations in Glass-Forming Systems*
10:10-10:40	**Alegria Angel**	*The Adam-Gibbs approach and the dielectric alpha-relaxation of polymer systems*

10:40-11:10 **Coffee break**

Chairman: **WÜBBENHORST MICHAEL**

11:10-11:30	Cangialosi Daniele, Alegria Angel, Colmenero Juan	*Dielectric relaxation and cooperative dynamics in non-polymeric glass-formers*
11:30-11:50	Köhler Melanie, Goncharov Yurii, Wehn Robert, Lunkenheimer Peter, Loidl Alois	*Relaxation dynamics of glass-forming propylene glycol oligomers*
11:50-12:10	Schwartz Gustavo, Paluch Marian, Alegria Angel, Colmenero Juan	*High Pressure Segmental Dynamics in Polymer/Plasticizer Binary Mixtures*
12:10-12:40	**Fothergill John**	*Making sense of the low-frequency dielectric spectrum*

12:40-14:20 **Lunch**

Chairman: **SERGHEI ANATOLI**

14:20-14:50	**Feldman Yuri**, Puzenko Alexander, Ben Ishai Paul	*Phenomenological manifestation of strange kinetics in dielectric response*
14:50-15:10	Dionisio Madalena, Viciosa Plaza María Teresa, Gómez Ribelles José Luis, Brás Ana Rita	*Molecular dynamics of n-ethylene glycol dimethacrylate followed by dielectric relaxation spectroscopy*
15:10-15:30	Nozaki Ryusuke	*Elementary process of the α relaxation of polyhydric alcohols: dielectric study from 10mHz to 2.5THz*
15:30-15:50	Böhmer Roland, El Goresy Tarek, Gainaru Catalin	*Dielectric studies of hydrogen bonds in pure and diluted monohydroxy alcohols*
15:50-16:10	Kahouli A., Sylvestre Alain, Sylvestre Alain, Jomni F., Yangui B., Robert J.-C., Berge B., Legrand J.	*Dielectric relaxation of Parylene C.*

16:10-16:30 **Coffee break**

Chairman: **SAITER JEAN-MARC**

16:30-17:00	**Nigmatullin Raoul**	*Detection of collective motions in dielectric spectra and the meaning of the generalized Vogel-Fulcher-Tamman equation*
17:00-17:20	Eker Sitki, Bozdemir Süleyman, Özdemir Metin	*A new simulation model for dielectric relaxation based on defect diffusion model and waiting time problems*
17:20-17:40	Fontanella John, Bendler J., Shlesinger M., Wintersgill M.	*Confinement, the Ratio EV*/H*, and the Defect Diffusion Model*
17:40-18:00	Matsumiya Yumi, Watanabe Hiroshi, Van Ruymbeke Evelyne, Vlassopoulos Dimitris, Hadjichristidis Nikos	*Viscoelastic and Dielectric Relaxation of a Cayley-Tree Type Polyisoprene: Test of Molecular Picture of Dynamic Tube Dilation*
18:00-18:20	Ben Ishai Paul, Feldman Yuri	*Structural Insights from the Cole-Cole Function*

19:30 **Evening Reception at « Grand Lyon »**

▨ *Invited lectures*

/// Wednesday 27th August

Heterogeneous and nanoconfined systems

Chairman: **KREMER FRIEDRICH**

8:30-9:00	**Wübbenhorst Michael**, Rotella Cinzia, Capponi Simona, Napolitano Simone	*Dielectric spectroscopy on ultrathin polymer films: new approaches and new insights*
9:00-9:20	Beiner Mario	*Crystallization behavior of acetaminophen in the bulk and under confinement*
9:20-9:40	Napolitano Simone, Wübbenhorst Michael	*Quantifying the deviations from bulk behaviour in ultrathin polymer films*
9:40-10:10	**Fukao Koji**	*Glassy dynamics in thin polymer films: Memory and rejuvenation effects of dielectric susceptibility and volume*

10:10-10:30 **Coffee break**

Chairman: **DIAZ-CALLEJA RICARDO**

10:30-11:00	**Torkelson John**, D. Priestley Rodney, Rittigstein Perla, Fukao Koji, J. Ellison Christopher, Kim Jungki, M. Mok Michelle, Dhinojwala Ali, Kim Soyoung	*Distributions of Tgs, Physical Aging Behavior, and Chain Dynamics in Nanohetereogeneous Polymers: Nanoconfined Films, Polymer Nanocomposites, and Gradient Copolymers*
11:00-11:20	Couderc Hugues, Saiter Allisson, Grenet Jean, Boiteux Gisèle, De Souza N., Saiter Jean-Marc	*Relaxation Study of PETg/Montmorillonite nanocomposites by dielectric spectroscopy*
11:20-11:40	Hallouet Béatrice, Desclaux Pauline, Wetzel Bernd, Pelster Rolf	*Analysing dielectric interphases and particle properties in polymer-based nano- and micro-composites*
11:40:12:00	Oleinik Eduard, Chmutin Igor, Ryvkina Natalia, Tatarenko Tatiana, Rudnev Sergei, Salamatina Olga, Kotelianskyi Mikhail	*Structural Dynamic and Thermodynamic Changes in Properties of Polymer Glasses Subjected to Plastic Deformation*

12.00-14.00 **Poster session**

Lunch

Chairman: **WILLIAMS GRAHAM**

14:00-14:30	**Runt James**, Fragiadakis Daniel, Atorngitjawat Pornpen, Masser Kevin	*Broadband Dielectric Spectroscopy of Multicomponent Polymer Systems: Crystalline and Associating Materials*
14:30-14:50	Makrocka-Rydzyk Monika, Jenczyk Jacek, Wypych Aleksandra, Glowinkowski Stanislaw, Kozak Maciej, Radosz Maciej, Jurga Stefan	*The phase structure and molecular dynamics in poly(styrene-b-isoprene) diblock copolymer*
14:50-15:10	Inoue Tadashi, Iwashige Tomohito, Watanabe Hiroshi	*Dielectric Relaxation of Polymer/Carbon Dioxide Systems*
15:10-15:30	Diaz-Calleja Ricardo, Sanchis Maria J., Dominguez-Espinosa Gustavo, Saez-Torres Patricia, Guzman Julio, Riande Evaristo	*Influence of the Structural Characteristics on the Broadband Dielectric Spectroscopy of naphtyl substituted acrylate Polymers*
15:30-15:50	Fillot Louise-Anne, Sotta Paul, Neyret-Duperray Hughes, Long D. Fort Alexandre, Royston Gareth, Rossi S., Tupinier D.	*Broadband dielectric spectroscopy characterization of the relaxations of polyamides plastified [or not] by solvents.*
15:50-16:10	Lund Reidar, Alegria Angel, Colmenero Juan, Willner Lutz, Richter Dieter	*Resolving Interfacial Fluctuations and its Effect on the Segmental Dynamics in Nano-segregated Block Copolymer Melts*
16:10-16:30	Wurm Andreas, Minakov Alexander A, Schick Christoph	*Simultaneous dielectric, calorimetric and saxs/waxs experiments during polymer crystallization*
16:30-17:00	**Serghei Anatoli**, Kremer F.	*Molecular dynamics of confined polymers: recent developments and challenges*

17:45 **Hermès boat excursion**

19:45 **Conference Dinner by « Abbaye de Collonges » Paul Bocuse**

POSTERS

Molecular dynamics

P1	hal-00262410	*Structural Insights from the Cole-Cole Function* Ben Ishai Paul, Feldman Yuri
P2	hal-00264142	*Dynamics of an ionic liquid supercooled with pressure* Rivera-Calzada Alberto, Kaminski Kamil, Leon Carlos, Paluch Marian
P3	hal-00264148	*Revisiting the molecular weight effects on dielectric relaxations of linear cis-polyisoprene1-4* Riedel Clement, Alegria Angel, Tordjeman Philippe, Colmenero Juan
P4	hal-00264250	*Conductivity and glass transition dynamics in imidazolium ionic liquids* Leys Jan, Preethy Menon Chirukandath, Rajesh Ravindran, Thoen Jan, Glorieux Christ, Nockemann Peter, Thijs Ben, Binnemans Koen, Longuemart Stéphane
P5	hal-00264275	*Dynamical properties of trans-Poly(isoprene) and its copolymers with styrene* Cerveny Silvina, Zinck Philippe, Terrier Michael, Alegria Angel, Colmenero Juan
P6	hal-00264468	*Dielectric relaxation processes in liquid supercooled and glassy states of a pharmaceutical drug: Ibuprofen* Correia Natália, Brás Ana Rita, Dionisio Madalena, Schönhals Andreas, Affouard Frédéric
P7	hal-00265706	*Broadband dielectric study on fructose-water mixtures from liquid to glass as a function of concentration* Yamamoto Wataru, Waragai Yamato, Iwata Yukino, Kita Rio, Shinyashiki Naoki, Yagihara Shin
P8	hal-00287148	*Molecular dynamics of perfluoropolyethers with medium-low molecular weight* Okrasa Lidia, Karolczak Stefan
P9	hal-00287714	*The diverse effect of plasticizer in the molecular dynamics of organic dye-doped polymers observed at different lengthscales* Kalogeras Ioannis, Pallikari Fotini, Aglaia Vassilikou-Dova
P10	hal-00297326	*Johari-Goldstein Relaxation in Glass Forming Flexible Molecules* Thayyil Mohamed Shahin, Capaccioli Simone, Prevosto Daniele, Ngai Kia, Rolla Pierangelo
P11	hal-00268003	*Segmental Dynamics in Polysiloxane Blends* Royston Gareth, Sotta Paul, Long Didier
P12	hal-00267233	*Dielectric relaxation in freeze-dried disaccharides and the potential significance to the moisture buffering of freeze-dried products* Ermolina Irina
P13	hal-00264287	*Properties and nature of the secondary relaxations in ethylcyclohexane and related materials at low and high temperatures* Mandanici Andrea, Huang Wei, Cutroni Maria, Richert Ranko
P14	hal-00199066	*Relaxations theory* Abdelguerfi Mériem, Soualmia A.
P15	hal-00264334	*Terahertz Time-Domain Spectroscopy of Hydrogen-bonding Liquids: Primary and Secondary Alcohols* Ryusuke Nozaki, Yuki Sato, Satoshi Okada, Tomobumi Mishina, Jun'Ichiro Nakahara, Yoshiki Yomogida, Kazuyoshi Yamakawa

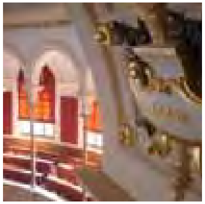
POSTERS

Heterogeneous and nanoconfined systems

P16	hal-00254742	*Dielectric properties of kaolinite intercalates - prospects of design of electromagnetic wave absorbers* Leluk Karol, Orzechowski Kazimierz, Slonka Tadeusz, Glowinski Jozef
P17	hal-00259452	*Experimental study on dielectric relaxation in Alfa fiber reinforced polyester composites* Ghallabi Zied, Rekik Houda, Arous Mourad, Boufi Sami, Kallel Ali
P18	hal-00262081	*Dielectric Studies of Tetraaryl and Triaryl Polycarbonates* Fontanella John, Bendler J., Wintersgill M., Boyles D., Filipova T.
P19	hal-00263597	*Relaxation processes in polymers filled with nanoparticles* Joel Lopez Ivan, Dolidze Vladimir, Aliev Fouad
P20	hal-00263659	*Broadband Dielectric Spectroscopy of poly (dimethoxybenzyl methacrylate)s* Diaz-Calleja Ricardo, Sanchis Maria J., Dominguez-Espinosa Gustavo, Alegria Luz, Gargallo Ligia, Radic D., Riande Evaristo
P21	hal-00264083	*Influence of low pressure on electrets behaviour at various air gaps* Viraneva Asya, Yovcheva Temenuzhka, Gencheva Elena, Mekishev Georgi
P22	hal-00264091	*Differential thermostimulated discharge current method for studying of electrets* Mekishev Georgi, Yovcheva Temenuzhka, Viraneva Asya, Gencheva Elena
P23	hal-00264254	*Dielectric relaxation in microemulsions with and without triblock copolymer* Wipf Robert, Stühn Bernd
P24	hal-00264265	*Dielectric relaxation of Polyethyleneoxide in porous alumina* Arrese-Igor Silvia, Alegria Angel, Colmenero Juan, Martín Pérez Jaime, Mijangos Carmen
P25	hal-00264295	*Rotational and translational diffusion of glass formic liquids in 2D confinement* Iacob Ciprian, Serghei Anatoli, Sangoro Joshua, Kärger Jörg, Kremer Friedrich
P26	hal-00264318	*Microwave dielectric properties and conductivity of aqueous solutions of polydiallylmethylammonium and diallylmethylammonium trifluoracetates* Lileev Alexsander, Lyashchenko A., Timofeeva L., Kleshcheva N.
P27	hal-00264320	*Influence of uniaxial stretching on dielectric response of miscible polymer blends* Lezak Emil, Alegria Angel, Colmenero Juan
P28	hal-00264331	*Investigation of interfacial polymer-clays properties through dielectric spectroscopy* Prevosto Daniele, Di Cuia Flavia, Lucchesi Mauro, Capaccioli Simone, Passaglia Elisa, Bertoldo Monica, Ciardelli Francesco, Rolla Pierangelo
P29	hal-00264350	*Peculiarities of high-temperature dielectric relaxation in vinylidene fluoride – hexafluoropropylene copolymers* Malyshkina Inna, Kochervinskii Valentin
P30	hal-00265875	*Real-time dielectric spectroscopy on ultra-thin layers of H-bondings liquids tuned by organic molecular beam deposition* Capponi Simona, Wubbenorst Michael, Rozanski S., Behrnd Norwid-Rasmus, Napolitano Simone, Couderc G., Hulliger Jürg
P31	hal-00266532	*Effects of SiO_2 Nanoparticles on Dielectric Properties and Thermal Stability of LDPE* Ciuprina Florin, Plesa Ilona, Panaitescu Denis, Zaharescu Traian, Radovici Constantin, Notingher Petru V.
P32	hal-00267418	*Dynamics of a nematic mixture confined to molecular sieves studied by broadband dielectric spectroscopy* Brás Ana Rita, Frunza Stefan, Guerreiro Liliana, Fonseca Isabel, Corma A., Frunza Ligia, Dionisio Madalena, Schönhals Andreas

POSTERS

P33	hal-00267440	*Molecular mobility studies in PCN/PUMA clay nanocomposites* Maroulas Panagiotis
P34	hal-00267476	*Dielectric spectroscopy on ultra-thin polymer films having free surfaces – a novel approach* Rotella Cinzia, Napolitano Simone, Wubbenhorst Michael, Caponi Simona
P35	hal-00267678	*Thermally stimulated currents in the electrospun poly(ethylene terephtalate) mats* Yovcheva Temenuzhka, Ignatova Milena, Viraneva Asya, Manolova Nevenka, Rashkov Iliya, Mekishev Georgi
P36	hal-00270297	*Dielectric relaxation studies in poly(ethylene oxide)/sodium montmorillonite nanocomposites* Wypych Aleksandra, Krzaczkowska Justyna, Strankowski Michal, Pietraszko Adam, Makrocka-Rydzyk Monika, Stefan Jurga
P37	hal-00271483	*Structure and Dielectric properties of hybrid Organic-Inorganic nanocomposites based on silsesquioxane* Fomenko A.O., Klepko V.V., Gomza Yu.P., Gumenna M.A., Shevchenko V.V.
P38	hal-00276727	*Study of confinement in semi-crystalline polymers* Nikaj Erisla, Stevenson Isabelle, Seytre Gérard, David Laurent, Boiteux Gisèle
P39	hal-00294731	*Glass transition of ultrathin supported polysulfone films studied by dielectric spectroscopy* Schönhals Andreas
P40	hal-00271493	*Microphase separation in polyurethane grafted onto styrene-styrene sulfonic acid copolymers* Jastrzebska Mariola, Dereszewska Alina, Rutkowska Maria
P41	hal-00266867	*Phase transformations in confined solid solutions* $NaNO_2$ – KNO_2 Naberezhnov Alexander, Fokin Alexander, Jagus P., Hansen Thomas, Koroleva Ekaterina, Korotkov Leonid, Rysiakiewicz-Pasek Ewa, Tovar Michael, Vakhrushev Sergey



POSTERS

Functional materials

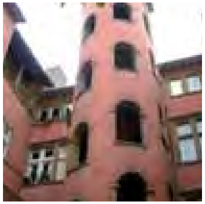
P42	hal-00225029	*Study of dielectric relaxation phenomena and electrical properties of conductive polyaniline based composite films* Vanga Bouanga Christele, Fatyeyeva Kateryna, Tabellout Mohamed
P43	hal-00255845	*Uniaxial pressure effect on Dielectric properties of $AgTaO_3$ single crystals* Suchanicz Jan, Kania A.
P44	hal-00258733	*Dielectric relaxation and cations hopping at aluminosilicate surfaces: water adsorption* Belarbi H., Giuntini J.C., Devautour-Vinot Sabine, Kharroubi M., Haouzi Ahmed, Henn F.
P45	hal-00260603	*Thermal-and Photo-switching of the dielectric permittivity of spin-crossover complex observed by broadband dielectric spectroscopy* Bonhommeau Sébastien, Demont Philippe, Guillon Thomas, Molnar Gàbor, Bousseksou Azzedine
P46	hal-00263518	*Dynamics of orientationally disordered mixed crystals sharing Cl-Adamantane an CN-Adamantane* Martinez-Garcia Cesar Julio, Capaccioli Simone, Diez Sergio, Lluís Tamarit Josep, Barrio María, Nestor, Veglio Carlos Pardo Luis
P47	hal-00264064	Characterization of lutetium oxide-based thin-film capacitors by impedance spectroscopy Wiktorczyk Tadeusz
P48	hal-00264079	*Reliability of advanced Cu/Low-k interconnects analyzed by impedance spectroscopy* Verriere Virginie, Sylvestre Alain, Guedj C., Roy D.
P49	hal-00264101	*Influence of solvent on the network structure formed by free radical polymerization of triethyleneglycol dimethacrylate: a dielectric study* Sabater I Serra Roser, Viciosa Plaza María Teresa, Dionisio Madalena, Andrio Balado Andreu, Gómez Ribelles José Luis
P50	hal-00264249	*A dielectric study near the critical point of the binary liquid mixture nitrobenzene-tetradecane: temperature and concentration dependence of the dielectric constant* Leys Jan, Cordoyiannis G., Losada-Perez P., A. Cerdeiriña C., Glorieux C., Thoen J.
P51	hal-00264267	*Orientational and phase change dynamics of 4-iodo-4'-nitrobiphenyl studied by broadband dielectric spectroscopy* Tsuwi Julius, Labat Gaël, Courderc Gaëtan, Berger Ricarda, Hulliger Jürg
P52	hal-00264322	*Dielectric relaxation in diepoxy nematics at elevated temperatures* Wlodarska Magdalena, Schönhals Andreas, Bak Grzegorz, Mossety-Leszczak Beata, Galina Henryk
P53	hal-00264324	*Dielectric Properties of SiO_2-$LiFe_5O_8$ Glass-Ceramics by Sol-Gel Processing* Graça Manuel Pedro, Silva Cleber, Cadillon Luis, Sombra António Sergio, Valente Manuel
P54	hal-00264325	*Dielectric properties of NaNO3 in porous glasses* Rysiakiewicz-Pasek Ewa, Poprawski R., Jagus P.
P55	hal-00264326	*Dielectric Properties Study of $xLiFe_5O_8$-(1-x) $LiNbO_3$ Composites Processed Using Microwave Energy* Graça Manuel Pedro, Silva Cleber, Gouveia Daniel, Cadillon Luis, Sombra António Sergio, Valente Manuel
P56	hal-00264327	*Dielectric Spectroscopy of $LiNbO_3$: Tm nanocrystals embedded in a SiO_2 glass matrix* Graça Manuel Pedro, Valente Manuel, Silva Cleber, Sombra Sergio
P57	hal-00264329	*Dielectric Spectroscopy of Lead-Free $NaNbO_3$-Based Relaxor-Like Ceramics* Bokov Alexei, Raevskaya Svetlana, Titov Victor, Raevski Igor, Porokhonsky Victor, Kamba S., Bovtun Viktor, Savinov Maxim, Petzelt Jan, Dellis Jean-Luc, Ye Z.-G.

POSTERS

P58	hal-00264788	*Dynamical Properties of Functionalized Polymers: Specific Chain Dynamics versus Matrix Plastification* Plaza Sandra, Lund Reidar, Alegria Angel, Jonoski Jonathan, Quirk Roderic, Colmenero Juan
P59	hal-00267162	*Peculiarities of the delta–and alpha-relaxations in polymers with cyanobiphenyl liquid crystalline side chains of different lengths* Salehli Ferid, Yildiz Sevtap, Ozbek Haluk, Uykur Ece, Hepuzer Gursel Yesim, Yuksel Durmaz Yasemin
P60	hal-00267254	*Comparison of dielectric and mechanical relaxations in different poly(vinylidene fluoride - hexa fluoropropylene) films* Fruebing Peter, Wang Feipeng, Gerhard Reimund, Wegener Michael, Jaunich Matthias, Stark Wolfgang
P61	hal-00267943	*Complex nature of the beta-relaxation in semi-crystalline PLLA: Influence of crystallinity* Brás Ana Rita, Malik Piotr, Dionisio Madalena, Mano João
P62	hal-00268006	*Broadband Dielectric Spectroscopy of Poly (2-ethoxyethyl methacrylate-co-2,3 dihydroxypropyl methacrylate) Membranes* Diaz-Calleja Ricardo, Carsi Marta, Sanchis Maria J., Guzman Julio, Riande Evaristo
P63	hal-00269104	*Dielectric spectroscopy of a macroscopic epoxy/silica interface submitted to an hygrothermal conditioning* Rain Pascal, Guillermin Christophe, Rowe Steve, Brun Emilie, Teissedre Gisèle
P64	hal-00269409	*Conductive polymer composites based on metallic nanofiller and polymer matrix as smart materials for temperature sensors* Rybak Andrzej, Boiteux Gisèle, Seytre Gérard
P65	hal-00270875	*Dielectric relaxation in the smectic E phase of 4-hexyl-4'- isothiocyanatobiphenyl (6BT)* Jasiurkowska Malgorzata, Kremer Friedrich, Serghei Anatoli, Massalska-Arodz Maria
P66	hal-00271477	*Investigation of molecular reorientation in poly(butylene terephthalate)/decylamine/fullerene nanocomposite* Wozniak-Braszak Aneta, Jurga Jan, Jurga Kazimierz, Brycki Bogumil, Holderna-Natkaniec Krystyna
P67	hal-00271488	*New information possibilities of the dielectric spectroscopy: investigation of the structural organization of the paraffin and vanadium oils* Saraev D., Lounev I., Yusupova T., Salehli Ferid
P68	hal-00271579	*Molecular Dynamics of a fluorinated cyano copolymer investigated by Dielectric spectroscopy* Meskini Ahmed, Raihane Mustpha, Stevenson Isabelle, Boiteux Gisèle, Seytre Gérard, Ameduri Bruno
P69	hal-00276726	*Molecular mobility at the interfaces of nanostructured systems* Nikaj Erisela, Stevenson Isabelle, Seytre Gérard, Laurent David, Boiteux Gisèle, Grohens Yves
P70	hal-00287652	*Studies of molecular dynamics in composites of carboxylated acrylonitrile-butadiene rubber containing silica* Pietrasik Joanna, Gaca Magdalena, Zaborski Marian, Okrasa Lidia, Gain Olivier, Boiteux Gisèle
P71	hal-00290056	*Analysis of interfacial polarisation relaxations in conducting composite films using the Maxwell-Wagner-Hanai effective medium theory* Tabellout Mohamed, Adohi Bibi Jean-Pierre, Vanga Bouanga Christele, Fatyeyeva Kateryna
P72	hal-00294867	*Dielectric and electrical study of PVC/MWCNT polymer nanocomposites* Levchenko Volodymyr, Mamunya Yevgen, Rybak Andrzej, Boiteux Gisele, Lebedev Eugene, Ulanski Jacek, Seytre Gérard
P73	hal-00264802	*Relation between the Distributed Nature of Processes in Polymer Materials and their Electrical Ageing Process* Lahoud Nadine, Martinez Vega Juan, Boudou Laurent

POSTERS

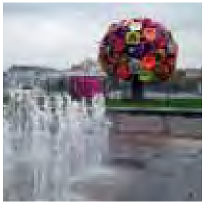
P74	hal-00274493	*Finite size effects in ferroelectric* $BaSrTiO_3$ *doped with* Fe_2O_3 *prepared by sol-gel technique* Battisha I.K.
P75	hal-00264274	*Conductivity characterization of redispersible polypyrrole composite nanoparticles* Mpoukouvalas Konstantinos, Wang Jianjun, Sun Ling, Wei Cheng, Beierlein Tilman, Muehlebach Andreas, Bonaccurso Elmar, Butt Hans-Jürgen, Wegner Gerhard
P76	hal-00285838	*Structure and dielectric studies of nano - composite Fe2O3:* $BaTiO_3$ *prepared by sol-gel method* Battisha I.K., Mahani R., Bellal A.
P77	hal-00271536	*Relaxation properties of Nanocomposites Zeolite-semiconductor Hbeta-ZnS* Voilov Dmitry, Novikov Gennadii Fiodorovich, Valerievna Meteleva-Fisher Yulia
P78	hal-00268741	*Back switching of ferroelectric polarization in PZT* Zhukov Sergey, Von Seggern Heinz, Fedosov Sergey
P79	hal-00259804	*Ac conductivity analysis and dielectric dispersion in unidirectional PZT fibres/epoxy resin composites* Hammami Helmi, Lagache Manuel, Arous Mourad, Kallel Ali
P80	hal-00267949	*Preparation and Characterisation of ferroelectric niobate crystals with tungstenbronze structure* Amira Yassine, Zegzouti Abdelwahed, Elaatmani M., Gagou Yaovi, Elmarssi Mimoun, Mezzane Daoud
P81	hal-00264264	*Dielectric properties of oxides coated fabrics for advanced shielding materials* Pospieszna Janina, Jaroszewski Maciej, Ziaja Jan
P82	hal-00264299	*Theoretical Approach for Characterization of Dielectric Properties of Metal Containing Nano-Composites* Trakhtenberg Leonid, Kozhushner Mortko, Gerasimov, Genrikh, Gromov Vladimir, Antropova Tatyana, Axelrod Ekaterina, Greenbaum Anna, Feldman Yuri

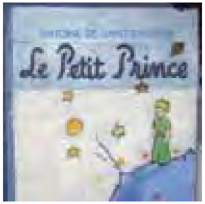


POSTERS

Charge transport

P83	hal-00260601	*Interplay between the charge transport phenomena and the charge-transfer phase transition in FeMn Prussian Blue Analogues using Broadband Dielectric Spectroscopy* Molnar Gàbor, Cobo Saioa, Vertelman Esther, Van Koningsbruggen Petra, Demont Philippe, Bousseksou Azzedine
P84	hal-00261529	*Determination of electronic structure by impedance spectroscopy* Niklasson Gunnar A., Malmgren Sara, Backholm Jonas
P85	hal-00262327	*Miscible polymer blends with dynamical asymmetry as a potential new class of materials for solid state electrolytes* Cangialosi Daniele, Alegria Angel, Colmenero Juan
P86	hal-00264257	*Dielectric properties of ionic liquids* Sangoro Joshua, Iacob Ciprian, Serghei Anatoli, Kremer Friedrich
P87	hal-00264374	*Anomalous Dielectric Relaxation in Binary Mixtures of Mesogenic Solvent / Non-mesogenic Solute* Jadzyn J., Bauman D., Dejardin J.-L., Ginovska M., Czechowski G.
P88	hal-00267288	*Dielectric and Thermal Properties of Some Supercooled Alkyl Halides* Berberian John
P89	hal-00271501	*Electrical properties of Li_2O-ZnO-P_2O_5 Glasses* Mogus-Milankovic Andrea, Pavica L., Reisb S.T., Dayb D.E.
P90	hal-00285604	*Dielectric and conductivity behaviors in $CaCu_3Ti_4O_{12}$ Glass* Yang Y. S.
P91	hal-00311653	*Electrical charge transport in deuterated oxalic acid dihydrate* Filipic Cene, Levstik Adrijan, Bobnar Vid, Levstik Iva, Hadzi Dusan
P92	hal-00311654	*Polaron conductivity mechanism in magnetoelectric $K_3Fe_5F_{15}$* Levstik Adrijan, Filipic Cene, Bobnar Vid, Tavcar Gregor, Zemva Boris
P93	hal-00267944	*Lithium conductivity and molecular mobility in poly(ethyleneoxide)-based polyester ionomers* Fragiadakis Daniel, Dou Shichen, Colby Ralph, Runt Jim





Biological systems

P94	hal-00201122	*Dielectric Study of the Anti-Plasticization of Trehalose by Glycerol* Obrzut Jan
P95	hal-00260619	*Scanning of the molecular mobility in a peptides/collagen system by thermal analysis* Tintar Doris, Samouillan Valérie, Dandurand Jany, Lacabanne Colette, Spina Michel, Naso F., Gandaglia A., Danesin R., Dettin M.
P96	hal-00263901	*How do sugars influence some structural vibrational and dynamical properties of proteins ? An Insight from Molecular Dynamics simulations* Affouard Frédéric, Lerbret Adrien, Guinet Yannick, Hédoux Alain, Descamps Marc
P97	hal-00264149	*High-frequency broadband dielectric spectroscopy on sugar alcohols below Tg* Nakanishi Masahiro, Nozaki Ryusuke
P98	hal-00264245	*Dielectric relaxation spectroscopy of aqueous amino acid solutions* Cerveny Silvina, Alegria Angel, Leza Lourdes, Colmenero Juan
P99	hal-00264247	*Using Impedance Spectroscopy to Monitor the Regeneration of Newt Tails* Hart Francis, Johnson Julie, Berner Nancy
P100	hal-00265771	*Broadband dielectric measurements of anhydrous and hydrated connective tissue* Fillmer Ariane, Gainaru Catalin, Vogel Michael, Böhmer Roland
P101	hal-00266081	*Boundary-element calculations for effects of low-frequency electric fields in a doublet-shaped biological cell* Sekine Katsuhisa, Asami Koji
P102	hal-00266570	*Single cell analysis using a scanning dielectric microscope* Asami Koji
P103	hal-00266739	*Chain Dynamics of Transformed Cassava Starch Using Dielectric Spectroscopy* Bello Alfredo, Laredo Estrella
P104	hal-00267757	*Identification of the molecular motions responsible for the slower secondary (β) -relaxation in sucrose* Hensel-Bielowka Stella, Kaminski K., Kaminska E., Chelmecka E., Paluch M., Ziolo J., Woldarczyk P., Ngai L.K.
P105	hal-00268399	*Dielectric Inspection of Biological Cells* Hayashi Y., Katsumoto Yoichi, Omori Shinji, Yasuda Akio, Asami Koji
P106	hal-00270311	*Influence of cationic surfactant on DMPC structure* Szpotkowski Kamil, Wypych Aleksandra, Kozak Maciej, Domka Ludwik, Jurga Stefan
P107	hal-00270313	*Structural and spectroscopic studies of DMPC/cationic surfactant system* Kozak Maciej, Wypych Aleksandra, Szpotkowski Kamil, Jurga Stefan
P108	hal-00272010	*Molecular Dynamics in Smart Hydrogel Systems* Bassil Maria, Davenas Joel, Boiteux Gisèle, El Tahchi Mario
P109	hal-00294109	*Glassy dynamics of proteins and effects of solvents: the case of spider silk* Papadopoulos Periklis, Serghei Anatoli, Kremer Friedrich, Gitsas Antonios, Floudas George

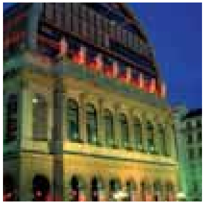
POSTERS

Broadband relaxation spectrodcopy and new developments

P110	hal-00260625	*Molecular mobility in a polyepoxy adhesive under hydrothermal ageing conditions by Broadband Dielectric Spectroscopy measurements* Dantras Eric, Chevalier Mathieu, Tonon Claire, Guigue Pascal, Lacabanne Colette, Puig Christian, Durin Christian
P111	hal-00260641	*Annealing effects of a polymer system by Broadband Dielectric Spectroscopy* Carsalade Elodie, Bernès Alain, Perraud Sophie, Lacabanne Colette
P112	hal-00262199	*The Assessment of the Influence of Temperature of Selected Parameters of the Approximation Method of Depolarization Current Analysis of Paper-Oil Insulation* Wolny Stefan, Kedzia Józef
P113	hal-00262341	*Positron annihilation lifetime response and broadband Dielectric Spectroscopy: (propylene glycol)* Bartos Josef, Schwartz G.A., Sausa O., Alegria Angel, Kristiak J., Colmenero Juan
P114	hal-00263898	*Nonlinear dielectric effect and critical phenomena of ternary critical mixture* Kosmowska Magdalena, Orzechowski Kazimierz
P115	hal-00263983	*Dielectric relaxation in double potassium yttrium orthophosphate $K_3Y(PO_4)_2$ and sodium yttrium orthophosphate $Na_3Y(PO_4)_2$* Szulia Sylwia, Kolodziej Hubert A., Szuszkiewicz Wladyslawa
P116	hal-00264115	*Generalization of the Ryabov-Feldman formula: the case of cylindrical symmetry* Arbuzov Andrey, Nigmatullin Raoul
P117	hal-00264154	*Features of Harmonic Spectrum of A_2BX_4 Crystals Related to Domain Wall Dynamics* Gorbatenko Vladimir, Gorbatenko Svetlana
P118	hal-00264221	*Entropy and Entropy Production in Dielectric and Magnetic Relaxation* Baker-Jarvis James
P119	hal-00264284	*Structural and Dynamical Aspects of the Cold Crystallization of a Flexible Polymer as seen by Time Resolved Neutron Scattering and Broadband Dielectric Spectroscopy* Lund Reidar, Alegria Angel, Goitiandia Luis, Colmenero Juan
P120	hal-00264300	*Observation of Polymer Crystallization through Ion Motion: Low Density Polyethylene* Anada Yuichi
P121	hal-00264448	*Dielectric study of cured epoxy resin with mesogenic unit* Wlodarska Magdalena, Bak Grzegorz, Schönhals Andreas, Mossety-Leszczak Beata, Galina Henryk
P122	hal-00265485	*Coupling Between the alpha Process and Boson Peak in Glycerol-Water Mixtures* Puzenko Alexander, Segev Ido, Feldman Yuri
P123	hal-00267937	*The analysis of isothermal current in terms of charge injection or extraction at the metal-dielectric contact* Neagu E.R., Neagu R.M., Dias C.J., Carmo-Lança M., Marat-Mendes J.N.
P124	hal-00267952	*Effect of Uniaxial Strain on the Dynamics of Elastomers* Fragiadakis Daniel, Martin Darren, Runt James
P125	hal-00267980	*Monitoring the crystallization in a low molecular weight compound by Dielectric Relaxation Spectroscopy* Dionisio Madalena, Viciosa Plaza María Teresa, Salmerón Sánchez M., Gómez Ribelles José Luis, Correia Natália
P126	hal-00268253	*Non Invasive Glucose Monitoring with a Dielectric Spectroscopy based Multi-Sensor Platform* Talary Mark, Falco Lisa, Dewarrat Francois, Caduff Andreas
P127	hal-00269976	*Review and improvement of a method for measuring losses in the dielectric materials by calorimetry* Obame Elysée, Aitken Frédéric, Gallot-Lavallée Olivier

POSTERS

P128	hal-00270334	*Broadband Dielectric and 1H NMR studies in semi-crystalline poly(ethylene oxide)* Orozbaev Bakyt, Fojud Zbigniew, Makrocka-Rydzyk Monika, Wypych Aleksandra, Wachowicz Marcin, Jurga Stefan
P129	hal-00271193	*In-situ monitoring of reactive thermoplastic composties* Hakme Chady, Boiteux Gisèle, Seytre Gérard, Stevenson Isabelle, Pantelelis Nikos
P130	hal-00271504	*In-line monitoring of polymer melt processing by conductivity spectroscopy: Carbon nanotube–polymer composites* Lellinger Dirk, Alig Ingo, Engel Martin, Skipa Tetyana, Pötschke Petra
P131	hal-00275222	*Electrical Properties of Polymer Nanocomposites based on Poly(butylene terephthalate) from Cyclic Butylene Terephthalate and MWCNT* Bardash Liubov, Boiteux Gisèle, Seytre Gérard, Fainleib Aleksander
P132	hal-00277561	*Dielectric phenomena of organic-inorganic polymer systems during polymerization and in solid state* Iurzhenko Maksym, Mamunya Yevgen, Boiteux Gisèle, Seytre Gérard, Lebedev Eugene
P133	hal-00294596	*Dielectric and Mechanical Properties of Polylactide and its Nanocomposites with Montmorillonite* Jeszka J.K., Pluta M., Pietrzak L., Boiteux G.
P134	hal-00271783	*Thermal and electrical behavior of a thermostable imide type polymer* Olariu Marius, Hamciuc Corneliu, Hamciuc Elena, Ciobanu Romeo
P135	hal-00271787	*Comparative study of the thermal and electrical properties of some poly (ether imide) thin films* Hamciuc Corneliu, Olariu Marius, Hamciuc Elena, Temneanu Marinel
P136	hal-00264290	*Impedance spectroscopy study of* $Pb_2(1-x)K_1+xGdxNb_5O_{15}$ *samples* Amira Yassine, Gagou Yaovi, El Marssi M., El Aatmani Mohamed, Zegzouti Abdelwahed, Mezzane Daoud
P137	hal-00305479	*Microscopic model on the electrode polarization* Serghei Anatoli, Kremer Friedrich



/// Thursday 28th ///

SESSION 1 LAPRADE AMPHITHEATRE

Functional materials

Chairman: **KLIEM HERBERT**

9:00-9:30 Gerhard Reimund **Maxwell-Wagner ferroelectrets**
Heterogeneous dielectrics with interface charges for transducer applications

9:30-9:50 Fedosov Sergey, Von Seggern Heinz Interrelation
Interrelation between conductivity and polarization phenomena in two-component ferroelectric polymers

9:50-10:10 Flores Suarez Rosaura, Mellinger Axel, Wirges Werner, Gerhard Reimund, Pham Cong-Duc, Petre Anca, Berquez Laurent, Marty-Dessus Didier
Time- and frequency-domain polarization imaging on poly (vinylidene fluoride-co-trifluoroethylene) films

10:10-10:30 Lerner Shimon, Ben Ishai Paul, Feldman Yuri, Mierzwa Michal, Paluch Marian
The effects of pressure on the cooperative and non-cooperative dielectric processes in KTN ferroelectric crystals

10:30-10:40 Dantras Eric, Capsal Jean-Fabien, Laffont-Dantras Lydia, Dandurand Jany, Lacabanne Colette Broadband
Dielectric spectroscopy of organic/inorganic ferroelectrics nanomaterials

11:15-15:00 **Poster session and Poster Prizes**

Lunch

Functional materials

Chairman: **NIKLASSON GUNNAR A.**

15:00-15:30 **Ezquerra Tiberio**
Broadband Electrical Conductivity of Polymer Nanocomposites based *on Carbon Nanoadditives*

15:30-15:50 Mamunya Yevgen, Levchenko Volodymyr, Rybak Andrzej, Boiteux Gisèle, Lebedev Eugene, Ulanski Jacek, Seytre Gérard
Structure, dielectric properties and conductivity of segregated PVC/MWCNT composites

15:50-16:10 Bovtun Viktor, Veljko Sergiy, Nuzhnyy Dmitry, Petzelt Jan, Knite Maris, Aulika Ilze, Fuith Armin
Theoretical Approach for Characterization of Dielectric Properties of Metal Containing Nano-Composites

16:10-16:40 **Kenny Josè**
Dielectric and Chemorheological behaviour of double-walled carbon nanotube-epoxy nanocomposites.

18:00 **Concert in UCB Lyon**
19:45 **« Wine and Cheese » Party**
21:00 **IDS Committee Meeting**

SESSION 2 GRAND AMPHITHEATRE

Charge transport

Chairman: **ULANSKI JACEK**

9:00-9:30 **Kremer Friedrich**, Serghei A., Sangoro J. R., Iacob C.
Charge transport and electrode polarisation in Ionic Liquids

9:30-9:50 Biermann Christine, Funke K.
KWW-type electrode polarization effects in glass

9:50-10:10 Martin Bjoern, Kliem Herbert
Space charges in solid electrolytes detected by the scanning Kelvin probe

10:10-10:30 Niklasson Gunnar A., Furlani Maurizio, Stappen Christopher, Mellander Bengt-Erik
Concentration dependence of ionic relaxation in lithium doped polymer electrolytes

10:30-11:00 Roling Bernhard, Ramaraj Mariappan C.
Electrical polarisation and space charge formation in bioactive glasses

11:00 **PETER DEBYE PRIZE FOR YOUNG INVESTIGATORS FOR EXCELLENCE IN DIELECTRIC RESEARCH**

11:15-15:00 **Poster session and Poster Prizes**

Lunch

Functional materials

Chairwomen: **OKRASA LIDIA**

15:00-15:30 **Floudas George**, Elmahdy M.M., Mondeshki M., Spiess H.W., Dou X., Müllen K.
Self-assembly, molecular dynamics and kinetics of structure formation in dipole functionalized discotic liquid crystals

15:30-15:50 Leys Jan, Glorieux Christ, Thoen Jan
Surface and disorder effects in aerosil dispersed liquid crystals

15:50-16:10 Aliev Fouad, Arroyo Edwin, Dolidze Vladimir
Influence of confinement on molecular and director reorientational dynamics of liquid crystals

16:10-16:40 **Dyre Jeppe C.**
Ac hopping conduction at extreme disorder takes place on the percolating cluster

18:00 **Concert in UCB Lyon**
19:45 **« Wine and Cheese » Party**
21:00 **IDS Committee Meeting**

Friday 29th August

SESSION 1 LAPRADE AMPHITHEATER

Biological systems

Chairman: **FELDMAN YURI**

8:30-9:00	**Bordi Federico**, Cametti Cesare, Sennato Simona, Tuzzolillo Domenico *Broadband Dielectric Spectroscopy as a tool to investigate polyelectrolytes and their interactions with biomembranes*
9:00-9:20	Raicu Valerica *Non-Debye dielectric behaviour and near-field interactions in biological tissues: when structure meets function*
9:20-9:40	Shinyashiki Naoki, Yokoyama Ayame, Yamamoto Wataru, Yagihara Shin, L. Ngai K., Capaccioli Simone *Glass Transitions and Dielectric Relaxations Observed in Partially Crystallized Protein-Water Mixtures*
9:40-10:00	Schiro' Giorgio, Cupane Antonio, Bruni Fabio, Natali Francesca *Dynamics of protein-solvent systems in hard confinement studied by Broadband Dielectric Spectroscopy and Neutron Scattering*

Chairman: **ASAMI KOJI**

10:00-10:30	**Ulanski Jacek**, Pastorczak M., Kozanecki M., Dominguez-Espinosa G., Okrasa L., Butt H.J., Koynov K., Pyda M., Kadlubowski S., Rosiak J.M. *The molecular dynamics in PVME hydrogels at sub-zero temperatures*
10:30-10:50	Rudowski Marek, Orzechowski Kazimierz, Rzaca Marek *Modified open-ended dielectric probe used for comparison between cancer and healthy breast tissues. Test of a new method*
10:50-11:20	**Coffee break**
11:20-11:40	Talary Mark, Falco Lisa, Dewarrat Francois, Puzenko Alexander, Caduff Andreas, Feldman Yuri *Approaching the inverse problem of the multi-layer skin system*
11:40-12:00	Gerecht Eyal *Terahertz Spectroscopy based on Heterodyne Detection Techniques*

Chairwoman: **VASSILIKOU-DOVA AGLAIA**

12:00:12:30	**Lacabanne Colette, Jafarpour Golnaz, Dantras Eric, Boudet Alain** *Dielectric study of macromolecular interactions in wood*
12:30-12:50	Carmo-Lança M., Neagu E.R., Dias C.J., Marat-Mendes J.N. *Dielectric spectra of natural cork and derivatives*
12:50-13:10	Paluch Marian, Kaminski Kamil, Wlodarczyk Patryk, Hensel-Bielowka Stella, Kaminska Ewa *Dielectric relaxation study of the dynamics of sugars*
13:10-13:30	Laredo Estrella, Bello Alfredo *Dielectric Relaxations and Moisture Effect in Native and transformed Cassava Starch*
13:30	**Conclusion**
13:45	**Farewell Party**

SESSION 2 GRAND AMPHITHEATER

Broadband relaxation spectrodcopy and new developments

Chairman: **DANTRAS ERIC**

8:30-9:00	**Schönhals Andreas** *Molecular Mobility of molecules in nanoscale confinement and close to surfaces*
9:00-9:20	Saiter Jean-Marc *Relaxation time at Tg measured by Dielectric spectroscopy and Thermally depolarisation current methods*
9:20-9:40	Jurga Stefan, Jancelewicz M., Nowaczyk G., Fojud Zbigniew, Kempka M., Makrocka-Rydzyk Monika, Maciejewski H. *Molecular dynamics in modified polydimethysiloxanes studied by DSC, rheology and NMR*
9:40-10:00	Novikov Gennadii *BDS Study of Photodielectric Phenomena in Semiconductors of AIIBVI Group*
10:00-10:20	Anastasiades C., Kanapitsas Athanasios, Tsonos Christos, Stavrakas I., Triantis D., Neagu E.R., Pissis Polycarpos *Dielectric Relaxation of ZnO varistor*
10:20-10:40	Amaral F., Valente M.A., Costa L.C. *Dielectric properties of* $C_aC_{u3}Ti_4O_{12}$ *(CCTO) doped with* GeO_2
10:40-11:10	**Coffee break**

Chairman: **DEBYE PRIZE WINNER**

11:10-11:40	**Alig Ingo**, Lellinger Dirk, Xu Donghua, Engel Martin, Pötschke Petra *Monitoring of polymer melt processing by dielectric spectroscopy*
11:40-12:00	Obrzut Jan *Shear induced conductor-insulator transition in carbon nanotube-polypropylene composites*
12:00-12:20	Bartos Josef, Majernik V., Sausa O., Kristiak J., Lunkenheimer P., Loidl A. *Positron annihilation lifetime response and broadband dielectric spectroscopy: propylene carbonate*
12:20-12:50	**Richert Ranko** *Time-resolved Nonlinear Dielectric Responses in Molecular Systems*
12:50-13:10	Soualmia Achour, Abdelguerfi Mériem *Dielectric spectroscopy study by Time Domain Reflectometry (TDR)*
13:30	**Conclusion**
13:45	**Farewell Party**

/// Listes of participants ///

NOM	PRENOM	PAYS
ABDELGUERFI	Mériem	ALGERIE
AFFOUARD	Frederic	FRANCE
ALEGRIA	Angel	ESPAGNE
ALIEV	Fouad	USA
ALIG	INGO	ALLEMAGNE
ALMEIDA VALENTE	Manuel	PORTUGAL
AMARAL	Filipe	PORTUGAL
AMIRA	Yassine	FRANCE
ANADA	Yuichi	JAPON
ANASTASIADIS	Cimon	GRECE
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In-Situ monitoring of reactive thermoplastic composites

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Abstract

The in-situ monitoring of the polymerization of cyclic butylene terephtalate (CBT) oligomers by dielectric and electrical sensing have been investigated under isothermal conditions at different processing temperatures [1, 2]. The change in conductivity depends on the increase of molecular weight but is also influenced by crystallization of the obtained c-PBT during or after polymerization. Dielectric sensing investigations are in good agreement with SEC and DSC analysis which confirm the polymerisation and crystallization kinetics. Unfortunately, the conductivity signal could not distinguish between the polymerization and crystallization when it occurs simultaneously at lower temperatures (<210 °C) but the crystallization remains detectable by the MWS relaxation which is related to the crystalline / amorphous interface.

Conductivity has been measured by dielectric measurements calculating the maximum of the imaginary impedance (Z’’max) [3] and the resistance by using a special DC monitoring system [4] (fig.1). A control system of the reactive moulding has been developed based on the Z’’max real-time monitoring of the CBT resin transforming to PBT (fig.2).

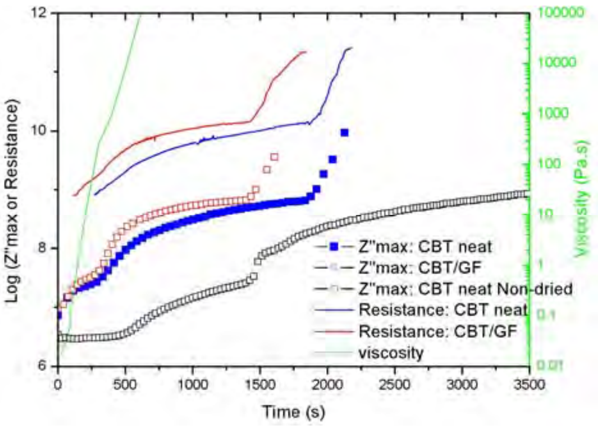

Figure 1. Monitoring the reaction of CBT using dielectrics (Z’’max) and DC measurements (Resistance) for neat and glassfibre filled resin.

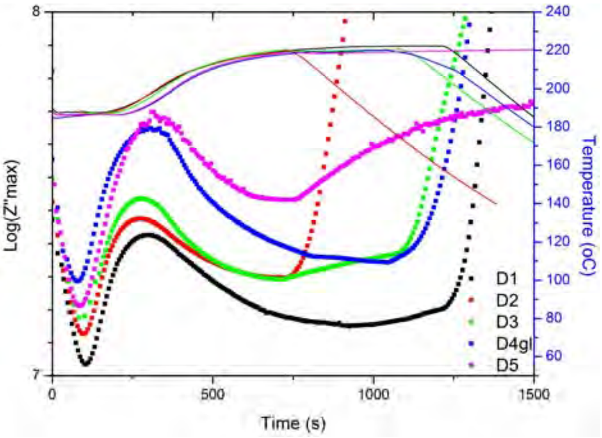

Figure 2. Monitoring repetitive cycles with neat CBT using the impedance Z’’max.

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Broadband Dielectric Spectroscopy as a tool to investigate polyelectrolytes and their interactions with biomembranes

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Although the dielectric method has been established for well over 100 years, it is still one of the most important techniques for studies of the structure and dynamics of polymer solutions due to the extremely wide range of characteristic times that can be investigated.

The dielectric and conductometric spectra of aqueous polyelectrolyte solutions, extending over a wide frequency range, present a very complex shape, involving three or more different, partially overlapping, contributions, each of them originated by different molecular level mechanisms [1]. The dielectric spectra of aqueous colloidal suspensions are complex as well [2-4], so that the interpretation of the spectra of mixed aqueous suspensions of polyelectrolyte *and* oppositely charged colloidal particles can easily become a real mess. Especially when the colloidal particles show a structure characterized by dielectric dishomogeneities, as is the case of liposomal vesicles [5] and, moreover, tend to aggregate in complex structures [6]. Nevertheless, dielectric spectroscopy and conductimetry applied to these systems provide extremely useful information on both the the dynamics of aggregation and the structure of the aggregates.

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UV-polymerization of neat HEMA and HEMA in a Matrix of Polyurethane by NIR and by Microdielectrometry

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The investigation of the kinetic of UV-polymerization of monomer 2-hydroxyethyl methacrylate (HEMA) in the matrix of polyuretane (PU) was carried out on-line by NIR and by microdielectrometry. The samples with different amount of monomer HEMA in the matrix of PU were analyzed in comparison with sample of neat monomer HEMA using the photoinitiator Irgacure 819. The vibrational band at 6163 cm^{-1} (assigned to the double bonds in monomer) was selected for investigation by NIR. The quartz sensors MS25 were used for investigation of UV-polymerization kinetic by microdielectrometry. Two quartz sensors were used to investigate the changes in Log Conductivity and Log Permittivity during the UV-polymerization in the surface and in the bottom of sample with thickness of 0.7 mm. It was shown that UV-polymerization of HEMA in the matrix of PU is quicker in comparison with UV-polymerization of neat HEMA: in the first case the conversion rate reached 94% after 5 minutes, in the second case the conversion rate reached 85% after 30 minutes. It was concluded that UV-polymerization of pure HEMA was inhibited by the oxygen of air. The monomer in the PU matrix is protected from the oxygen, and UV-polymerization occurred quicker. It was shown that UV-polymerization of HEMA in the bottom of PU sample started 3 minutes later in comparison with the surface due to the gradient of UV light.

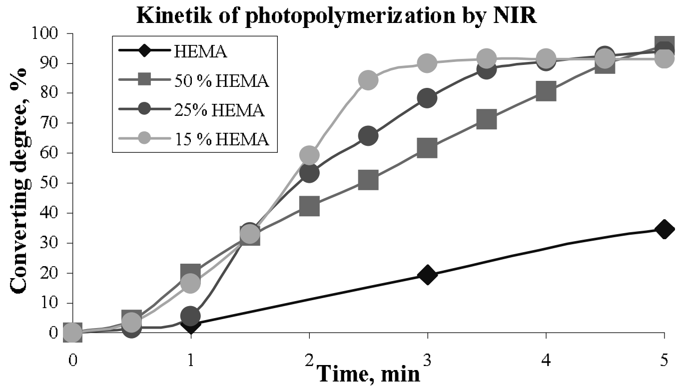

Figure 1. The conversion degree of neat monomer HEMA and 15%, 25% and 50% of XEMA in the matrix of Polyurethane

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Dielectric and Chemorheological behaviour of double-walled carbon nanotube-epoxy nanocomposites

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Carbon nanotubes (CNTs) are promising fillers for composite materials to improve mechanical behavior and electrical and thermal transport [1]. Nevertheless intrinsic difficulties and unresolved issues related to the incorporation of carbon nanotubes as conductive fillers in polymer matrices and the interpretation of the processing behaviour have not yet been resolved. The nanotube dispersion and compatibilization in polymer matrices remains an open issue to be overcome and represents a topic object of large investigation as reported in the literature CNTs [2-6]. Double-walled carbon nanotubes (DWNTs) [7] consists of two coaxial single-walled carbon nanotubes and represents a class of emerging materials. Thus, the functionalization of these nanofillers represents an open issue for the preparation of DWNT based nanocomposites. Grafted- N-methyldiethanolamine on carboxy-functionalized DWNTs will be presented and investigated in terms of chemorheological behaviour during the cure reaction of an epoxy system. A chemorheological model has been also developed for this new type of nanocomposite [8]. Moreover the interaction of the amine groups with the carboxy functionalities of the tubes would have a direct effect on the network for the following reasons: (1) the amine groups reacts with the carboxylic groups; (2) this modified system should affect the total mean-square dipole moment. The principal objective of this study is to elucidate by means of the dielectric spectroscopy how this interaction affects the dielectric relaxation of the neat epoxy/amine networks.

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A microscopic model for the electrode polarization

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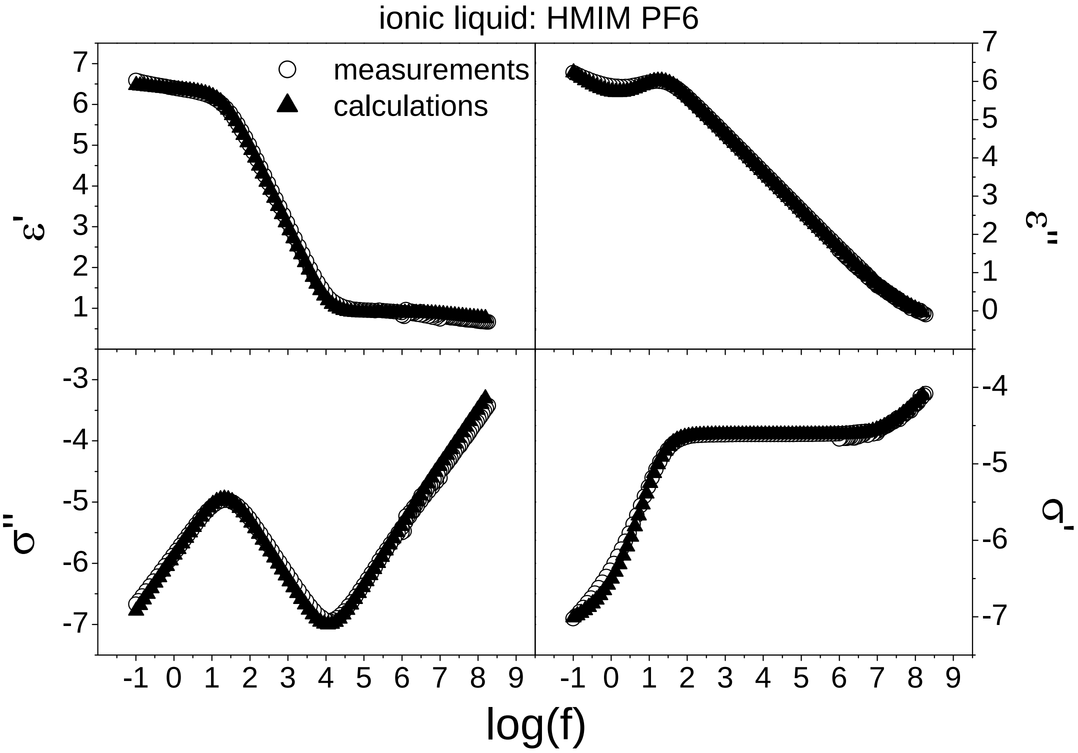
Electrode polarization is a phenomenon manifested when the diffusion of charge carriers is (partially) blocked due to the presence of interfaces. It causes pronounced changes of the dielectric function and hence of the complex conductivity. These changes show a peculiar dependence on the length of the sample cell and on the material of the electrodes. In the present contribution a microscopic model for electrode polarization is discussed in detail. It basically relies on the assumption that the hopping rate of the charge carriers decreases by many orders of magnitude in the nanometric vicinity of the electrodes, due to the coloumbic interactions. It can shown that this "minimal" assumption leads to dielectric spectra which exhibit – on a qualitative as well as quantitative level – all experimental features of the electrode polarization:

(i) the characteristic spectral dependence of the dielectric response.
(ii) the experimental observation that the electrode polarization shifts to higher frequencies with increasing temperature.
(iii) the scaling in respect to the temperature variation.
(iv) the dependence on the length of the sample cell: the electrode polarization shifts to higher frequencies when decreasing the sample length
(v) the experimental observation that the dielectric response does not scale in respect to the variation of the sample length.
(vi) the dependence on the material of the electrodes, by allowing different thicknesses of the interfacial layer.
(vii) the experimental observation that the dielectric response does not scale in respect to the variation of the electrodes material.



Molecular dynamics of confined polymers: recent developments and challenges

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Polymers represent a class of glass-forming materials of special technological importance. With the rise of nano-technology in the recent years, novel approaches have to be developed to enable one a direct experimental access to the polymer dynamics in samples having nanometric dimensions. This challenge is discussed in the present contribution, which will be focused on the molecular glassy dynamics of ultra-thin polymer layers. The following topics will be emphasized:

(i) it will be shown that, due to preparative factors, metastable states in the molecular dynamics can be induced in thin films, which show deviations from the bulk behavior and, hence, may take the appearance of confinement-effects.

(ii) several microscopic mechanisms leading to shifts in the position and broadening of the dynamic glass transition in thin polymer films will be discussed.

(iii) a recently developed experimental approach will be demonstrated, which allows one a direct access to the glassy dynamics of polymers in the immediate (nanometric) vicinity of solid interfaces. This renders to Broadband Dielectric Spectroscopy – traditionally a volume specific technique – the ability to measure the interfacial dynamics of polymers in systematic dependence on the interfacial interactions with a supporting substrate.

(iv) this recent development allows furthermore measurements on the molecular dynamics in polymeric systems resembling a statistical ensemble of single polymer chains, and rises thereby the possibility to address the question of whether a single polymer chain could have a glass transition.

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Charge transport and electrode polarisation in glass-forming ionic liquids

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The mechanism of charge transport in imidazolium based ionic liquids is analyzed by combining Broadband Dielectric Spectroscopy (BDS) and Pulsed Field Gradient Nuclear Magnetic Resonance (PFG NMR). The dielectric spectra are dominated – on the low-frequency side – by electrode polarization effects while, for higher frequencies, charge transport in a disordered matrix is the underlying physical mechanism. Using the Einstein and Einstein-Smoluchowski equation enables one to determine – in excellent agreement with direct measurements by PFG NMR – the diffusion coefficient of the charge carriers. By that, it becomes possible to extract from the dielectric spectra separately the number density and the mobilities of the charge carriers and the type of their thermal activation. It is shown that the observed VFT dependence of the DC conductivity can be traced back to a similar temperature dependence of the mobility while for the number density an Arrhenius-type thermal activation is found. Extrapolating the latter to room temperature indicates that nearly all charge carriers are participating to the conduction process. In the second part charge transport and glassy dynamics of a variety of glass-forming ionic liquids (ILs) are investigated in a wide frequency and temperature range by means of Broadband Dielectric Spectroscopy, Differential Scanning Calorimetry and Rheology. While the absolute values of dc conductivity and viscosity vary over more than 11 decades with temperature and upon systematic structural variation of the ILs, quantitative agreement is found between the characteristic frequency of charge transport and the structural α-relaxation. This is traced back to *dynamic glass transition assisted hopping* as the underlying mechanism of charge transport.

In the third part of the talk electrode polarisation - a common effect in ion-containing systems - will be discussed. It is characterized in its frequency and temperature dependence by a special signature of the complex dielectric function resp. the complex conductivity which can be *quantitatively* understood.

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Phenomenological manifestation of “strange kinetics" in dielectric response of complex systems.

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The paper considers several examples of non-Debye dielectric response in complex heterogeneous media such as porous materials, colloid systems, glass formers, doped ferroelectric crystals, polymers composites and biological systems. The percolation phenomenon and Cole-Cole (C-C) relaxation in disordered matter are discussed in detail [1]. In addition, the origins of "strange kinetic" phenomena were discussed based on statistical physics and fractional time evolution ideas. A phenomenological classification of different C-C relaxation systems in terms of their dependencies on the various thermodynamic parameters is presented. This classification is used for a deeper understanding of colloid and biological systems where interface dynamics often exhibit C-C relaxation.

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DETECTION OF COLLECTIVE MOTIONS IN DIELECTRIC SPECTRA AND THE MEANING OF THE GENERALIZED VOGEL-FULCHER-TAMMAN EQUATION

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Abstract

Based on the reduction property of dielectric spectra associated with the power-law function [$\sim\left(j\omega\tau\right)^{\pm\nu}$] in the frequency domain one can develop an effective procedure for detection of different collective motions (described by the corresponding power-law exponents) with the help of separation procedure in the cases, when an extreme point is *hidden* (or visually undetectable). If the power-law exponent ν is related with characteristic relaxation time τ by the relationship $\nu \sim \ln\left(\tau/\tau_s\right)/\ln\left(\tau/\tau_0\right)$ (here τ_s, τ_0 are the characteristic times characterizing a movement over fractal cluster that defined in paper [1]) and the simple temperature dependence of $\tau(T) = \tau_A \cdot \exp(E/T)$ obeys the traditional Arrhenius relationship then one can prove that *any* extreme point figuring in the complex permittivity spectra (characterized by the values [ω_m, $y(\omega_m)$]) obeys the generalized Vogel-Fulcher-Tamman (VFT) equation. This important statement confirms the existence of the 'universal' response (UR) (discovered and classified by A.K. Jonscher) and opens new possibilities in detection of the 'hidden' collective motions in the dielectric spectra of many complex (heterogeneous) systems. It gives also the extended interpretation to the VFT equation and allows differentiate collective motions passing through an extreme point. This differentiation, in turn, allows to select the proper fitting function containing one or two (at least) relaxation times for the fitting of the complex permittivity function in the limited frequency domain. This conclusion gives a certain chance for classification of dielectric spectroscopy as the spectroscopy of *collective* motions, which are described by different power-law exponents on the mesoscale region. The verification of this approach on available DS data (Poly(Ethylene Glycol) –based – single ion conductors) completely confirms the basic statements of this theory and opens new possibilities in general classification of different collective motions that can be detected in analysis of the complex dielectric permittivity spectra.

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Keywords: Dielectric spectroscopy; 'universal' response; collective motions; the generalized Vogel-Fulcher-Tamman equation; self-similar (fractal) systems

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Recent progress in understanding relaxation of complex interacting systems

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The glass transition problem is still an unsolved problem in condensed matter physics and chemistry. In this paper we critically reexamine experimental data and theoretical interpretations of dynamic properties of various processes seen over a wide time range from picoseconds to laboratory times-scales. In order of increasing time, the processes considered include the dynamics of caged molecular units with motion confined within the anharmonic intermolecular potential and no genuine relaxation has yet taken place, the onset of the Johari-Goldstein secondary relaxation involving rotation or translation of the entire molecular unit and causing the decay of the cages, the cooperative and dynamically heterogeneous motion participated by increasing number of molecules or length-scale, and finally the terminal primary α-relaxation with maximum cooperative length-scale allowed by the intermolecular interaction and constraints of the glassformer. Some general and important properties found in each of these processes are shown to be interrelated, indicating that the processes are connected with one being the precursor of the other following it. In addition to published data, new experimental data are reported here to provide a collection of critical experimental facts that has impact on current issues of glass transition research and serves as a guide to the construction of a complete and successful theory in the future.

Dielectric spectroscopy on ultrathin polymer films: new approaches and new insights

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Ultrathin polymer films are an intriguing subject in soft condensed matter physics since they often show pronounced effects of the film thickness on their thermo-physical properties. Typical manifestations of such *confinement effects* are marked deviations in the glass transition dynamics and alterations in the visco-elastic properties. For film having no free surface (capped films) or a single free surface (supported films), the specific role of substrate/polymer interactions and the existence of mobility gradients has been established in the last years.

Freely-standing films (FSF), by definition, don’t suffer from potential effects of a solid substrate and appear in fact to be the most challenging polymer film geometry. For polystyrene FSF, spectacular reductions in the glass transition temperature (T_g) by more than 70 K have been reported, however, all experimental results so far are based on density-related (dilatometric) measurements.

The aim of this paper is to present the first successful studies on freely-standing films of PS as measured by dielectric spectroscopy. The investigations rely on a new experimental approach using specifically designed interdigitated comb-electrodes (cf. poster by ROTELLA et.al.) that appears to be sensitive enough to obtain broadband dynamic information on samples in a true FSF geometry. The results from our systematic studies will be presented in detail and basically confirm the consistency between the temperature dependence of the *dielectric α-process* and the dilatometric T_g-data reported by the Canadian groups. First ideas to rationalize this peculiar glass transition dynamics will be discussed.

Johari-Goldstein Relaxation in Glass Forming Flexible Molecules

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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 are some widely studied flexible small molecular glassformers like low molecular weight phthalates [3-4] and benzophenone[5], which, in addition to a fast secondary γ-relaxation due to dipoles coupled to intramolecular 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 benzophenone), 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 [6].

We investigate such suggestion on several glass formers and we report the data on small molecular phthalates *viz.* dimethylphthalate (DMP), diethylphthlate (DEP), diisobutylphthalates (DiBP) and benzophenone by dissolving small quantities of these in apolar glassformers of much higher glass transition temperature, like oligostyrenes or ortho-terphenyl. We were able to move the α-relaxation further away from the γ-relaxation, and find the JG β-relaxation for the first time in these glassformers. Interestingly, the secondary γ-relaxation observed in the mixtures is situated at the same temperature/frequency range as in the neat phase with same activation energy as expected for an intramolecular process [4-5]. Some of these mixtures were studied at elevated pressures: the slower JG β-secondary process moved to lower frequencies on applying pressure giving additional evidence that it of intermolecular origin [7], while the γ-relaxation showing insensitivity to the pressure.

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Distributions of Tgs, Physical Aging Behavior, and Chain Dynamics in Nanoheterogeneous Polymers: Nanoconfined Films, Polymer Nanocomposites, and Gradient Copolymers

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Many types of polymeric materials reportedly exhibit unusual breadth of glass transition response and strong perturbations of chain dynamics at temperatures near and below the glass transition temperature, T_g. Among these include ultrathin supported and unsupported polymer films, polymer nanocomposites containing low levels of well-dispersed nanoparticles, and a novel class of polymers known as gradient copolymers. Here we describe results of our recent novel studies and plans for future investigation related to these nanoheterogeneous polymers.

With thin films, the perturbations of chain dynamics from bulk response are associated with the presence of free surfaces (polymer-air interfaces) that may reduce requirements for cooperativity in dynamics and attractive polymer-substrate or polymer-nanofiller interactions, e.g., hydrogen bonds, that increase requirements for cooperativity in dynamics. When perturbations are dominated by free-surface effects, T_g reductions (relative to bulk T_g) are often observed at thicknesses of some tens of nanometers. When perturbations are dominated by attractive interactions, increases in T_g are commonly reported at thicknesses of up to 100 nm. Using a combination of optically-based experimental investigations (fluorescence spectroscopy and ellipsometry) that in some cases allow for determinations of distributions of responses, we have found that the length scale over which T_g and physical aging response can be perturbed by interfaces can extend well beyond 100 nm. We have also shown that these effects can be nearly eliminated via the inclusion of small levels of low MW diluent molecules in the polymer. A proof-of-principle study will also be described in which dye-labeled polymer is used in conjunction with unlabeled polymer to demonstrate the presence of a distribution of dynamics across the confining dimension of a thin polymer film.

In the case of “real” and “model” nanocomposites, we have found that attractive interactions involving secondary bonding between polymer and nanoparticle or substrate as well as covalent attachment of polymer to nanoparticle lead to large increases in T_g and major suppressions of physical aging response. The latter result suggests a novel application of nanocomposites related to the production of glassy-state polymeric materials that exhibit long-term stable properties. We have also found that the strength of the dielectric response associated with certain dynamics is strongly suppressed in the presence of as little as a fraction of a volume percent of nanofiller, providing insight into the molecular scale origin of the strong suppression of physical aging.

Finally, gradient copolymers (with a composition gradient of comonomers along the length of the copolymer chain) can undergo nanophase separation similar to that of block copolymers but in which the composition profile across lamellae is sinusoidal rather than step-change in nature. We demonstrate the unique glass transition response that can be obtained in such systems and suggest opportunities for study using dielectric spectroscopy.

Making sense of the low-frequency dielectric spectrum

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At the low end of the dielectric spectrum, typically below 1 Hz, charge carrier movement often dominates over dipolar relaxation. This region of the spectrum is sometimes dismissed or overlooked as simply "DC conduction" or interfacial polarisation. Jonscher was particularly keen to show that low frequency dielectric behaviour was important (e.g. [1]) This talk will attempt to show that this sub-hertz region is worth further exploration and may be able to show subtle variations in behaviour that are difficult to observe in other ways.

The talk will provide various examples including:

1. The effect of electrical ageing on printed circuit board substrates; these are epoxy reinforced with "e-glass matting". It is observed that, prior to ageing the activation energy for low frequency carrier movement changes; this is probably due to delamination of the glass from the epoxy [2]
2. The effect of humidity on epoxy containing silica nano-particles. Under certain circumstances, in which water collects around nano-particles a percolation-like conduction behaviour is observed in the low frequency spectrum. However, where water is prevented from accumulating around the particles, a behaviour closer to true DC conduction is observed [3].
3. Insulating oil was studied as it became contaminated with conducting particles. An interesting study was conducted, which included an unusual effect of thickness on capacitance. By consider the low-frequency spectrum it was possible to consider the fractal paths through which conduction took place [4].
4. The ageing of polyethylene is of great interest to electrical engineers in establishing whether extruded power cables, in an aged distribution network, are in need of replacement. It is found that, the activation energy for carrier flow can change reproducibly with cable ageing but also that the slope of the low-frequency dispersion varies with temperature. This is related to the crystallinity of the material [5].

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Dielectric and electrical study of PVC/MWCNT polymer nanocomposites.

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The dielectric and electrical properties of polyvinylchloride-multiwalled carbon nanotube (PVC/MWCNT) nanocomposites in the broad frequency range 10^{-1} to 10^{6} Hz were investigated. PVC/MWCNT nanocomposites with different contents of MWCNT varying in the interval 0.013-0.672 vol. % were prepared by hot compacting. This method enables to create the conductive network around pressed polymer particles. Measurement of DC conductivity σ_{DC} shows a presence of ultralow percolation threshold with value φ_c = 0.045 vol. %. The AC conductivity versus frequency demonstrates percolation character of curves at the same value of φ_c. AC conductivity of pure PVC and nanocomposites with concentration of MWCNT less than 0.054 vol. % increases linearly with frequency which is the characteristic of a dielectric material. However, σ_{AC} of the PVC/MWCNT with high content of MWCNT becomes independent on frequency that indicates the electron type of the charge transport.

The curves of the temperature dependence of σ_{DC} for pure PVC and nanocomposites below φ_c consist of two regions with different values of activation energy. In the first region σ_{DC} increaseas slowly with increasing of temperature. In the second region (at temperature higher of 86^0C) dependence of σ_{AC} on temperature is more considerable. The temperature T=86 ^{0}C is associated with glass transition temperature. The values of σ_{AC} for composites with concentrations higher than φ_c are independent on temperature that indicates the electron type of the charge transport.

Dielectric spectroscopy investigation shows the changes of frequency behavior for $\varepsilon'$and ε'' parameters of composites at transition through the percolation threshold. At concentration from 0.013 to 0.044 vol. % of MWCNT the nanocomposites have a constant ε' and ε'' values for the whole range of frequency. The ε' and ε'' values of nanocomposites with concentration higher than 0054 vol.% decrease with increasing the frequency. The value of ε' of the nanocomposites increase with increasing MWCNT content and temperature. The jump of ε' in the temperature region 100-130 ^{0}C for all nanocomposites corresponds to the glass transition.

Glass transition of ultrathin supported polysulfone films studied by dielectric spectroscopy.

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Broadband dielectric spectroscopy (10^{-2} Hz to 10^{7} Hz) was employed to study the glassy dynamics of ultra thin supported polysulfone layers. The ultra thin films were prepared between two aluminum electrodes. Glass slides, cleaned in an ultrasound alkaline bath, rinsed in pure chloroform, and dried under nitrogen flow, were used as supporting substrates. Thin polymer films were spin-coated from a chloroform solution at 3000 rpm. The film thickness from microns down to below 10 nm was adjusted by changing the concentration of the polymer in solution. After spin-coating, the samples were annealed at a temperature well above the bulk glass transition ($T_{ann}=T_{g,Bulk}+35$ K). As a main result, for carefully annealed samples no change of the glass transition temperature with the decreasing film thickness is observed in contradiction to literature results. A more detailed analysis using a derivative technique shows that the Vogel temperature increases und the fragility parameter decreases with decreasing film thickness.

Further the dielectric strength $\Delta\varepsilon$ decreases with decreasing d. This is discussed by the formation of a surface layer of adsorbed polysulfone segments having a reduced molecular mobility with regard to the time scale characteristic for glassy dynamics of bulk polysulfone. Plotted versus inverse film thickens $\Delta\varepsilon$ decreases linearly with 1/d and becomes zero for an extrapolated length scale of 10 nm. From that it is concluded that the thickness of the adsorbed boundary layer is about 5 nm. It is also shown that preparation details like annealing conditions strongly influences the glass transition of supported ultra-thin films.

Molecular Mobility of molecules in nanoscale confinement and close to surfaces.

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During recent years the investigation and understanding of the behavior of molecules in nanoscale confinements and close to surfaces attracts a growing interest. From the point of basic research the influence of finite size effects on the structure and dynamic of matter can be investigated experimentally and compared with theoretical approaches. On the other side the confining of molecules to nanopores is of importance for many practical applications for instance in chemistry and medicine.

Dielectric spectroscopy in the frequency range from 10^{-2} Hz to 10^{9} Hz is employed to study different systems:

1. The unusual relaxation behavior of water molecules confined to nanopores and to layered structures.[1-4]
2. Molecular dynamics of liquid crystals confined to the nanopores of molecular sieves with different pore sizes.[5-7]
3. Molecular fluctuations of molecules adsorbed nearly in a monolayer onto the surface of silica nanoparticles[8-10]

In several cases the results obtained by dielectric spectroscopy are compared with data from broadband specific heat spectroscopy and inelastic / quasielastic neutron scattering.

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Dielectric and Mechanical Properties of Polylactide and its Nanocomposites with Montmorillonite

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Influence of preparation method on dielectric properties of polylactide and its nanocomposites with an organoclay (Cloisite® 30B) is investigated. The samples obtained by solution casting and hot pressing are compared. Two types of not compatibilized nanocomposites containing 3wt% or 10wt% of the organoclay were studied to reveal the effect of the filler concentration on the nanostructure and physical properties of such systems. The 3wt%-nanocomposite was also additionally compatibilized in order to improve the nanoclay dispersion.

Polylactide with the compatibilizer processed in similar conditions were also studied. X-ray diffractograms showed the presence of exfoliated nanostructure in 3wt%-nanocomposite. Compatibilization of such system noticeably enhanced the degree of exfoliation of the organoclay. Dielectric properties of the nanocomposites show a weak influence of the nanoclay on segmental (α_S) and local (β) relaxations in PLA, except for the highest nanoclay content. Above T_g a strong increase of dc conductivity attributed to ionic species in the clay is observed. It gives rise also to the Maxwell-Wagner-Sillars interfacial polarization and both real and imaginary parts of ε strongly increase.

In the temperature dependence of low frequency dielectric constant and mechanical moduli (at 1 Hz) an additional maximum around 80-90 ^{0}C is observed due to cold crystallization of PLA. Viscoelastic spectra (DMTA) also showed an increase of the storage and loss moduli with the increase of the organoclay content and dispersion.

Glassy dynamics of proteins and effects of solvents: the case of spider silk

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Spider silk is one of the toughest known materials, composed of two high-molecular-weight proteins, rich in alanine and glycine. Several studies have revealed a semi-crystalline nanostructure, where alanine-rich crystals are interconnected by glycine-rich amorphous chains [1]. The dominant controlling factor of the mechanical properties is the molecular order and the dynamics of the matrix. Mechanical studies suggest the existence of relaxation processes with long characteristic times at room temperature [2], which may be sigificantly affected by temperature and humidity [3]. These findings suggest that the matrix is glassy [4], similar to synthetic semi-crystalline polymers. It is evident that the complete understanding of silk properties requires the study of its relaxation. In addition, reproducing the spinning process also requires the study of peptide solutions.

Dielectric spectroscopy is one of the most frequently employed techniques for the study of glassy systems, because it can be applied to very broad frequency and temperature ranges. Our previous studies on a series of polyaminoacids and aminoacid block copolymers, including poly(L-alanine) and polyglycine which are similar to spider silk proteins, revealed that the „glass transition“ is an intrinsic feature of these systems, independent of the presence of solvent [5][6]. Here we show that spider silk exhibits a T_g in the same temperature range. In addition, we trace the effects of solvent to model polypeptides. Small amounts of solvent lower the T_g of the system, which maintains a single relaxation process associated with the glass transition, reflecting the flexibility of the peptide backbone. At higher solvent concentrations two separate T_g's are observed, corresponding to the solvent and peptide. These effects may help understand silk spinning process and „supercontraction“, that is the shrinking after wetting.

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Ac conduction in the extreme disorder limit takes place on the percolating cluster.

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We first briefly review the phenomenon of percolation in general. Then the role of percolation in determining the dc conductivity activation energy for the case where the barriers vary very much is reviewed. This is done be reference to the random barrier model, that is the reference point throughout the paper. This model is characterized by five simplifying assumptions: 1) All charge carrier interactions including self-exclusion are ignored; 2) Charge carrier motion takes place on a cubic lattice; 3) All lattice sites have same energy; 4) Only nearest-neighbor jumps are allowed; 5) Jump rates have random activation energies with. The main focus of the talk is on ac conduction, which is know to be universal in the extreme disorder limit, i.e., when the jump rates cover many orders of magnitude [1]. Traditional approaches for rationalizing the role of the percolation cluster are reviewed; these focus on finite clusters of high jump rate links and their statistics. In contrast, it has been proposed that these are not important for understanding the universal ac conductivity, but that this take place almost exclusively on the infinte percolating cluster (like the dc conductivity) [1]. This has very recently [2] been confirmed by extensive computer simulations that are detailed in the talk. Contrary to the previous belief that only some unspecified subset of the percolating cluster is important for the universal ac conductivity, we now find that in fact the entire percolating cluster is important. This gives rise to an excellent analytical approximation the universal ac conductivity with no fitting parameters except overall scalings of frequency and conductivity.

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Maxwell-Wagner ferro- and piezoelectrets - Heterogeneous dielectrics with interface charges for transducer applications

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Polymer-based piezoelectrics (and pyroelectrics) come in several different types:

(1) Semi-crystalline polar polymers such as polyvinylidene fluoride (PVDF) and some of its copolymers as well as some polyamides exhibit useful piezoelectric coefficients if their “hard” crystalline phase is ferroelectric so that the dipole density within the “soft” amorphous phase changes upon mechanical or electrical stressing (“secondary piezoelectricity”).

(2) Micro- or nano-composites of “hard” inorganic ferroelectric particles e.g. from lead zirconate titanate (PZT) or barium titanate (BT) in a “soft” highly insulating polymer matrix exhibit the same dipole-density effect, but also a significant stress dependence of the polarization in the ferroelectric particles themselves (“primary piezoelectricity”).

(3) Cellular-polymer ferroelectrets [1] contain internal voids with bipolar space charge. When these “man-made” dipoles are mechanically or electrically deformed, direct and inverse piezoelectricity is observed (a new variant of “primary piezoelectricity”).

Here, we discuss a further concept: “Hard” disks (e.g. platelets) of an inorganic dielectric such as silicon dioxide or mica are dispersed in a “soft” highly insulating polymer matrix, and bipolar charge layers are deposited at the internal interfaces between the two components [2]. This concept is an extension of the previously demonstrated two- and multi-layer sandwiches of “soft” and “hard” dielectrics with interface charges. In contrast to cellular ferroelectrets [3], the “man-made” dipoles of the new piezoelectrets are the “hard” phase so that the material exhibits essentially only “secondary piezoelectricity” (dipole-density effect). In contrast to polymer composites with ferroelectric particles, the dipoles of the new piezoelectrets originate from interface charges. An electric polarization from such interface charges has long been known as Maxwell-Wagner polarization, but is usually not considered to be useful. Consequently, the new materials, whose applications-relevant properties are based on this often unwanted polarization, may be called “Maxwell-Wagner piezoelectrets”.

The fundamental relations for piezoelectricity in heterogeneous soft-hard two-phase systems will be considered. Examples of possible materials concepts and their relevance for transducer applications will be briefly discussed.

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The molecular dynamics in PVME hydrogels at sub-zero temperatures

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Stimuli-responsive hydrogels are a group of materials especially promising for their potential application in pharmacy, medicine and cosmetics [1, 2]. Hydrogels prepared of poly (vinyl methyl ether) (PVME) are interesting due to a volume-phase-transition which they exhibit at ca. 37°C [3]. Solutions of PVME reveal also peculiar, not still fully understood, properties in sub-zero temperatures, resulted from water-polymer interactions [4-7]. When crosslinked by mean of electron-beam irradiation (which also sterilises system in one-step procedure [8]) the obtained hydrogel exhibits more complex supramolecular architecture than the simple solution. Knowledge of their molecular dynamics as well as of the intermolecular interactions constitutes a crucial aspect in understanding the structure-properties relationship allowing to design and synthesize materials of desired properties.

Presented work concern molecular dynamics in series of PVME hydrogels crosslinked by different doses of irradiation i.e. different crosslinking degrees. Molecular relaxations in these systems were investigated with use of Broadband Dielectric Spectroscopy (BDA) in the temperature range: -100 ÷ +50°C and Dynamical Mechanical Analysis (DMA) (temperature range: -150 ÷ +5°C). Both applied techniques revealed presence of the processes of the polymer as well as of water origin. Correlation between processes observed in BDS and DMA was found. What is more, with use of Differential Scanning Calorimetry (DSC) the amounts of bounded water in studied hydrogels were estimated. Raman spectroscopy measurements in a temperature range: -173 ÷ +50°C enabled to correlate the observed relaxation processes with the changes in water-polymer and water-water intermolecular interactions.

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Analysis of interfacial polarisation relaxations in conducting composite films using the Maxwell-Wagner-Hanai effective medium theory

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A new approach to explain the interfacial polarization phenomenon in conducting composite films is proposed. Poly(ethylene terephthalate) (PET) and polyamide-6 (PA-6) matrices with embedded polyaniline (PANI) particles as filler were investigated and analyzed, combining dielectric spectroscopy, Raman spectroscopy and AFM electrical images with the effective medium theory (EMT) analysis. Up to three relaxation peaks attributed to the interfacial polarization phenomena were detected in the studied frequency range (0.1Hz-1MHz) consequently to the HCl doping process [1]. A double layered structure for both films was found by Raman spectroscopy: a conductive composite layer with PANI clusters distributed in the matrix and a pure matrix layer. The AFM electrical images revealed that the doped PA-6/PANI composite layer can be modelled as a single-type particle medium and the PET/PANI one as a two-type particle medium. A simple dielectric loss expression was derived from the Maxwell-Wagner-Hanai's (MWH) mixture equation [2] and was applied to the experimental data to identify the interfaces involved in each of the relaxation peaks. The parameter values (permittivity, conductivity, volume fraction of the PANI particles) were found to agree well with the measured one and hence validated the models.

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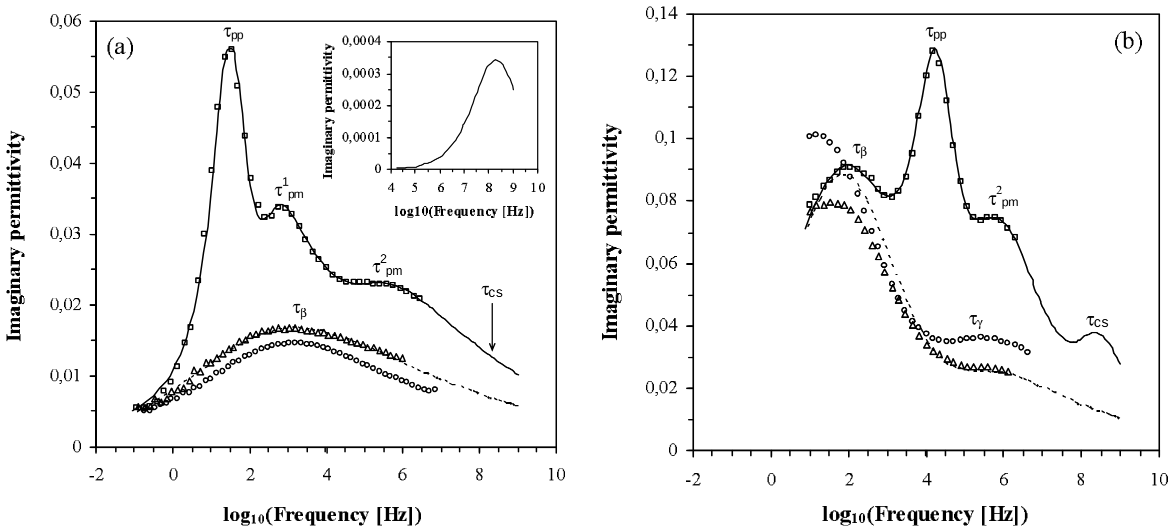

Figure 1: Frequency dependence of the imaginary permittivity at 233K: the PET (a) and the PA-6 ((b) based samples;: Δ Virgin film; ○ dedoped matrix/PANI layer; □ HCl-doped matrix/PANI layer; — Model;

Dielectric dispersion and ionic conduction behaviour of montmorillonite clay loaded poly(vinyl pyrrolidone)−poly (ethylene glycol) blends

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The pressure-sensitive adhesive properties of poly(vinyl pyrrolidone)−poly(ethylene glycol) (PVP−PEG) blends find their extensive use in pharmaceutical, biological and medical applications [1]. The molecular dynamics, H-bond interactions and ionic conduction behaviour of the PVP−PEG blends have been explored by broadband dielectric measurements [2-4]. The montmorillonite (MMT) clay loaded polymers results polymer-clay nanocomposites and have remarkably enhanced physical and mechanical properties of the materials [5,6]. In the present paper the dielectric dispersion of MMT clay loaded PVP−PEG blends were investigated over the frequency range 20 Hz to 1 MHz. The 10 wt% PVP concentration blend of PVP−PEG is used. The 1, 2, 3, 5 and 10 wt% MMT clay concentration of the weight of PVP was added for the preparation of MMT clay loaded PVP−PEG blends. The dielectric dispersion, ac conductivity, electric modulus and impedance properties plots of these blends shows the relaxation processes corresponds to PVP segmental motion, ionic conduction and electrode polarization phenomena. The dc ionic conductivity, ionic conductivity relaxation time, polymer segmental relaxation, and electric double layer (EDL) dynamic relaxation time, have been evaluated for these blends. It is observed that the addition of 10 wt% PVP in PEG reduces the dc conductivity and increases the ionic conductivity and EDL relaxation times. The loading of clay in the PVP−PEG blends linearly increases the dc conductivity with clay concentration and simultaneously reduces the ionic conductivity and EDL relaxation times. Results suggest that the loading of MMT clay in PVP−PEG blend provides a convenient way to obtain a composite material with tailored ionic conduction properties. The dielectric behaviour of the blends were discussed by considering the hydrogen bond formation between the hydroxyl groups (–OH) of PEG, carbonyl groups (C=O) of PVP monomer units, and the –OH groups of the clay sheets surfaces in the MMT loaded PVP−PEG blends.

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Structural studies of sodium montmorillonite layers in polymer/clay mineral nanocomposites

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The aim of the study was to determine structural differences in tetrahedral and octahedral sodium montmorillonite layers arrangements in polymer/clay mineral nanocomposites [1]. Synthetic and naturally occurring clay minerals were used for nanocomposites synthesis. The ^{27}Al, ^{23}Na MAS NMR and FTIR spectroscopy were applied to characterize the investigated system [2]. The structure changes connected with polymer intercalation into the sodium montmorillonite galleries were studied by the spectral position of Al and Na NMR lines and spectral parameters of Si-O stretching vibrations bands analysis. We have observed that polymer molecules do not affect aluminum ions in the octahedral layers of the clay but influence rigidity of the tetrahedral layers. The structure of tetrahedral and octahedral layers in pure synthetic and natural sodium montmorillonites are fundamentally different. This phenomenon is connected with thermal history of the system [3]. The ^{23}Na NMR spectra studies indicate two different sodium ions environments in the nanocomposite samples. First arrangement is connected with the sodium ions with a close contact with polymer, second one occurs as bulk ions in the clay gallery. Sodium ions perform a role of the nanocomposite structure stabilization or take part in ion-exchange processes which lead to polymer intercalation in the clay structure.

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The diverse effect of plasticizer in the molecular dynamics of organic dye-doped polymers observed at different lengthscales

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The solid-state dye laser performance largely depends on the dye-matrix interactions at the nanoscopic scale. The current work deals with blends of a comparatively inert dye host, poly(methyl methacrylate) (PMMA), with non-ionic/apolar (substituted perylenes) and ionic/polar (Rhodamine 6G, Pyrromethene 567) dyes at $\approx 10^{-4}$ mol L^{-1} loading. Differential scanning calorimetry (DSC) and thermally stimulated current (TSC) were used to explore the relative strength of inter- and intra-molecular guest-host interactions by monitoring blending-induced modifications of the high-temperature signals: the segmental relaxation, the space-charge relaxation and the liquid-liquid transition. Both techniques revealed the anti-plasticising role of the oligomeric organics on the relaxation dynamics of polymer segments, evidenced by clear glass-transition temperature upshift. This is in contrast to the observed plasticization of the low-temperature relaxation mechanisms of PMMA, observed by TSC. It becomes apparent that the above effects are independent of the size, polarity and ionicity of the dopant, signifying a common mechanism underway. It is suggested that, at least for the dyes under investigation, the chromophores simply fill the voids within the matrix, imposing strong steric hindrances on the rearrangement of the long-range structure.

Studies of molecular dynamics in composites of carboxylated acrylonitrile-butadiene rubber containing silica

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Rubber additives are used in order to improve its properties, such as tensile strength, wear resistance, performance and processing. In many applications additives are fillers like silica, carbon black or zinc oxide, cross-linking agents, dispersants and anti-degradants.

Filler particles are mostly composed of the primary particles but can be strongly bonded to other primary particles to form aggregates and agglomerates. The dispersion of silica, especially that having very fine particles is difficult. Even a prolonged effort to grind materials does not result in a change of their aggregates' size. Forces holding individual particles together are sufficiently strong to resist even under very intensive grinding or mixing. Agglomeration processes are very complex in nature but their prevention is necessary for the design of reinforced rubber. Numerous efforts have been made in order to obtain homogenous dispersion of primary particles in polymer matrix. Using the coupling agents, surfactants or synthesis of silica in situ, are the most common examples.

Within this research silica filler particles were synthesized directly in an elastomeric matrix by the sol-gel process [1-5] using N-2-aminoethyl-3-aminopropyltrimethoxysilane. Furthermore, the amino groups on the alkyl substituents of the silane acted as the cross-linking moieties for the carboxylated acrylonitrile-butadiene rubber.

It was of interest to determine the mobility of the system crosslinked with ionic bonds, created by the interactions of amino groups of the silane and carboxyl groups of the rubber. Moreover, the subsequent hydrolysis and condensation reactions of methoxy groups provided the silica filler with better dispersion when compared to the composites containing the silica added during the preparation of rubber mixes. In this work we discuss the molecular dynamics of the obtained organic-inorganic hybrid materials by means of the dynamic mechanical and dielectric analysis.

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Molecular dynamics of perfluoropolyethers with medium-low molecular weight

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Perfluoropolyethers (PFPEs) are the family of medium-low MW polymers composed entirely of carbon, fluorine and oxygen atoms. These compounds exhibit liquid phase behaviour over very wide temperature range (-100°C to 450°C) and possess high thermal oxidative stability, low volatility, nonflammability, excellent tribological properties, high transparency in far UV region, biological inertness etc. PFPEs found application in a number of diverse and demanding applications such as: high vacuum pump fluids, lubricants for jet-engines, turbines and recently for magnetic recording media and satellite instrumentation. Hydrophobic and lyophobic nature of these compounds render them suitable for use in biomedical and cosmetic products

Number of commercially available linear and branched, nonfunctionalized PFPEs namely: Krytox, Fomblin Z, and Fomblin Y products of DuPont and Solvay-Ausimont respectively has been studied. Functionalized polymers such as Krytox-OH, Fomblin ZDOL (PFPE diol) and Galden H-(dihydroperfluoroether) were also investigated. Finally three new lubricants/additives: X-1P, X-100 (X-Lube) and A20H (Moresco) were included. The last mentioned compounds are derivatives of cyclotriphospazene molecule.

Molecular dynamics in these systems were investigated by means of dielectric relaxation spectroscopy (DRS). Glass transition temperatures were determined by differential scanning calorimetry (DSC). In the DRS spectra, for the investigated materials one can distinguish generally three relaxation processes. At the lowest temperature range the subglass relaxation attributed to the local motions is observed. The α-relaxation seen at higher temperature is related to their glass transition and is in good agreement with the DSC results. At the highest temperature range the normal mode correlated with the flow of the materials is observed. This last one in some materials is hidden by the ionic conductivity process. The PFPE materials have generally very low dielectric constant, which depends strongly on the chemical structure of these materials. The incorporation of the hydrogen atoms instead of fluorine in the end groups is enough to increasing the dielectric constant from 2,5 to 5 at room temperature. Also the molecular relaxation strongly depends not only on the chemical structure but also on molar mass. The differences in the glass transition in this family are even tens degrees. So the desirable properties can be tailored by only slight change of structure.

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Structure and dielectric studies of nano - composite Fe_2O_3: $BaTiO_3$ prepared by sol-gel method

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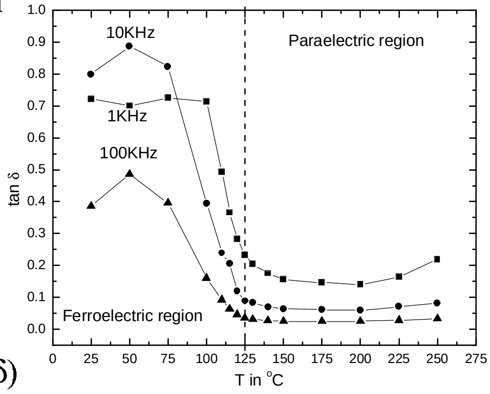
Abstract

Nano-structure pure barium titanate ($BaTiO_3$) and that was doped with 30 % of iron oxide (Fe_2O_3), have been prepared by sol-gel method, using barium acetate (Ba(Ac)2) and titanium butoxide (Ti(C4H9O)4), as precursors. The as-grown prepared samples by sol-gel technique were found to be amorphous, which crystallized to the tetragonal phase after synthesized at 750°C in air for 30 minutes as detected from the XRD patterns. The XRD data were confirmed by transmission electron microscope (TEM). The dielectric properties namely; dielectric constant and loss tangent (tanδ) in the frequency range between 42 Hz and 1 MHz, at range of temperature 25°C-250°C were investigated. The temperature dependence of tanδ for $BaTiO_3$ at 1 KHz, 10 KHz and 100 KHz is shown in the presented Figure. tanδ increased rapidly with decreasing temperature below 125°C (Curie temperature), see the vertical dashed line. While above this temperature, tanδ shows temperature independent. As a result, below and above Curie temperature, ferroelectric phase and paraelectric phase of $BaTiO_3$ can be obtained, respectively.



Dielectric and conductivity behaviors in $CaCu_3Ti_4O_{12}$ Glass

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We have investigated the frequency and temperature dependence of dielectric properties for the $CaCu_3Ti_4O_{12}$ (CCTO) glass. CCTO crystal has a cubic perovskite structure, nonferroelectric characteristics, and has attracted attention because it has ultra high dielectric constant, showing relaxor behavior. While investigations on the dielectric response, impurity and grain boundary effects of the CCTO polycrystalline ceramics have been reported, there has been a lack of the study for the CCTO glass. We have achieved the CCTO glass by using the twin roller quenching method. The frequency dependence of the electrical data has been analyzed in the frameworks of the universal power law and the impedance Cole-Cole plot. We have observed a broad dielectric peak with dielectric constant ~10^2 over the wide temperature range above room temperature in a glass state. Activation energy of electrical conduction obtained from the distribution of the relaxation time in the Cole-Cole formalism is similar to the value 0.36 ~ 0.52 eV of the power law, indicating that both methods provide information to demonstrate the conduction and dielectric relaxation mechanisms for the CCTO glass.

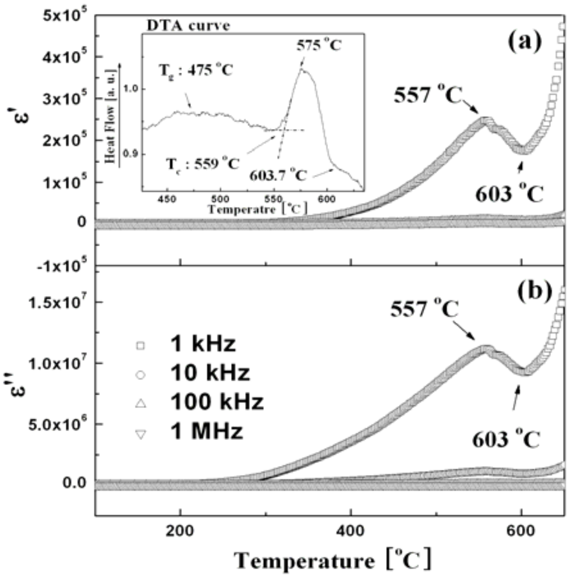

Figure: Temperature dependence of dielectric constant for (a) the real and (b) imaginary parts of $CaCu_3Ti_4O_{12}$ glass. The inset is the differential thermal analysis curve and shows a glass state below the crystallization temperature T_c = 559 ℃.

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Theory of Dielectric Permittivity of Mixtures of Polar Substances and its application to Studying Supramolecular Ordering in Mixtures

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The extension of the Fröhlich's approach on permittivity and dipole correlation factor of the individual liquids [1] to mixtures of polar substances given for the first time in [2,3] with applications to studying supramolecular organization of liquid solutions has been considered. The Eqn. (1) for the permittivity of the mixtures obtained [3] is as follows

$$\frac{9k_BTV_m}{4\pi N_A\varepsilon_S}\sum_{j=1}^{k}\left(\frac{\varepsilon_S-\varepsilon_{\infty j}}{2\varepsilon_S+\varepsilon_{\infty j}}\right)\varphi_j^o=\sum_{j=1}^{k}\left(\frac{\varepsilon_{\infty j}+2}{2\varepsilon_S+\varepsilon_{\infty j}}\right)^2 x_j^o\mu_j^2 g_j^{dip}. \tag{1}$$

In Eqn. (1) k_B, N_A are the Boltzmann constant and Avogadro's number, T - temperature, V_m, ε_S - the molar volume and permittivity of the mixture, $\varepsilon_{\infty j}$, φ_j^o, x_j^o - the deformation permittivity, volume and molar fraction of the j-th component, μ_j and $g_j^{dip} = <\boldsymbol{\mu}_j\boldsymbol{\mu}_j^*> /\mu_j^2$ ($j = 1,2,...,k$) are the dipole moment and the correlation factor of the j-th component.

The analytical expressions for g_j^{dip} (1), which relate them to structural parameters of chain-like aggregates of arbitrary composition and thermodynamics of their aggregation in the mixtures, were obtained in [2]. At present the results on g_j^{dip}, Eqn. (1) [2] are considered in the framework of the Quasichemical Model of Non-Ideal Associated Solution (QCNAS) (see, e.g., [4, 5] and refs. therein).

This approach has been developed and tested in application to dielectric as well as to thermodynamic, optic and kinetic properties of liquid mixtures with complex supramolecular organisation (chain-like, cyclic, branched comb-like and star-like aggregates) in the whole composition range of the mixture and in the wide temperature and pressure intervals (from melting point to supercritical conditions) [4-6].

The results on analysis of the permittivity of mixtures with different types of supramolecular ordering up to nanoscale range are discussed. The supramolecular aggregates with long-range molecular correlations have been revealed at the common parameters of the state. The structure and thermodynamics of their formation have been studied in detail.

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Semiconducting Properties of Passive and Oxide Films Formed on Stainless Steels

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Thin passive and oxide films are formed on AISI 304 stainless steel and in-situ investigated by different spectroscopic techniques. The Auger Electron Spectroscopy (AES) show that the films are in all cases composed by an inner region of a mixed chromium-iron oxide and an external region of iron oxide. In other part, the potential formation does affect the distribution of elements within the oxide. However, the outer layer of the film is essentially formed of Fe_2O_3 thin oxide. The Electrochemical Impedance Spectroscopy (EIS) show that the films can be represented by an equivalent circuit composed of different resistances and capacitances. The investigation of the frequency dispersion was performed by analysing the Bode plots through the impedance measurements. In other part, the impedance results as the applied potential indicate that the electronic structure of the films is comparable to that of a p-n heterojunction. This structure is due to the development of space charge layers in the outer iron oxide region at the film/electrolyte interface and in the inner chromium oxide region at the film/metal interface. The photoelectrochemical impedance spectroscopy results show that the films present the same photoresponse variation as the applied potential and the incident energy light revealing behaviour similar to that of semiconductor electrodes. However the quantum efficiency values markedly change with the formation conditions (potential, temperature,…). The electronic structure of these films can be discussed on the base of spinell oxide with a very thin lattice. These considerations can be applied and translated to the nano-materials concept.

Broadband Electrical Conductivity of Polymer Nanocomposites based on Carbon Nanoadditives

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A nanocomposite can be defined as a nanofilled system in which the total interfacial phase becomes the critical parameter instead of the filler concentration[1]. The electrical conductivity of the nanocomposite varies from that of the polymer matrix to that one of the carbon additive depending on the additive concentration due to the formation of a percolative network of the conducting additive at a certain critical concentration. Low percolation critical concentrations are highly desirable in order to remain as close as possible to the mechanical properties of the polymer matrix. In the past a lot of attention has been devoted to polymer composites based on carbon black[2,3]. More recently, polymer composites based on carbon nanoadditives, either carbon nanofibres(CNF) or carbon nanotubes(CNT) have begun to be intensively investigated mainly due to the particular properties of nanocomposites as compared with those of traditional composites. The small diameter and the high aspect ratio of both CNF and CNT favour percolation at very low concentrations[4-8]. Both the direct current (dc) and the alternating current (ac) electrical conductivity of polymer nanocomposites based on multi wall carbon nanotubes (MWCNT) and single wall carbon nanotubes (SWCNT) has been recently discussed[4-8]. Different conduction models, including anomalous diffusion in percolating clusters and hopping, have been proposed to explain the frequency dependence of the conductivity on CNT-nanocomposites. However a clear picture about the conduction mechanism in nanocomposites is still under discussion. In this talk broad band (up to 10^9 Hz) electrical conductivity data of two families of polymer nanocomposite based in either MWCNT or CNF will be presented and discussed. By comparing the broad band electrical conductivity of the two systems information about the conduction mechanism in nanocomposites with carbon additives can be extracted[9].

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Dielectric phenomena of organic-inorganic polymer systems during polymerization and in solid state

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Organic-inorganic polymer systems (OIS) are the perspective material for electrical industrial applications [1, 2] due to their properties owing to the specific chemical structure of OIS that includes chemically bonded organic and inorganic blocks [3, 4]. In accordance to that the studies of their electrical and dielectric properties take one of the main parts of investigations of OIS. In the present work the changes of dielectric parameters (ε', ε'' etc) and electrical characteristics (σ_{AC}, σ_{DC} etc) during OIS polymerization and in solid state depending on chemical structure were fulfilled.

OIS were obtained in the reactive mixture as a result of reaction between the organic component, which contains free isocyanate groups, with metal silicate (MS), that was used as inorganic component. Organic component of OIS was the mixture of two isocyanate-containing products: urethane oligomer (UO), with 3,6% of free NCO-groups, and isocyanate-containing modifier (IM), which contains 32 % of free NCO-groups. Using of a mixture of UO and IM enables to vary the content of NCO-groups in the organic component and therefore to change the OIS structure.

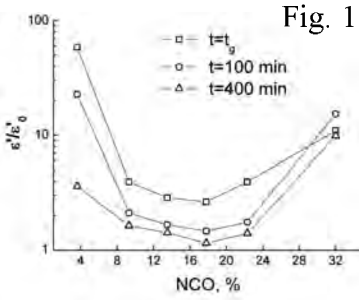

Fig. 1

In **figure 1** the changes of dielectric permittivity ε'/ε'$_0$ (where ε'$_0$ – the dielectric permittivity of cured system) during polymerization depend on content of free NCO-groups are shown. As it is obvious, the non-monotonic dependencies of electrical parameters with increasing of the content of NCO-groups were found. This tendency was explained by specific reactions which run between reactive groups of organic and inorganic components. **Figure 2** demonstrates dependencies of ε' and tan δ on content of NCO-groups. In the range of NCO-groups content equal to 3.6-17.8 % the values of ε′ and tan δ sharply decrease, and within the interval of 17.8-32 % they become constant. Such effect was explained by the presence of two types organic-inorganic interpenetrating networks, which are formed in OIS with phase inversion in a sample with 17,8% of NCO-groups.

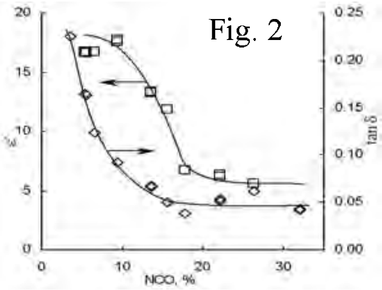

Fig. 2

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Study Of Confinement In Semi-Crystalline Polymers

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The mobility of the semi-crystalline polymers has been studied by several authors [1,2], but the link between cristallinity and confinement of the amorphous phase by the crystalline lamellae is not yet completely clear. In this study the behaviour of Poly(ethylene-2,6-naphthalate) (PEN) will be studied. The samples of PEN were crystallized from the glassy state at different crystallisation temperatures during different crystallisation times [3,4]. The link between crystallinity and molecular mobility is discussed in order to see the influence of confinement, using the results of BDS, SAXS, WAXS and DSC. It appears that the molecular mobility of the crystallized samples is lower than the amorphous sample mobility (Fig.1,2). For the lower crystallisation temperatures (165°C ($X_c \approx 26\%$) and 180°C ($X_c \approx 28\%$)), Tα increases with the crystallization time (Fig. 1). For higher crystallization temperatures (220°C ($X_c \approx 32\%$) and 245°C ($X_c \approx 33\%$)), Tα is less sensible to the crystallization time (Fig. 1). The SAXS measurements confirmed these results: at high crystallization temperatures the amorphous thickness is higher than the amorphous thickness of the samples crystallized at lower temperatures. This means that the amorphous phase is more confined for the low crystallization temperatures and that is the reason why the mobility is more affected in this case.

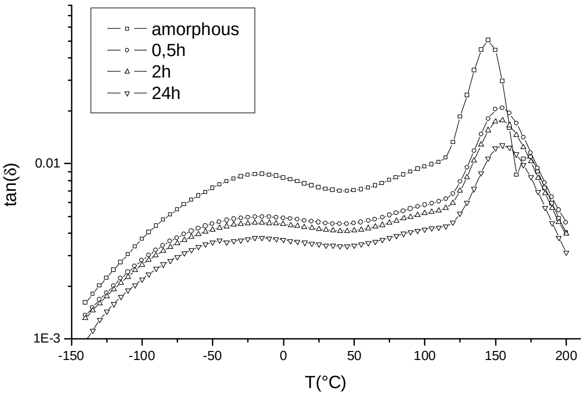

Fig. 1: Tan(δ) versus temperature for PEN crystallized at 165°C (a) during 0.5, 2 and 24h (f = 1950Hz)

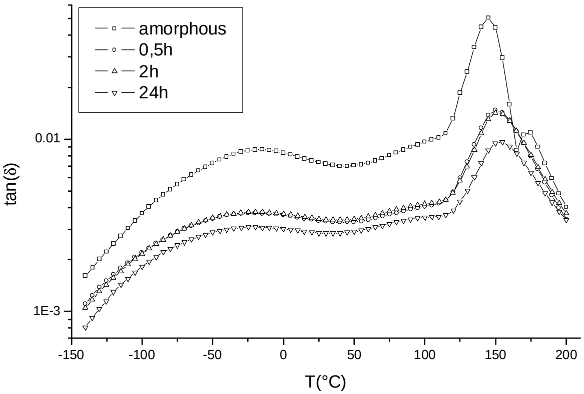

Fig. 2: Tan(δ) versus temperature for PEN crystallized at 245°C during 0.5, 2 and 24h (f = 1950Hz)

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Molecular Mobility At The Interfaces Of Nanostructured Systems

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As nowadays nanostructured systems are more and more used in industry, the organisation of polymers in the nanometric scale has to be better understood. The molecular dynamics of these systems has not been clarified yet, especially in the interfacial regions. The Broadband Dielectric Spectroscopy is an interesting method to evaluate the molecular mobility of these systems. In this work two systems have been studied: nanocomposite films (PA6/MMT and PLA/MMT) and ultra thin films of PLA. The films of PA6 filled MMT (6, 10 and 13%) are obtained by extrusion and a Novocontrol Concept 40 α-analyzer, interfaced to the sample by a Broadband Dielectric Convertor (BDC, Novocontrol), was used to measure the complex dielectric function. It results from this study that the mobility of the polymer varies with the filler fraction and that for the filled samples a new MWS relaxation appears due to the interfaces (Fig.1) [1]. The films of PLA are obtained by pressing the compounds (PLA filled with 3% MMT) at 200°C for 5 minutes and then quenching them in iced water [2]. In this case there is no significant difference between the neat sample and the composites because of the low filler content.

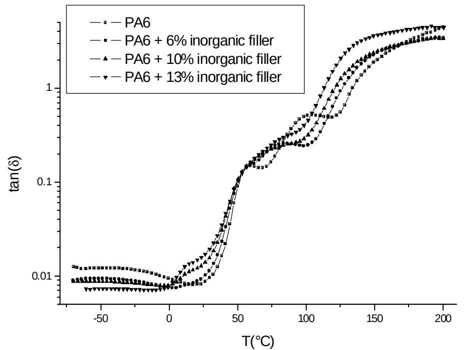

Fig.1: Tan(δ) versus temperature for PA6 compounded MMT at 1950Hz

The dielectric spectroscopy of thin films of PLA was carried out on interdigited electrodes. The films were obtained by spin-coating and the thickness was measured by AFM. This study showed a slowing down mobility for the thin film compared to the mobility of the bulk (Fig.2) [3].

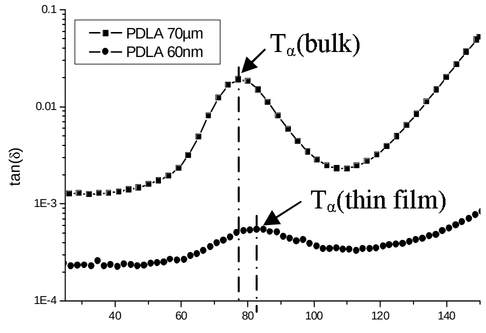

Fig.2: Tan(δ) versus temperature for PDLA thin film and bulk at 122Hz

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Dielectric study
Of macromolecular interactions in wood

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As the most common form of biomass, wood concentrates suddenly a high interest. One of the problems encountered with this biocomposite is the strong interactions between the various components - cellulose, hemicellulose and especially lignin - .Consequently, biotechnological researches are focused on the modification of the lignin content. A complementary approach is to improve the knowledge of the physical structure of wood. Developments of dielectric spectroscopies allow us to perform an investigation of the supramolecular organization in cell wall i.e. cellulose, via inter and intra molecular interactions.

Dielectric measurements performed in a very broad temperature and frequency range take advantage of dipolar species whose relaxations are characteristic of order at a nanometric scale. In this work, Thermo Stimulated Current (TSC) analyses combined with Dynamic Dielectric Spectroscopy (DDS) have been applied to the investigation of molecular mobility in poplar cell wall [1] in comparison with its major macromolecular components (cellulose, hemicellulose, and lignin)

The molecular origin of the various dielectric relaxations has been determined], [2]. The influence of hydration on cellulose molecular mobility has been investigated at different molecular scales. Cellulose and lignin contributions in wood dielectric response were distinguished. The correlation between results obtained by both dielectric methods allows us to follow molecular mobility involved in delocalized movement as primary relaxation mode. For these two major components of wood, the evolution of relaxation times involve in α relaxation mode is explained using the strong/fragile pattern. We compared the cellulose and lignin *in-situ* and *ex-situ* responses to interpret wood compound behaviour. The importance of structural wood interactions which modified the molecular mobility of polymer components will be underlined.

Such investigations based on the analysis of molecular mobility involved in phase transitions and dielectric relaxations exhibit the major role of macromolecular interactions on macroscopic functionality of this highly complex polymeric biocomposite.

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Electrical Properties of Polymer Nanocomposites based on Poly(butylene terephthalate) from Cyclic Butylene Terephthalate and MWCNT

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Nanocomposites containing carbon nanotubes (CNTs) are of a great interest nowadays. Due to the complex of their unique properties (semiconducting, electromagnetic, optical) they attract much attention in industrial world. It has been found that nanofilled polymer composites also exhibit remarkable improvement of thermal, mechanical and physicochemical properties when compared with pure polymers and their conventional microcomposites, even at very low filler concentrations due to the nano-level interactions with the polymer matrix [1]. In the present work the Cyclic Butylene Terephthalate oligomers (CBT) were used in reason of very low viscosity of their melt that can promote a good dispersion of nanoparticles. Under the action of heat and catalyst CBT converts to linear Poly(butylene terephthalate)–cPBT [2]. The Multi-Walled Carbon Nanotubes (MWCNT) were mixed with CBT for preparing of conductive polymer nanocomposites [3].

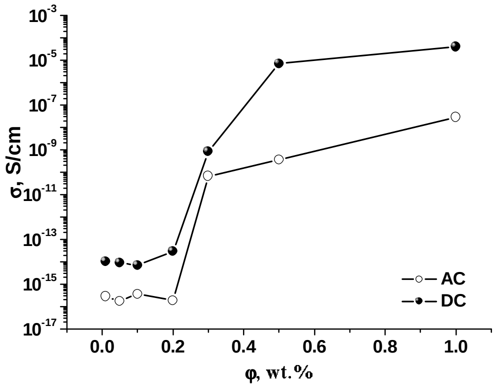

Figure 1: The percolation threshold for cPBT/MWCNT

Before processing CBT and MWCNT were dry mixed by intensive shaking in order to break the agglomerates of nanotubes. The samples have been processed in twin-screw DSM laboratory miniextruder at 230°C with screw rotation 100 min^{-1} during 10 min and then pressed at 240°C under the pressure of 90 Bar. MWCNT concentration in composites was varied from 0.01 to 1 wt. %.

The samples of nanocopmosites prepared have been characterized by dielectric measurements carried out on Keithley 237 High Voltage Source Measure Unit (direct current measurements) and the results were compared to those of alternative current measurements performed on Broadband Dielectric Spectrometer Novocontrol. The measurement results are represented on Fig.1. The dielectric measurements shows a percolation threshold equal to 0,3 wt. % of MWCNT.

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Finite size effects in ferroelectric BaSrTiO$_3$ doped with Fe$_2$O$_3$ prepared by sol-gel technique.

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Nano-structure BaTiO$_3$ and Ba$_x$ Sr$_{1-x}$ TiO$_3$ have been prepared by sol- gel technique in powder and thin film forms, using barium acetate (Ba(Ac)$_2$), and titanium butoxide (Ti(C$_4$H$_9$O)$_4$), and strontium bromide as precursor materials. The powders prepared by sol-gel technique were found to be amorphous, which crystallized to the tetragonal phase after synthesized at 750^{o}C in air for one hour. The crystallite sizes of both samples, was found to be in the nanometer range. The XRD data were confirmed by transmission electron microscope TEM. The dielectric properties will be elucidate by mesuaring the dielectric spectra in the frequency range 42 Hz – 5 MHz, at temperatures between 25°C and 250°C.

Electrical polarisation and space charge formation in bioactive glasses

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Bioactive glasses are capable of binding to bone tissue via the formation of hydroxyapatite interfacial layers. Recently, it was discovered that the hydroxyapatite growth rate depends on the surface charge of the glasses and can therefore be influenced by means of electrical polarisation [1, 2]. During the polarisation experiments, the glasses are heated to temperatures typically between 200 °C and 500 °C while applying a voltage typically between 100 V and 1 kV. Then the glasses are cooled down to room temperature under the applied voltage. At higher temperatures, the migration of mobile ions and electrochemical processes lead to the formation of interfacial layers at the electrodes. These interfacial layers contain internal electric fields which are frozen in when the glass is cooled down to room temperature. The interfacial layer under the positive electrode is characterised by a negative charge density which causes an enhancement of the bioactivity, i.e. of the hydroxyapatite growth rate.

Up to now, the electrical and electrochemical processes leading to the formation of the interfacial layers are not properly understood. Therefore, we carried out electrical polarisation experiments on Na-Ca-phosphosilicate bioactive glass and have characterised the chemical composition and the electrical properties of the interfacial layers by means of scanning electron microscopy with energy-dispersive X-ray analysis (SEM-EDX), ^{15}N nuclear reaction profiling, impedance spectroscopy and thermally stimulated depolarisation current measurements. The interfacial layer under the positive electrode is characterised by sodium ion depletion, and the layer is much thicker than expected from standard space charge theories [3, 4]. This indicates that the negative charge density due to sodium ion depletion is partially compensated by other mobile charge carriers. We discuss possible charge compensation mechanisms.

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Design and Analysis of a Class D Amplifier with high-efficiency and low-distortion

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Abstract :
Audio amplifiers play an important role in every system that involves audible sound. General power amplifiers till recently have been very inefficient, bulky and unreliable. Though Class AB amplifiers have major market share in the audio industry because of their efficiency compared to previous classes of amplifiers such as Class A and Class B, recent demand for smaller devices with longer battery life has resulted in replacement of class AB amplifiers (linear amplifiers) with Class D(switching amplifiers). Class D amplifiers provide the balance between efficiency and distortion required by portable devices, hi-fi audio systems, as they utilize the switching operation where the transistors are either fully on or fully off resulting in amplification with zero power dissipation ideally.

The main focus of this thesis is to analyze various design issues involved in implementation of class D amplifiers. As many designers in the future will be switching to Class D amplifiers because of the recent advances in switching amplifiers, an effort was made to develop the thesis so as to be able to serve as a basic reference guide which gives them a good understanding of existing architectures, challenges in efficient power amplifier design, modulation methods, power stage topologies and implementation of class D amplifiers.

A detailed study of parameters and parasitics that affect the performance of class D amplifiers has been carried out with design, implementation, and simulation of various stages. Various component selection decisions and layout issues have been discussed for an efficient, EMI free, low distortion class D amplifier.

I. Introduction

A Class D audio amplifier is basically a switching amplifier or PWM amplifier. There are a number of different classes of amplifiers. We will take a look at the definitions for the main classifications as an introduction:

Class A – In a Class A amplifier, the output devices are continuously conducting for the entire cycle, or in other words there is always bias current flowing in the output devices. This topology has the least distortion and is the most linear, but at the same time is the least efficient at about 20%. The design is typically not complementary with high and low side output devices.

Class B – This type of amplifier operates in the opposite way to Class A amplifiers. The output devices only conduct for half the sinusoidal cycle (one conducts in the positive region, and one conducts in the negative region), or in other words, if there is no input signal then there is no current flow in the output devices. This class of amplifier is obviously more efficient than Class A, at about 50%, but has some issue with linearity at the crossover point, due to the time it takes to turn one device off and turn the other device on.

Class AB – This type of amplifier is a combination of the above two types, and is currently one of the most common types of power amplifier in existence. Here both devices are allowed to conduct at the same time, but just a small amount near the crossover point. Hence each device is conducting for more than half a cycle but less than the whole cycle, so the inherent non-linearity of Class B designs is overcome, without the inefficiencies of a Class A design.

Efficiencies for Class AB amplifiers is about 50%.

Class D – This class of amplifier is a switching or PWM amplifier as mentioned above. This class of amplifier is the man focus of this application note. In this type of amplifier, the switches are either fully on or fully off, significantly reducing the power losses in the output devices.

Efficiencies of 90-95% are possible. The audio signal is used to modulate a PWM carrier signal, which drives the output devices, with the last stage being a low pass filter to remove the high frequency PWM carrier frequency.

From the above amplifier classifications, classes A, B and AB are all what is termed linear amplifiers. We will discuss the differences between Linear and Class D amplifiers in the next section. The block diagram of a linear amplifier is shown below in fig 1. In a linear amplifier, the signals always remain in the analog domain, and the output transistors act as linear regulators to modulate the output voltage. This results in a voltage drop across the output devices, which reduces efficiency.

Class D amplifiers take on many different forms, some can have digital inputs and some can have analog inputs. Here we will focus on the type, which have analog inputs.

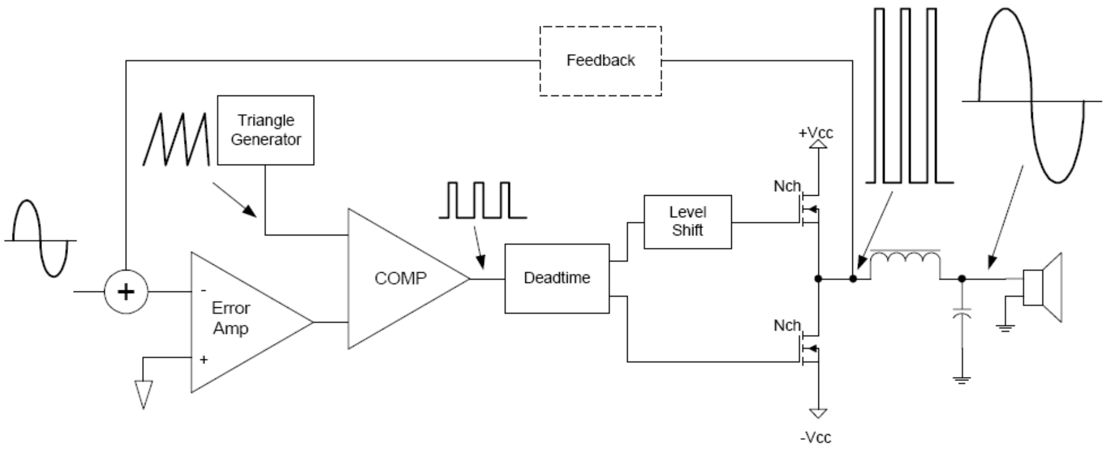

Fig 1: Block Diagram of a class D Amplifier

Fig 1 above shows the basic block diagram for a Half Bridge Class D amplifier, with the waveforms at each stage. This circuit uses feedback from the output of the half-bridge to help compensate for variations in the bus voltages.

So how does a Class D amplifier work? A Class D amplifier works in very much the same way as a PWM power supply (we will show the analogy later).

Let’s start with an assumption that the input signal is a standard audio line level signal. This audio line level signal is sinusoidal with a frequency ranging from 20Hz to 20kHz

typically. This signal is compared with a high frequency triangle or saw tooth waveform to create the PWM signal as seen in fig 2a below.
This PWM signal is then used to drive the power stage, creating the amplified digital signal, and finally a low pass filter is applied to the signal to filter out the PWM carrier frequency and retrieve the sinusoidal audio signal (also seen in fig 2b).

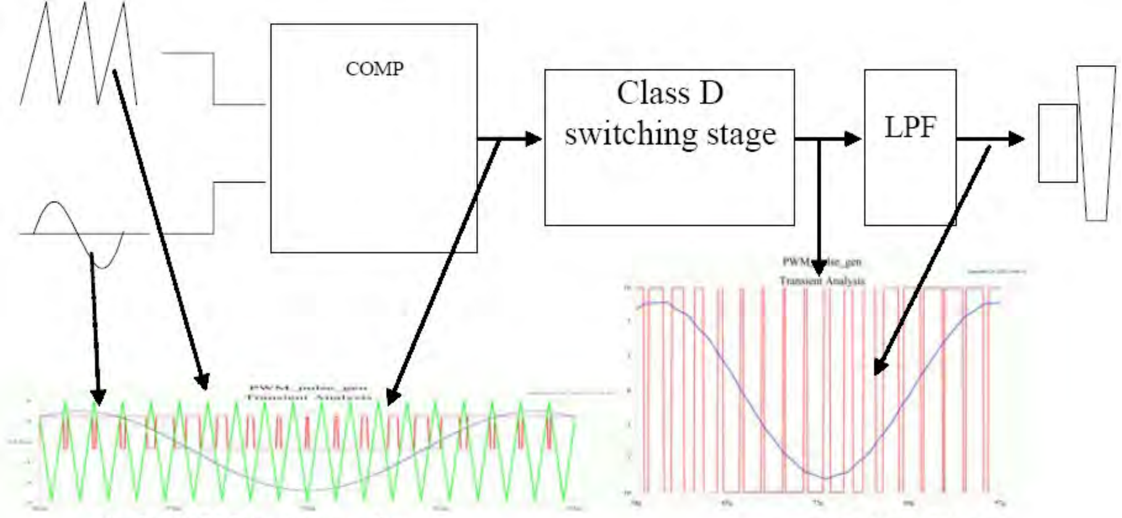

Fig 2a PWM Signal Generation

Fig 2b Output Filtering

Fig 2: Class D Amplifier Waveforms

II. Design Challenges

A. Top view

The top schematic view of Class-D amplifier Fig. 3 is composed by a main part (inverting input integrator, triangle generator, PWM modulator, gate driver and MOSFET H-bridge) and secondary parts like common mode voltage and bias current generator, startup and protection circuit, input gain selector and shifter.
Two analog power supplies (tailed together with decoupling capacitor on the circuit board) are used [1], PVDD/PGND supply the MOSFET H-bridge where as AVDD/AGND supply the rest of circuit. A digital VDD is used to supply level shifter.
ESD protection and bonding are not shown is this schematic but have been taken into account for simulation.

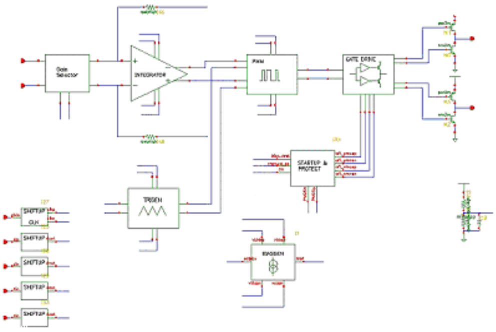

Fig 3: Class D schematic

B. Triangle ramp Generator

The proposed ramp is generated by constant charging current into the capacitors C1 and C2, which is connected between the ground and successively current source and current sink. The value of two capacitors is C1=C2=C=25pF (fig.4)**.**

The current through R1 is the charging current, kept constant by forcing the voltage across R1 to equal VDD/2 by op amp, configured as follower voltage.

The ramp slope is:

$$\frac{dVramp}{dt} = \pm\frac{Vdd}{2R1*C} \qquad \text{(Eq. 1)}$$

The resistance R1 is adjusted by four digital bits Trim<3:0> for adjust finally the current charging, the ramp slope and Vramp peak-to-peak to equal Vdd/5.

The charge make in two phase Φ1 and Φ2:

- In the phase Φ1 ,the switches Φ2 will be open and the switches Φ1 will be closed ,the capacitor C1 will be in charge by constant current and the ramp output is the charge voltage of C1, thus Vout will be :

$$Vout(t) = \frac{Vdd}{2R1*C}t + (\mathrm{Vdd/2} - \mathrm{R2*I}) \qquad \text{(Eq. 2)}$$

At the same time the capacitor C2 is in pre-charge state.

V_{C2} (t) = (Vdd/2+R_2I) (1-exp (-t/R_2C))

- In the phase Φ2 , the switches Φ1 will be open and the switches Φ2 will closed ,the capacitor C2 will be in discharge by constant current, thus Vout will be :

$$Vout(t) = -\frac{Vdd}{2R1*C}t + (\mathrm{Vdd/2} + \mathrm{R2*I}) \qquad \text{(Eq. 3)}$$

In the same way the capacitor C1 is in RC discharge.

V_{C1} (t) = (Vdd/2+R_{2*}I) (2*exp (-t/R_{2*}C) -1)

The resistor R2 is adjusted by four digital bits Trim<7:4> to adjust the value of outp and outn, such that ΔV=0 (Fig.7).

The condition to get the continuity of the ramp output is Trim<7:4>=0001, i.e. the value of R2=23.4Kohms.

The condition to get ramp slope or ramp output peak-to-peak equal VDD/5 is Trim<3:0>=0101, i.e. the value of R1=105Kohms.

The third condition is that the half period T/2 will be large enough such that C2 voltage achieves 95% of its final value (i.e. Vdd/2+R_2I), thus:

$$\exp\left(\frac{-T}{2R2C}\right) = 0.05 \qquad \text{(Eq. 4)}$$

So the minimum input clock period is T_{min}=2*R_2C*ln20 = 3*R2*C = 1.725us

So the maximum input clock frequency F_{max} = 580 kHz

At top classD level, we can adjust the value of two resistors R1 and R2, by putting on both inputs (positive and negative) of the class-D a constant signal equal to VDD/2 (i.e. a zero differential input signal is going to the class-D).

Then we adjust the value of Trim such as to have on both outputs of the class-D a square signal with duty cycle equal 50%.

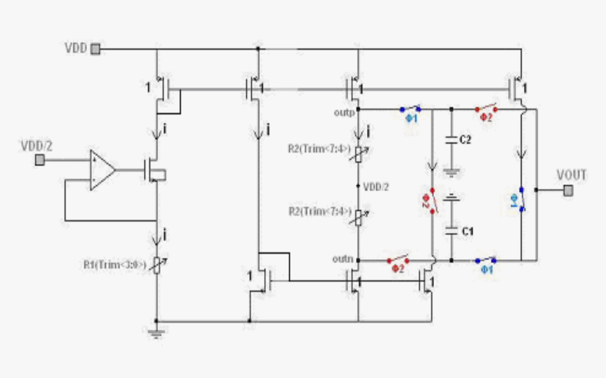

Fig 4: **proposed triangle Generator Schematic**

III. EXPERIMENTAL RESULTS

The class D audio amplifier has been integrated in a 0.5um, double-poly, triple-metal, BiCMOS process, occupying an area of 1.5 x 1.2 mm2. The measured output peak current was measured to be 0.35A into an 8 ohm load, using a 3.6V supply voltage. The IC consumed 2.5mA of quiescent current under those conditions with an rms output power of 0.5W and a power efficiency of 79%. A power efficiency of 86% was achieved at a

supply voltage of 6.5V. Fig. 10 shows the efficiency versus power curve. The total harmonic distortion plus noise (THD+N) was measured with an Audio Precision (AP) measurement system. A low pass filter had to be used at the output since the AP measurement system can not handle pure class D audio amplifiers because of the high frequency PWM waveform. The THD+N measured under the above-mentioned conditions varies from under 0.04% at low frequencies to a maximum of 0.4% at 7 kHz. Fig. 5 shows a plot of the THD+N versus the power under different supply voltage levels. Fig 6 shows layout of Amplifier Class D with process 0.5 um. Table 1 summarizes the measured results. The output offset is higher than predicted in the simulations because of mismatch in the feedback and in the input resistors.

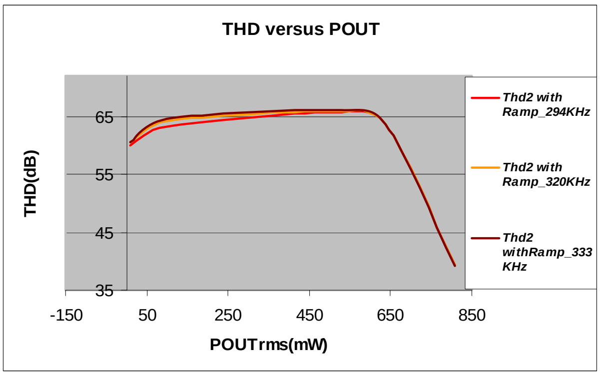

Fig 5: shows the THD+N versus the power.

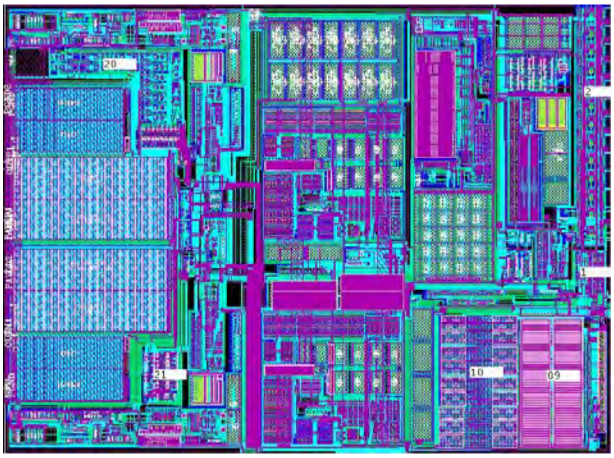

Fig 6: Layout of Amplifier Class D with process 0.5um of Texas Instrument.

Parameters	measurements	unity
Supply Voltage	3.6 -5.5	V
Output Power	1.4	V
Speaker Load	4 or 8	ohm
Total Harmonic Distortion Plus Noise *THD+N*	0.11	%
Common Mode Rejection Ratio CMRR	69	dB
Power Supply Rejection PSRR	75	dB

TABLE I: SUMMARY OF MEASUREMENT RESULTS

IV. CONCLUSIONS

We have presented a new class D audio amplifier for low voltage applications with high efficiency and minimum system solution size. The amplifier is a great improvement over its class AB counterparts where it comes to battery powered application since it dissipates less power in the amplifier itself.

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High temperature hopping conductivity in CdTe:Cl crystals

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In this work we present the results of experimental investigations of dielectric properties of CdTe:Cl single crystals. Temperature dependence of dielectric permittivity of CdTe samples at frequency of 10^6 Hz was studied in the temperature region of 20 – 150°C. About 1 mm thick plates with chemically polished facets were prepared from ingots with different chlorine concentrations for this purpose. Condensers were made by depositing a silver containing mixture on their opposite large sides with about 10 mm^2 area followed by firing. Capacity measurements were conducted by means of digital measuring devices connected with PC.

The obtained results can be satisfactorily explained taking into consideration the contribution of hopping conduction. It is known that this type of conductivity is very often observed in compensated semiinsulating CdTe:Cl crystals and became a predominant mechanism of carrier transport at low temperatures. But we found out that electrons hopping between the neutral defects also cause activation character of dielectric permittivity increasing with temperature rise in high temperature region. These defects create the deep levels in cadmium telluride band gap. The activation energy of the hopping conductivity was calculated from the temperature dependence of dielectric permittivity. The value of ~0.9 eV was obtained. Also, electron hopping between neighboring neutral defects leads to the formation of the dipole electric moments, which results in the material additional polarizing.

Glassy dynamics in thin polymer films: Memory and rejuvenation effects of dielectric susceptibility and volume

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Glassy dynamics was investigated for thin films of poly(2-chlorostyrene) (P2CS) through complex electric capacitance measurements using dielectric relaxation spectroscopy. During the isothermal aging process the real part of the electric capacitance increased with time, whereas the imaginary part decreased with time. It follows that the aging time dependences of real and imaginary parts of the electric capacitance were primarily associated with change in volume (film thickness) and dielectric permittivity, respectively. This results are similar to those observed in thin films of atactic polystyrene (a-PS), although the glass transition temperature is by 20 K higher in P2CS than in a-PS.
The aging behavior is discussed in terms of the change in volume and dielectric susceptibility during the aging process. Further, dielectric permittivity showed memory and rejuvenation effects in a similar manner to those observed for poly(methyl methacrylate) thin films. On the other hand, volume did not show a strong rejuvenation effect.

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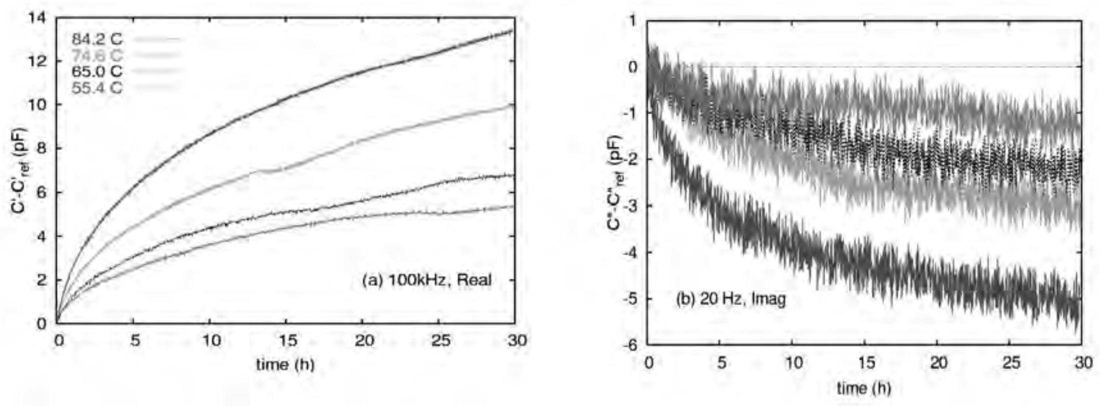

Fig.1: Aging time dependence of C'-C'$_{ref}$ and C"-C"$_{ref}$ for isothermal aging at 55.4 C – 84.2 C for frequency 100 kHz and 20 Hz, respectively

Relaxation Time At Tg Measured By Dielectric Spectroscopy And Thermally Depolarisation Current Methods

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The glass transition temperature (Tg) is defined for a material as the temperature which separates the like liquid state from the glassy states. For a given material it is now well known that this temperature depends upon the thermal history of the material (Which includes the value of the cooling rate used to prepare the glass). On the other hand, the passage of the like liquid state to the glassy state is associated to a drastic change of temperature dependences of the relaxation times which characterize the molecular dynamic in the two phases. In this work we show that a correct knowledge of the value of the relaxation time at Tg and a correct value of the glass transition temperature can be obtained by making the complete relaxation map of the material. This can be done by coupling three independent types of measurements. With dielectric spectroscopy the alpha and beta relaxation can be analysed, by thermally depolarization current measurement, the relaxation time in the glassy state as a function of the temperature can be obtained, finally by means of calorimetry the value of Tg is determined. The three independent measurements must converge at Tg and by this way we may with a great accuracy determine the value of the relaxation time at Tg. This method has been applied to PET, PETg, PETG montmorillonite and PC. One of the main conclusion concern the assumption often proposed in the literature for a constant value of $\tau_{(Tg)}$ = 100 s which is found not in fact not valid.

Molecular Dynamics in Smart Hydrogel Systems

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Partially hydrolyzed Polyacrylamide (PAAM) can be defined as lightly crosslinked polymers with high affinity to water [1]. They absorb and retain a large volume of water or biological fluids while keeping its solid-like properties due their chemically crosslinking network. Such hydrogels interact with their environment in a preprogrammed and intelligent manner. They can sense the external stimulation, such as, a change in pH, ionic strength or an applied electrical field, and in response change their swelling rate which results in actuation. Their lifelike movements and biocompatibility [2] makes them suitable for application in tissue engineering, biosensors and valves [3].

The main task in PAAM intelligent behavior is based on the volumetric changes occuring in such systems. Thus the study and understanding of the fundamental phenomena and molecular mechanisms of their expanding, contracting and bending mechanisms is necessary in order to respond to emerging technology demands for high performance materials.

In this study, the charge transport inside the hydrogel matrix when it's subjected to an electrical stimulation is studied.

Then the ion exchange, between the hydrogel and its environment, induced by a chemical stimulation is investigated in different physiological and pHs solutions. Finally the molecular dynamics responsible of volumetric changes in PAAM gel systems is explained based on the osmotic pressure which induces the ion diffusion phenomenon and determines the equilibrium volume of the network.

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Broadband Dielectric Measurement of Sandstones, Shales and Other Geological Materials

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Many of the mechanisms which affect the dielectric behaviour of rock samples also influence other physical properties of interest, such as strength, amount of clays and oil saturation [1]. For instance, moisture present within the rock which gives rise to dipole dielectric behaviour as well as low frequency space-charge polarization, may be expected to lubricate the clay mineral platelets and so lead to a reduction in shear strength [2]. CSIRO Petroleum is well equipped for porosimetry, permeametry, X-ray tomography, and mechanical strength testing, and in recent years we have developed a range of measurement techniques to facilitate dielectric analysis of all possible rock sample types provided by industry. These include: a 16mm diameter loaded coaxial transmission line [3], which is used for small solid samples, liquids and packed powders prepared from drill cuttings, in the range from 300KHz to 1GHz; a parallel plate capacitor for offcuts of core samples, in the range from 100Hz up to 10MHz; an Agilent 85070 style endloaded transmission line [4], which is suitable for small quantities of pastes prepared from drill cuttings in the range from 1MHz to 3GHz; and a 1.5” diameter uniaxially loaded coaxial transmission line (using some principles from ref [5]), which is used for standard industry core samples in the range from 300KHz to 1GHz at elevated pressure.

We present examples of broadband dielectric measurements made in our laboratories on a range of rock samples with the different methods and test cells. We show how dielectric spectroscopy can help in solving problems of practical interest to the oil and gas industry, such as predicting the strength and chemical sensitivity of shales in unstable well bores, and assessing the relative wetting tendencies of different types of reservoir rocks.

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Comparative study of the thermal and electrical properties of some poly(ether imide) thin films

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The aim of the proposed paper is to present a set of measurements made on some poly(ether imide)s which can be successfully used in a large number of applications due to their good solubility in organic solvents and excellent combination of physical, chemical and mechanical properties. The polymers have been synthesized by solution polycondensation technique in two steps. In the first step poly(amic acid)s were prepared by the reaction of an aromatic diamine, namely 4,4'-(1,3-phenylenedioxy)dianiline, with some bis(ether anhydride)s which contain isopropylidene or hexafluoroisopropylidene groups, at room temperature, in N-methylpyrrolidone as solvent. In the second step the resulting solutions of polyamic acids were heated, under a nitrogen stream, at 180-185°C, to perform the cyclodehydration reaction to the corresponding imide structures. The properties of these polymers such as solubility, inherent viscosity, thermal stability, glass transition temperature, film forming ability have been investigated. Thin polymer films were studied via Broadband Dielectric Spectroscopy, Thermally Stimulated Discharge Currents and Dynamic Mechanical Analysis. The electrical measurements were made on virgin samples but also on conditioned ones. The conditioning consisted on thermal and electric stressing for a period of time varying from hours to days. The results recommend the use of these polymers for application in different industry domains like microelectronics and related fields.

Keywords: TSDC, good solubility, thin films, thermal stability, dielectric constant

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Thermal And Electrical Behavior Of A Thermostable Imide Type Polymer

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The interest of worldwide researchers for developing new dielectric materials suitable for high performance applications represents a common target of world's scientific community. In conjunction with the above issue the proposed paper presents a study on a thermostable imide type polymer. The polymer has been synthesized by solution polycondensation reaction at high temperature of 4,4'-oxydiphthalic anhydride with an aromatic diamine having ether bridges between phenylene rings, namely 4,4'-(1,3-phenylenedioxy)dianiline. It was easily soluble in polar organic solvents such as N-methylpyrrolidone and N,N-dimethylformamide, as well as in low boiling-point organic solvents like chloroform, and can be cast from solutions into thin, flexible films.

Beside classical measurements performed in order to obtain information about polymer's characteristics (Broadband Dielectric Spectroscopy, Differential Scanning Calorimetry and Thermogravimetric Analysis) we were interested in observing how the material acts under an applied electric field action, that's why we focused in analyzing the behaviour of charge carries with the help of TSDC (Thermally Stimulated Discharge Currents).

Keywords: TDSC, thin films, thermal stability, dielectric constant

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Molecular Dynamics of a Fluorinated Cyano Copolymers Investigated by Dielectric Spectroscopy

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High dielectric constant polymers are becoming crucial components in advanced electronic devices : such as memory and dielectrics gate for integrated circuits, stationary power generation and miniature capacitors for telecommunication.[1] The exchange of electrical energy and mechanical energy in sensors, transducers, and actuators also benefits from the materials with high dielectric constant.[2] Compared to the traditional electroactive ceramics, polymeric dielectric materials enjoy inherent advantages, such as high mechanical elasticity, high electrical breakdown strength, ease of processing of large areas, low cost, and self-healing ability. However, unlike their inorganic counterparts, the permittivities of most polymers are in a limited region ranging from 2 to 12.[3] Ferroelectric poly(vinylidene fluoride) and its copolymers are the most important dielectric polymers due to the polarization originating from C—F bonds and the spontaneous of dipoles of the crystalline phases[4]. Polymers containing polar substituents such as cyano (nitrile) groups are interesting for the development of advanced electrical and optical materials because of the large dipole moment from the polar substituent (CN)[5)]. First described by Miyata and al., the piezoelectric activity of the amorphous alternating copolymer of vinylidene cyanide (VCN) and vinyl acetate (VAc)[6)] explains why there has been a growing interest in the copolymerization of cyano monomers with various acrylic, vinylic or styrenic comonomers.

In the frame of a research aiming at developing new dielectric polymers containing C-CN and C-F substituents with strong dipole moments, we describe in this work the dielectric behaviour of bloc copolymers prepared by iodine transfer polymerization (ITP) based on three cyano monomers: vinylidene cyanide, acrylonitrile and methacrylonitrile with vinylidène fluoride (VDF) as the fluorinated comonomer.

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Relaxation Properties Of Nanocomposites Zeolite-Semiconductor Hbeta-Zns

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By method of broadband dielectric spectroscopy were obtained the dependencies of the complex dielectric permittivity for Hbeta zeolite and nanocomposites Hbeta-ZnS in the frequency range 10^{-1}–10^{5} Hz and temperature range -160 ÷ +300°C. The samples of nanocomposites were synthesized by the procedure of solid-state ion exchange of Hbeta zeolite (Si/Al=45) with cadmium chloride followed by hydrogen sulphide treatment.

We have found the difference in a disperse of real and imaginary part of dielectric permittivity of Hbeta-ZnS nanocomposite in comparison with a source zeolite. Approximation of dielectric spectrum by the Havriliak-Negami functions has allowed calculating the distribution of times of dielectric relaxation with a few maximums, which correspond to a few relaxation transitions for both nanocomposites and source zeolite. However, in the nanocomposite in the temperature range 170-230°C we have observed a new relaxation transition. Temperature dependence of relaxation time for this transition is linear in the Arrhenius coordinates with activation energy ~ 2.0 eV

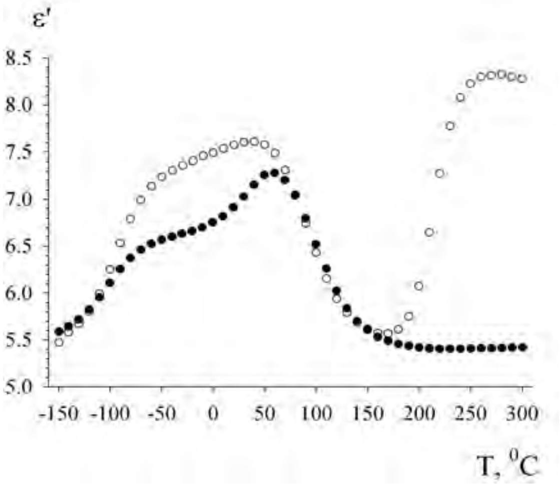

Fig. 1. Dependence of the real part of dielectric permittivity at frequency of electric field 10^{5} Hz on the temperature for: filled dotes – Hbeta, blank dotes – nanocomposite Hbeta-ZnS

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In-line monitoring of polymer melt processing by conductivity spectroscopy: Carbon nanotube –polymer composites

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In recent years, the applications of carbon nanotubes (CNT)-polymer composites has grown rapidly. Although, first CNT-polymer composites are commercially available a major restraint in market acceptance is the wide variations in electrical conductivity as function of the processing conditions.
In order to study the influence of extrusion conditions on electrical properties experiments have been performed in a slit die flanged to the outlet of a twin screw extruder (**Figure 1**). The measurement slit die contains two electrodes in plate-plate geometry [1]. AC conductivity and the related complex permittivity were measured in the frequency range between 20 to 10^6 Hz for different extrusion conditions (melt temperature, screw speed, throughput etc.) and after stopping the extruder (**Figure 2**). The investigations have been performed during melt processing of polycarbonate (PC) and polyamid-6 (PA6) containing 0.5 – 2 wt% and 0.7 -2.7 wt% of multi walled carbon nanotubes (MWNT), respectively, for different processing temperatures.

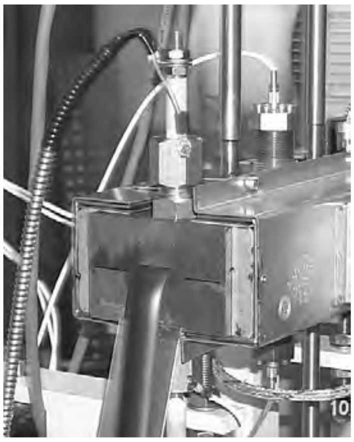

Figure 1: Measurement slit die

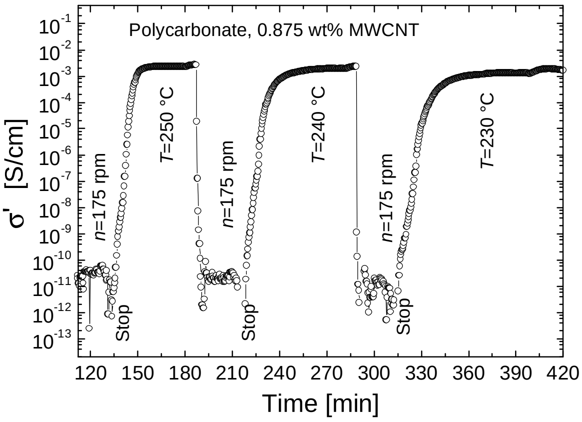

Figure 2: Conductivity during extrusion and after stopping of the extruder for a PC-CNT composite (0.875 wt% MWNT)

It was found for all samples that during extrusion the conductivities were in the order of magnitude of the matrix polymer. After the extruder was stopped (model experiment for injection molding) the conductivity shows a tremendous increase with time (conductivity recovery after shearing). This process was more pronounced for samples with CNT content close to the percolation threshold. The finding can be explained by the reorganization of the conducting network-like filler structure which was (at least partially) destroyed under shear. The reformation kinetics of filler clusters is due to a cooperative aggregation [2], which is related to the kinetics of cluster-cluster aggregation in a percolating system.

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Electrical properties of Li_2O-ZnO-P_2O_5 Glasses

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ABSTRACT

Lithium zinc phosphate glasses of the composition xLi_2O-$(40-x)ZnO$-$60\ P_2O_5$ ($0<x<40$), mol% were prepared by melting and analyzed by different thermal analysis (DTA), Raman and Impedance spectroscopy in the frequency range from 0.01 Hz to 4 MHz and temperature range from 303 to 473 K.

The systematic change in the variety of properties, such as glass transition temperature, T_g, and density at 20 mol% Li_2O is explained by changes in the nature of the oxygen bonds in glass network. The Raman spectra predominantly show the metaphosphate structure with barely detectable pyrophosphate units for all glasses in the series. However, replacing ZnO with Li_2O in these glasses leads to the compositional dependent changes. This dependence is explained by different structural cross-linking of phosphate chains with increasing Li_2O, which is correlated with the unusual T_g minimum at 20 mol% Li_2O.

The electrical conductivity as a function of Li_2O concentration measured at lower temperatures (298 and 333 K) passes thought a minimum at 20 mol% whereas linearly increases at higher temperatures. This suggests that the conductivity enhancement is directly related to the thermally stimulated mobility of Li^+ ions in the high temperature region. The observed minimum in electrical conductivity at 20 mol% Li_2O is related to the structural reorganization of the glass network.

With increasing Li_2O content up to 40 mol% the values of electrical conductivity increases for five orders of magnitude indicating the ionic conductivity.

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Dielectric Relaxation of ZnO varistor

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Varistor (variable resistor) ceramics have become technologicaly important because of their highly nonlinear electrical characteristics enabling them to be used as reversible solid state switches with large-energy-handling capabilities.

Zinc oxide-based ceramic compositions are among the most widely investigated varistors, the applications of witch include voltage stabilization transient surge suppression in electronic circuits and electronic power systems.

Broadband dielectric relaxation spectroscopy in wide frequency (10^{-1} – 10^{7} Hz) and temperature range (-150 up to 150^{0}C), thermally stimulated depolarization currents (TSDC, -150 up to 200^{0}C), electrical current – voltage (V – I) measurements, isothermal depolarization current measurements, scanning electron microscopy and thermal analysis techniques used in this work in order to study the dielectric, electrical and thermal properties and morphology features of industrially producted ZnO varistors.

Microphase Separation In Polyurethane Grafted Onto Styrene-Styrene Sulfonic Acid Copolymers

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The exploration of the phase behaviour of partly sulfonated polystyrene containing polyurethane grafts was the object of this study. Similarly to other multicomponent polymeric systems, the properties of the polyurethane grafts depend strongly on the miscibility of components. A widely accepted criterion of miscibility in polymer systems is the existence of a single glass transition at an intermediate temperature between the glass transitions of the components typically measured by dynamic mechanical thermal analysis [1]. If a spectroscopic technique is employed to investigate molecular mobility, such a dielectric relaxation spectroscopy, this criterion corresponds to measuring two loss peaks due to the segmental (α) relaxation of the components (dynamic glass transition) in immiscible heterophase systems and single loss peak in miscible system [2-4]. It was interesting to compare the dielectric results with dynamic mechanical properties.

The synthesis was accomplished by stepwise grafting onto partly sulfonated polystyrene of N-methyldiethanoloamine followed by chain growth on the hydroxyl sites of a wide range of the polyurethane structures [1]. Molecular relaxations in relations to microphase separation in polyurethane grafts were characterized by dielectric relaxation spectroscopy using a dielectric analyser DEA 2970 from TA Instruments coupled to a 2100 thermal analyser and by dynamic mechanical analysis using the Polymer Laboratories dynamic mechanical thermal analyser. The dynamic mechanical properties and the dielectric properties thereof are discussed in terms of microphase separation. If the grafts consist of only hard segments, then a single glass-transition temperature is observed. For the grafts with short soft segments one glass-transition temperature is also observed. If, on the other hand, longer soft segments are included in the grafts, then these phase-separate and yield a new glass-transition temperature [1]. However the dielectric behaviours of the grafts with long and even short soft segments show the presence of two the glass temperatures and confirm their heterogeneity. It was shown that the dielectric properties can be a more sensible criterion of an existence of separation in polyurethane grafts than the dynamic mechanical studies.

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Infrared dispersion of liquid *iso*–propanol

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The spectra of the real and imaginary components of the complex refractive index were determined from thin film transmission studies of liquid *iso*-propanol (propan-2-ol) using a method, which takes into account the dispersion of the refractive index in the visible range and requires integration over the entire absorption range in the NIR, IR and FIR regions [1].

From these data the spectra of both components of the complex electric permittivity and complex polarizability of liquid *iso*-propanol 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.

The molar vibrational polarization related to various spectral ranges has been determined. It has been found to be extremely small for overtone bands. The main contribution stems from the region of deformation modes of the molecule and from the vibrations of the hydrogen-bonded OH group. The total molar vibrational polarization originating from internal vibrational modes in the 12000 - 350 cm^{-1} region amounts to 2.57 cm^3 $mole^{-1}$, contributing ca. 12.7 % to the distortion polarization. The results have been compared with those obtained for the related *n*-propanol (propan-1-ol) [2].

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Study of molecular dynamics in methacrylic based diblock copolymers

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The ability of block copolymers to form separate microphases, which often develop highly organized domains of various morphologies of nanometer scale, is of great theoretical and practical importance. In the present work the molecular dynamics within different ordered microphases (lamellar and cylindrical) in diblock copolymers based on poly(alkyl methacrylates) is investigated by means of broad-band dielectric spectroscopy.

Diblock copolymers of poly(methyl methacrylate) (PMMA) and poly(pentyl methacrylate) (PPMA) as well as the corresponding homopolymers were prepared by anionic polymerization providing samples with narrow molecular weight distribution and high purity. Diblock copolymers having different compositions and block lengths were prepared and studied. Microphase separation takes place in the diblocks under study, while depending on the composition and block length different supermolecular structures (lamella and cylinders) of nanometer scale were detected by small angle X-ray scattering (SAXS) and atomic force microscopy (AFM) techniques. Molecular mobility was investigated by dynamic and static dielectric techniques including dielectric relaxation spectroscopy (DRS) (10^{-1}-10^{6} Hz) and thermally stimulated depolarization currents (TSDC) (10^{-3}-10^{-4} Hz) in a broad temperature range (-150 – 190 °C).

The β, α and αβ relaxations of PPMA and PMMA blocks were followed. Information regarding the time scale of the relaxations was extracted from the isothermal and isochronal plots of dielectric losses, while the strength and the shape of the relaxations was estimated by analyzing the isothermal data with model functions. By comparison with the homopolymers no significant shift of the β relaxations was detected in the diblocks, while shift toward higher temperatures/lower frequencies for the α and αβ relaxations of PPMA block was recorded. The results are discussed in terms of constraints imposed on the PPMA domains by the PMMA being in the glassy state and incorporation of blocks of one type to the phase formed by the other.

New information possibilities of the dielectric spectroscopy : investigation of the structural organization of the paraffin and vanadium oils

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Recent advances in dielectric spectroscopy drastically change attitude to this method and transform it in effective method for investigation of complex heterogeneous systems, particularly for investigation oil dispersion systems and phase transitions in that systems [1-3], that allows to obtain quite new conception about structural features of the oils. In this work by the use of the time domain dielectric spectroscopy in frequency range 10^1 – 10^9 Hz and temperature range -160 ^{0}C – 100 ^{0}C it were made investigations of the association processes of the supramolecular structures in paraffin oils with degraded physicochemical properties at the expense of the oxidation and crystallization processes of the solid hydrocarbons and in high-viscous vanadium oils with different concentration of the asphalten components. Complex investigations of the rheologic, dielectric and thermodynamic properties of the paraffin oils let us find differences in formation of the aggregative state with solid hydrocarbons in the form of:

- macrocrystalline phase, bonding supramolecular structure units asphaltenes in big aggregative pseudocrystalline organizational structure or,
- microcrystalline structure, entering in nuclei of the complex structural unit of the asphaltene components, that are responsible for formation of the aggregative stability of the nanostructures themselves. Temperature increasing in the second case leads to occurrence of the cooperative processes, conditioned by the dipoles space correlation. It was find out that anomalous formation of the collective motions in the system with increasing of the temperature (T) is related with activation of the polar groups as a result of the desorption process of the solvation sphere of the nanostructures.

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Dielectric Properties Of Gamma-Irradiation Thermoplastic Polyethylene Composites

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The dielectric properties of thermoplastic composites on recycled high- density polyethylene - HDPE^R , ethylene-propylene –diamine – EPDM and ground tire rubber- GTR bases has been investigated : HDPE^R:EPDM (1), HDPE^R:EPDM:GTR (2) and plastized composite HDPE^R:EPDM:GTR/plast (3).

The dielectric loss and permittivity study was performed using E8-4 bridge. The testing temperature was varied from – 150 to 120°C at a heating rate of 2 K/min and a frequency of 1kH. The TDV samples were γ-irradiated in liquid nitrogen at different dose of the irradiation (γ–source Co^{60} with energy of 1.25 MeV).

The experimental data obtained shows significant differences between dielectric properties different samples, as well as between the unirradiated and γ-irradiated samples. The dielectric losses curve of γ-irradiated composites are characterized by presence of sharp peak at the temperature of about 20°C (for dose 20 kGy), and the peak is shifted to higher temperatures with increasing dose both for sample HDPE^R:EPDM and for composite HDPE^R:EPDM:GTR. It is connected with increase in polar group content (data of IR (FTIR) measurements) and, as consequence, with the strengthening of inter-chain interaction.
For TDV - HDPE^R:EPDM:GTR/plast (sample 3) the losses intensity raising (growth of the tg δ maximum) is occurred only at doses above 500kGy and the peak shifts to the higher temperature region. That also can be connected with formation of unstable peroxide radicals.

Under irradiation up to dose of 50 kGy the permittivity raising is observed; it may be connected not only to oxidizing processes but also to the presence of peroxides - long-lived products of radiolysis of composites. At the further irradiation up to dose of 100 kGy the permittivity diminution for TDV - HDPER:EPDM and HDPER:EPDM:GTR was pointed out, that is the consequence of radiation-stimulated cross-linking formation.

The work was supported by EC (the STCU Project № 3009).

Structure And Dielectric Properties Of Hybrid Organic-Inorganic Nanocomposites Based On Silsesquioxane

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Organic-inorganic hybrids have large prospect for obtaining new materials with the improved properties as a result of the great possibilities in the combining of the functions of organic and inorganic components. Recently special interest has the study of hybrid organic-inorganic systems based on polyhedral oligomeric silsesquioxane (POSS). The structure and dielectric properties of POSS-containing hybrid systems of different morphology and different content of organic and inorganic components were investigated by SAXS and dielectric relaxation spectroscopy. It was shown that with the formation of hybrid systems based on POSS the processes of microphase separation with the formation of the nanodimensional inorganic regions (9-30 nm) are passed. A variation in the ration of organic and inorganic fragments influences the sizes, the polydispersion and the nature of the spatial distribution of such regions and practically does not change the overall level of the microphase separation of hybrid systems. The study of dielectric properties and conductivity showed that a variation in the composition of hybrid organic-inorganic systems leads to a change of conductivity levels to 1-2 orders. It was determined that the dependence of conductivity as a function of inorganic components content is extremal.

Investigation Of Molecular Reorientation In Poly(Butylene Terephthalate)/Decylamine/Fullerene Nanocomposite

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Molecular dynamics in poly(butylene terephthalate)-decylamine-fullerene nanocomposite has been studied by NMR method. The poly(butylene terephthalate) PBT is a commercial engineering thermoplastic, resistant to solvents, mechanically strong and heat-resistant. PBT is widely used because of its good mechanical properties, rapid crystallization rate and excellent moldability [1]. This polymer is used among other things as packaging material. The problem is that a significant number of free radicals remain after its synthesis and processing. It is suggested that modification of PBT with fullerene C_{60} would decrease the number of free radicals in this polymer and give new attractive nancomposite material both with improved chemical and physical properties [2].

The molecular dynamics of the nancomposite has been studied using solid-state pulse NMR spin-lattice relaxation method and NMR off-resonance technique [3]. The basis of this technique is to measure the spin-lattice relaxation times $T_{1\rho}^{off}$ in the presence of an off-resonance rf field. The obtained rates of relaxation times as a function of angular frequency were fitted into equation:

$$\frac{1}{T_{1\rho}^{\mathrm{off}}} = \frac{K}{4}\sin^2\theta J(\omega_e, \tau_c, \beta) + \frac{1}{T_1},$$

using the following density function given by Davidson and Cole:

$$J(\omega_e, \tau_c, \beta) = \frac{2\alpha}{\omega_e}\left[\frac{\sin(\beta \arctan(\omega_e \tau_c))}{(1+\omega_e^2\tau_c^2)^{\frac{\beta}{2}}}\right].$$

The correlation cut-off times were found in different temperatures, below and above the glass transition temperature, respectively. The temperature dependence of the spin-lattice relaxation time T_1 for PBT-decylamine-C_{60} is different from that of pristine PBT with the same measurement frequency. The obtained spin-lattice relaxation times T_1 in the laboratory frame and $T_{1\rho}^{off}$ in the off-resonance rotating frame demonstrate that the electron – nuclear spin interaction was decreased, which confirms the lower content of free radicals.

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The phase structure and molecular dynamics In poly(styrene-b-isoprene) diblock copolymer

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Polymer systems such as block copolymers are under intense experimental and theoretical studies because of their current and potential applications. Properties of such systems depend on both the properties of individual components and on the interaction between the components [1]. The immiscible polystyrene (PS) and polyisoprene (PI) systems exhibit the ability to self-organize by phase separation. The investigated poly(styrene-b-isoprene) diblock copolymer (SI) was nearly symmetric in composition, comprising PS and PI chain blocks of the molecular weight of 11500 and 10500 g/mol, respectively.

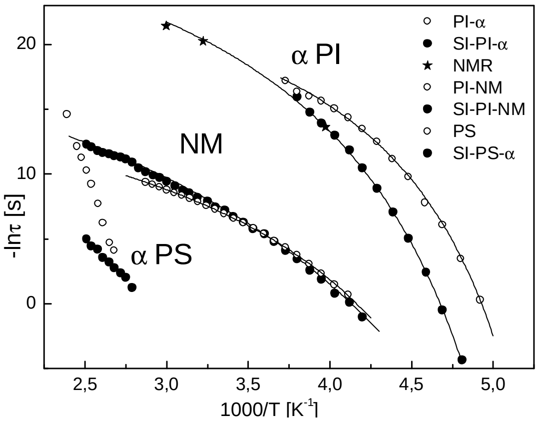

Fig. 1 BDS relaxation map for copolymer and neat polymers.

The NMR and BDS studies were applied to characterize molecular motions in SI and its neat components. The molecular dynamics in the copolymer reflects the molecular behaviours of neat PI and PS. The observed motions (Fig.1) are: (i) segmental motions relevant to the glass transition primary relaxations (α-processes) of PI and PS parts of the copolymer, (ii) normal mode motions of PI chains, which involve the fluctuations of the end-to-end vector (visible in BDS measurements) and (iii) the rotation of methyl groups (observed only in NMR experiments). However, the existence of flexible and stiff blocks (PI and PS, respectively) in the SI modifies their molecular dynamics, as compared with the neat systems. The increase in the glass transition temperature for PI (T_g^{PI}) and decrease in the glass transition for PS (T_g^{PS}) are observed [2]. Moreover, the distribution of relaxation times connected with this motion becomes broader as compared to the same processes observed in the neat PI and PS. It is assumed that these changes result from the tethered chains mutual interactions, in which PS blocks impose spatial confinement effect on the dynamics of PI chains, whereas the flexible PI acts as plasticizer for PS blocks. In order to estimate the size of PS domains the NMR and SAXS experiments were also performed.

Acknowledgements

This work is supported by 6th Framework Programme under SoftComp Grant No 502235-2.
A Wypych expresses her appreciation to the Ministry of Science and Higher Education in Poland for a Postdoctoral Fellowship (POL-POST III).

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Molecular dynamics in modified polydimethysiloxanes studied by rheology, NMR and dielectric spectroscopies

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Silicoorganic polymers belong to the family of water resistant molecular silicates, of wide application in science and industry [1]. The aim of the study was to check the effect of random incorporation of alkyl side chains (C_7H_{18}) into the PDMS chain on its molecular motion. Molecular dynamics of linear and modified polydimethylsiloxane (PDMS) was studied using rheological, NMR and dielectric techniques, whereas its thermal behaviour was determined by DSC.

It was found that modified polymers have amorphous structure, while the linear polymer is partially crystalline. The increase in vitrification temperatures with increasing amount of the modifier fraction was observed.

Results of NMR measurements made it possible to distinguish two relaxation processes: rotation of methyl groups around the Si-C bond (low temperature process) and segmental motions of the main chain (high temperature process).

The increase in the modifier amount in the polymer leads to the slowdown of the main chain segmental motions connected with the glass transition as reflected by NMR (Fig.1), dielectric (Fig.2) and rheological measurements.

Rheological and dielectric studies revealed also slow molecular motions (normal mode processes) above glass transition temperatures in modified compounds.

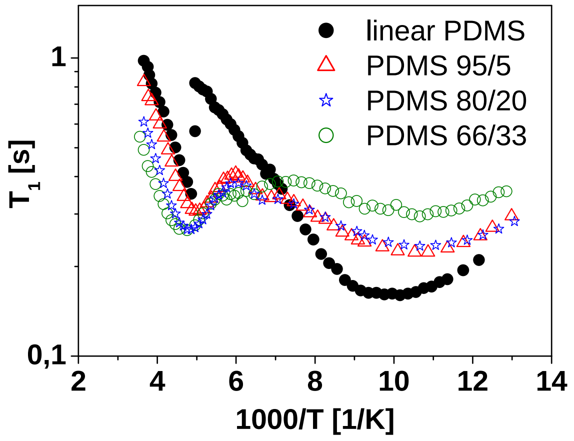

Fig. 1. Temperature dependence of proton spin-lattice NMR relaxation time.

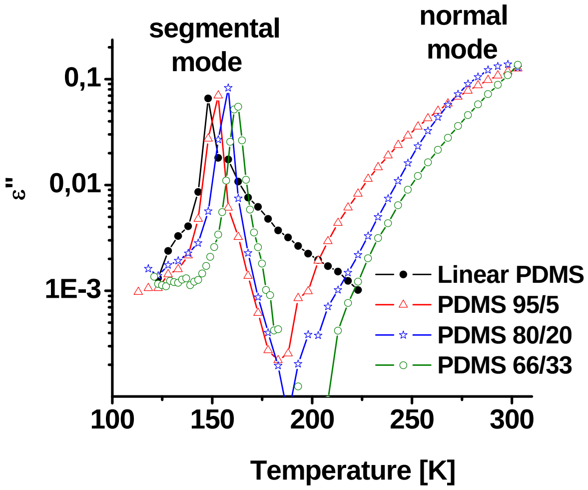

Fig. 2. Dielectric loss vs. temperature for modified polydimethysiloxanes

This work is supported by 6th Framework Programme under SoftComp Grant No 502235-2

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Terahertz Spectroscopy based on Heterodyne Detection Techniques

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Spectroscopy at terahertz frequencies have great potential for healthcare, plasma diagnostics, and homeland security applications. Terahertz frequencies correspond to energy level transitions of important molecules in biology and astrophysics. Because of its shorter wavelength, terahertz radiation also offers higher spatial resolution than microwaves or millimeter waves.

We are developing hot electron bolometer (HEB) mixer receivers for heterodyne detection at terahertz frequencies (0.5 THz up to 5 THz). HEB detectors provide unprecedented sensitivity and spectral resolution at terahertz frequencies. Terahertz imagers based on HEB technology have sufficient sensitivity to operate in a passive imaging mode, thus eliminating the need for active illumination. We have developed receivers and focal plane arrays operating near the quantum noise limit for astrophysical applications. We have recently demonstrated a low-noise heterodyne two-element focal plane array (FPA) operating at 0.85 THz. The integrated mixer block consists of NbN hot electron bolometric (HEB) detectors and state-of-the-art MMIC low-noise amplifiers in a compact design. HEB technology is becoming the basis for advanced terahertz imaging and spectroscopic technologies for the study of biological and chemical agents over the entire terahertz spectrum.

The terhertz spectrum presents certain challenges for developing instrumentation and techniques for imaging and spectroscopy. Current and future capabilities of spectroscopy at terahertz frequencies will be discussed.

BDS Study of Photodielectric Phenomena in Semiconductors of $A^{II}B^{VI}$ Group

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In the present paper the BDS studies of photogeneration and loss processes (due to recombination, trapping or capture) of charge particles in Semiconductors of $A^{II}B^{VI}$ group are discussed. The examples of application of the method are shown on fig. 1 and 2.

The changes of relaxation time distribution (G(τ)) with wavelength's (λ) in CdS thin films are shown in fig. 1. If the photon energy is greater than the band-gap energy the considerable changes in G(τ) spectra are observed. In this case the dipoles of trapped geminate electron-hole pairs provide the photosensitive part of relaxation spectra. And the energy depth's of electron and hole traps and the dependences of extinction coefficients on light energy determine G(τ) function.

The studies of photodielectric effects (PDE) in microwave region enable to obtain data on properties of electrons and holes in semiconductors. In fig. 2 the PDE in solid solutions based on CdTe in the frequency rage of 10^{10} Hz is shown. Free electrons along with entrapped electrons can contribute to changes of complex dielectric permitivity. By the time of coming of the electron equilibrium (5̃0-1000 ns) between traps and conduction band a contribution of free electron becomes substantially smaller than a contribution of entrapped electrones. This fact allows to obtain the life time of free electrons before the trapping.

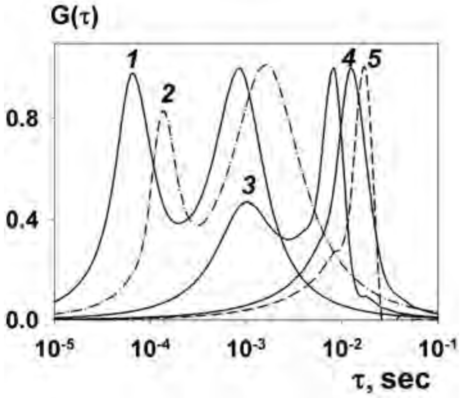

Fig. 1 Relaxation time distribution G(τ) in CdS film: 1 – λ = 370 nm, 2 - 520 нм, 3 - 620 нм, 4 - 960 нм, 5 - dark.

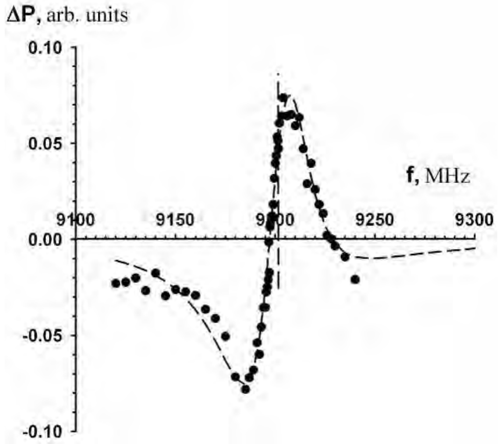

Fig. 1. Dependence of the reflected power on microwave frequency in polycrystallic CdTe, contained 0.015 mol.% GaTe. Time is 100 ns after laser impulse, λ=440 nm, light dose is 10^{14} photon·cm^{-2} per impulse. The resonance frequency is 9202 MHz. The broken line is approximation.

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Dielectric relaxation in Glycerol at long-time exposure to low temperatures

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This paper deals with the dielectric relaxation in glycerol at different temperatures (down to 25 K) for protracted periods of time. Two relaxation maxima were observed. The peak at lower frequencies was ascribed to the relaxation α-process of glycerol proper; the peak at higher frequencies differed in samples from different manufacturers, so that it represents rather a relaxation peak associated with contaminants and not the true β-process in glycerol. The α-process was considerably masked by the conductivity component. During a long-time exposure of glycerol to a low constant temperature, the relaxation spectrum shifts with increasing time to lower frequencies, reaching a steady position after about 20 hours.

Keywords: dielectric spectrum, dielectrics, physical aging, glycerol.

Introduction

The objective of the research was to obtain more detailed data on dielectric relaxations in glycerol and subsequently to develop a concept of the microscopic nature of dipole orientations. Glycerol is a widely studied low-molecular-weight hydrogen-bonded glass-former (CH2OH CHOH-CH2OH), whose dielectric behavior has been summarized e.g. in [1,2]. At room temperature glycerol is liquid, its melting point being Tm = 291 K and its calorimetric glass transition temperature being Tg = 185 K [3,4]. Glycerol molecule contains three polar hydroxyl groups (-OH). In the present paper we studied the dielectric relaxation of glycerol in the frequency range 10 Hz – 10 MHz and in the temperature range 25 K – 298 K. The objective of our studies was to find the origin of relaxation processes, to determine dielectric spectrum at different temperatures and to observe what would happen if the glycerol sample was exposed to cooling for a longer time.

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In-Situ Monitoring Of Reactive Thermoplastic Composite

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Abstract

The in-situ monitoring of the polymerization of cyclic butylene terephtalate (CBT) oligomers by dielectric sensing have been investigated under isothermal conditions at different processing temperatures. The change in conductivity depends on the increase of molecular weight but is also influenced by crystallization of the obtained c-PBT during or after polymerization. Dielectric sensing investigations are in good agreement with SEC and DSC analysis which confirm the polymerization and crystallization kinetics. Unfortunately, the conductivity signal could not distinguish between the polymerization and crystallization when it occurs simultaneously at lower temperatures (<210 °C) but the crystallization remains detectable by the MWS relaxation which is related to the crystalline / amorphous interface.

Relaxation and Conductivity in Hyaluronic Acid and Its Salts

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The subject of this paper is the investigation of dielectric and conductivity properties of hyaluronic acid (HA) and its salts. HA is a high molecular weight (~10^6 Da) polysaccharide composed of alternating molecules of N-acetyl glucosamine and D-glucuronic acid. In neutral conditions (pH=7), the hyaluronan molecule is a very large polyanion with associated exchangeable cations (Na^+, H^+) to maintain charge neutrality. The main physical properties are given by the polymeric chain and are only little affected by the cation type. HA is mostly used in biomedical applications in skin treatment, in particular for transdermal drug delivery administration. The objective of our research was to analyze the frequency and temperature behaviour of HA. In particular, it was desirable to determine, whether a relaxational (movement of charges at short distances only) or conductivity phenomena would prevail in the general HA behaviour in electric field.

Recently, it has become apparent that dielectric relaxation measurements in the relatively easily accessible radio frequency range can be a useful tool in investigating electrical properties of biosystems and the variations in these induced by various physical and chemical agents. In particular, the DRS technique allows the determination of both conductivity (a measure of the overall ionic transport) and permittivity (a measure of the dynamics of polar groups) of the material concerned.

A pronounced feature of the HA behaviour was the absence of any relaxation peak in the temperature and frequency range available, i.e., 198 K – 300 K, 100 Hz – 1 MHz. The conductivity of the sample was rather large (~$1E^{-8}$ S/m) so that it masked any relaxation peaks. HA exhibits a steady-state (constant) conductivity at low frequencies and a monotonous (power-law) increase at high frequencies. The onset of the increase of conductivity with frequency depends on temperature. At the lowest temperature of 198 K, the constant part of the conductivity is more or less clearly pronounced, whereas at the room temperature (in the log-log coordinates) only a gradual increase with frequency was observed. Also, the width of the transition region – between the constant part and the power-law increase – increases with temperature. The observed conductivity followed a slightly superlinear power law as $\sigma \sim \omega^{1.06}$. The value of the activation energy obtained from the low-frequency parts of conductivity spectra is around 5.4 MJ/kmol. No distinctions were found between samples with diffterent cation types.

The existence of the power-law in the frequency dependence of the HA conductivity which is a ubiquitous phenomenon in low-molecular-weight matter has been proved also for materials with very high molecular weight. This finding points to the idea that the frequency power-law for conductivity might be associated rather with the existence of spatial confinements and barriers to the motion of electrically charged particles rather than with their physical carriers themselves.

Dielectric elaxation in the smectic e phase of 4-hexyl-4'- isothiocyanatobiphenyl (6bt)

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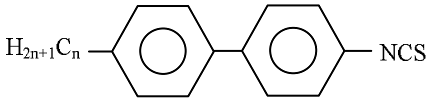
In calamitic liquid crystalline substances a variety of smectic phases can be devided into two classes: liquid-like phases with no arrangement of the molecular centres of mass in the layers (smectic A and C) and crystal-like phases where such arrangement within the layers is substantial (smectic B, E, K, G. etc.) [1]. Despite the close-packed arrangement in all smectic phases the molecules perform rotational motions around their short and long axes.

The sixth member of the well-know 4-n-alkyl-4'-isothiocyanatobiphenyl homologous series (abbreviated as *n*BT) was studied by Broadband Dielectric Spectroscopy. The chemical formula is shows in Scheme 1.



Scheme 1. Structure of the 4-n-alkyl-4'-isothiocyanatobi-phenyl homologous series (nBT)

The substance studied (6BT) exhibits only one liquid crystalline phase, the smectic E phase (SmE) [2,3].

Complex dielectric permittivity measurements were performed in the frequency range from 0.03 Hz to 10^5 Hz in a wide temperature range. The dynamics of molecules in the vicinity of the glass transition was studied. Crystallization kinetics and activation energies estimated in stable and supercooled SmE phase will be discussed.

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Broadband Dielectric and ^{1}H NMR Studies in Semi-crystalline Poly(ethylene oxide)

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In many polymer systems, the molecular ordering has a significant influence on physical properties, like molecular dynamics, temperature of the glass transition and others. In the substances in which two different types of arrangements can be found, like crystal and amorphous regions, semi-crystalline areas are characterized by different types of motions. The results collected by using dielectric and NMR spectroscopy, especially Fast Field Cycling relaxometry method (FFC), have pointed to the occurrence of the processes of three types: β, γ , γ ‘ in poly(ethylene oxide) (PEO) of two molecular weights: $M=2\cdot10^6$ and $M=1\cdot10^5$ g/mol.

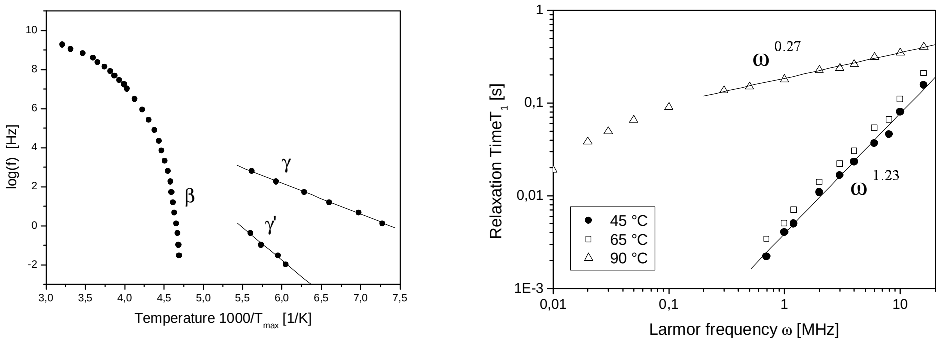

Fig.1. Dielectric relaxation map and dispersion of NMR relaxation times for high molecular weight PEO.

The relaxation process detected at high temperature and low frequency limit called β relaxation can be related to motions of amorphous PEO segments, while the γ-process has been assigned to local motions of PEO chains [1, 2]. The γ’ process observed between the β and γ-relaxation is assigned to the movements of segments in the interphase region. It should be marked that γ’ relaxation is poorly identified in literature [1].

Acknowledgements

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A. Wypych expresses her appreciation to the Ministry of Science and Higher Education in Poland for a Postdoctoral Fellowship (POL-POST III).

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Structural and Spectroscopic Studies of DMPC/cationic Surfactant System

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Each biological cell is enclosed by the membrane, which consists of phospholipids and proteins. Phospholipids conformation is strongly dependent on temperature. The phase transition of lipids is associated with formation of the *gauche* conformers as a consequence of increasing temperature [1]. Dielectric spectroscopy (DS) enables determination of the main phase transition (“melting” of hydrophobic chains) and microscopic parameters of the dynamics of the zwiterionic head groups in the polar region of the bilayer [2]. The bicellar structures are very useful as models of biological membranes in structural studies. Bicelles are used to study the function of peptides and their conformational changes as well as integral membrane protein [3,4].

Aqueous suspension of 1,2-dimyrilstoyl-sn-glycero-3-phosphocholine (DMPC) has been investigated by dielectric spectroscopy, small angle scattering of synchrotron radiation (SAXS), Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC). It was evidenced that even low concentrations of a surfactant initiate transition from the lamellar to bicellar phase.

An addition of dodecyldimethyl(dodecyloxymethyl)ammonium chloride (DDMDDAC) to DMPC water solution, induces bicelle formation, which has been revealed by SAXS studies. The radius of bicelles depends on the concentration of the surfactant. The presence of the surfactant has been found to decrease the phase transition temperature, as indicated by the DS and FTIR results. The small step in the dielectric constant plot vs. temperature can be connected with a transition from the gel to liquid crystal phase, which is supported by the temperatures dependencies of the symmetric and antisymmetric CH_2 band frequencies from FTIR measurements. DSC results are in a good agreement with the DS and FTIR data.

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A. Wypych expresses her appreciation to the MSHE for a Postdoctoral Fellowship (POL-POST III). The data collection at DESY Hamburg was supported by Integrating Activity on Synchrotron and Free Electron Laser Science to the EMBL Hamburg Outstation, contract number: RII-CT-2004-506008.

Influence of Cationic Surfactant on DMPC Structure

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Biological membranes play very important role in living organisms. The structural basis of biological membranes are phospholipids. The main phase transition of lipids, often called the chain melting, is generally associated with the transition from the gel or crystalline to the fluid phase [1]. Apart from temperature there are other agents such as e.g. surfactants, which can interact with phospholipids and influence their organization or induce bicellar phase formation [2].

The aim of the study was to analyze the effect of the cationic surfactant(benzyloxymethyl)dodecydimethylammonium chloride (BzMDDACl) on the structure of 1,2-dimyristoyl-sn-glycero-3-phosphocholine (DMPC). The small angle synchrotron radiation scattering (SAXS), dielectric spectroscopy (DS), Fourier transform infrared spectroscopy (FTIR) and differential scanning calorymetry (DSC) were used. DS in a microwave range is a useful method for detection of conformational changes in proteins and lipids in water solution [3].

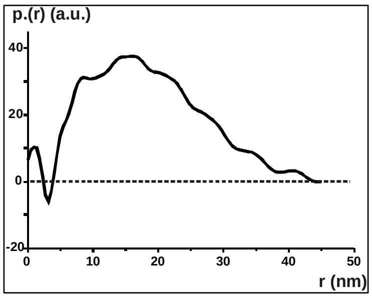

Fig.1 The distance distribution function p(r) calculated for DMPC/BzMDDACl 0.5%

The SAXS curves confirm that even a very low concentration of the surfactant initiates a transition from the lamellar phase to bicellar phase (Fig.1). The size of bicelles, ranging from about 20 to 45 nm, depend on the surfactant concentration.

Fig 2. presents the dielectric constants (ε') vs. temperature. The small jump on the curve can be connected with the phase transition onset being a result of increasing flexibility of the molten phospholipids chains, which has been confirmed by FTIR measurements. As a result of surfactants addition, the temperature of the main phase transition decreases and the interval over which the transition takes place broadens. DSC measurements confirmed the ranges of phase transition in systems investigated, detected by DS.

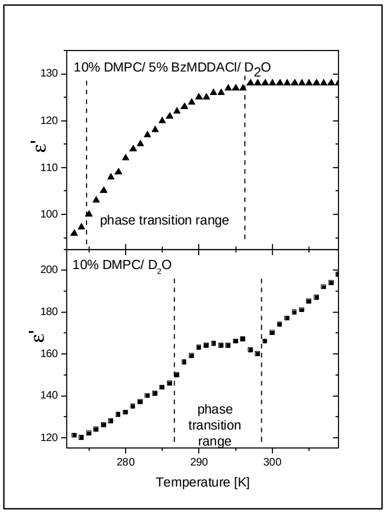

Fig. 2. The high frequency permittivity of DMPC and DMPC/surfactant water solution as a function of temperature

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A. Wypych expresses her appreciation to the MSHE for a Postdoctoral Fellowship (POL-POST III). The data collection at DESY Hamburg was supported by Integrating Activity on Synchrotron and Free Electron Laser Science to the EMBL Hamburg Outstation, contract number:RII-CT-2004-506008.

Dielectric Relaxation Studies in Poly(ethylene oxide)/sodium Montmorillonite Nanocomposites

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Nanocomposites of poly(ethylene oxide) with sodium montmorillonite (PEO/Na$^+$MMT) have attracted the attention of scientific community for the last few years due to their interesting electromechanical responses, rendering them potential candidates for applications as electrolytes in solid state batteries [1]. In order to obtain PEO/Na$^+$MMT, PEO intercalation from water/sodium montmorillonite suspension technique was applied for preparation nanocomposites' samples with 5% montmorillonite concentration. In the present studies PEO, with different molecular weights, were used. Differential Scanning Calorimetry (DSC) measurements exhibited that melting points of investigated nanocomposites (95 PEO / 5 Na$^+$MMT) are similar to relevant neat polymers.

In order to define the molecular mobility of PEO/Na$^+$MMT nanocomposites, broadband dielectric spectroscopy (BDS) and NMR spectroscopy, especially fast field cycling relaxometry (FFC), have been used. In the case of PEO systems and its nanocomposites different molecular relaxations below its melting point can be found. They were referred to the α, β and γ processes, with decreasing temperature, respectively. The α relaxation is a process associated with the crystalline phase and generally it is hardly observed in dielectric studies [2]. The β relaxation can be related to motions of amorphous PEO segments, while the γ-process may be assigned to the local motions of PEO chains. The γ' process located between β and γ relaxations is probably connected with the interphase region between them. BDS results of investigated nanocomposites revealed that Na$^+$MMT addition to PEO systems strongly influence the dielectric strength of low temperature relaxations: γ and γ', without significant change of their activation energies. The β process is less affected, however the broader distribution of relaxation times can be observed in PEO/Na$^+$MMT systems.

X-ray diffraction and NMR data show that in the intercalated nanocomposites PEO chains reside between the layers of the inorganic Na$^+$MMT galleries forming thin films with diameters of few nanometers. This confined phase is usually amorphous, while PEO phase outside the Na$^+$MMT galleries is mainly crystalline.

In summary, it can be concluded, that inclusion of Na$^+$MMT in the polymer network of PEO reduces its molecular mobility in amorphous part.

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A. Wypych expresses her appreciation to the Ministry of Science and Higher Education in Poland for a Postdoctoral Fellowship (POL-POST III).

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Structure, dielectric properties and conductivity of segregated PVC/MWCNT composites.

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This study is devoted to dielectric and electrical properties of nanocomposites based on PVC and multiwalled carbon nanotubes. The composites possess segregated (sintered) structure due to a method of preparation, compacting of PVC-MWCNT powder mixtute. Nanofiller creates the network round pressed polymer particles with high local concentration in the walls of network. Such a structure and high aspect ration of carbon nanotubes result in ultralow value of percolation threshold, namely φ_c=0.00045. Equation $\sigma = \sigma_0(\varphi - \varphi_c)^t$ for DC conductivity gives the value of critical exponent t = 3.5 that indicates nonstatistical distribution of filler. Temperature dependence of conductivity demonstrates a transition from ionic conductivity in pure PVC and in filled PVC below percolation threshold to ohmic conductivity along the MWCNT phase in the composites above percolation threshold.

Dielectric spectroscopy investigation shows the changes of frequency behaviour for ε', ε'' and σ parameters of composites at transition from below to above percolation threshold. AC conductivity gives the value of σ coincident with DC measurements for the filled composites. Frequency dependence of dielectric losses ε'' shows a presence of peak that is shifting to higher frequencies with filling of the composites. It can be related to interfacial polarization according to the MWS model. Temperature dependence of dielectric constant reveals a jump of ε' in the temperature region 100-130 ^{0}C that is higher of glass transition temperature T_g. This jump becomes more intensive with higher content of filler that can be caused by creation of loose surface layer of polymer on the surface of filler and intensification of molecular mobility in it.

Thermomechanical analysis shows the appearance of pronounced region of high-elasticity on the curve of deformation versus temperature at MWCNT content above percolation threshold. This effect is a result of creation of the filler network in the PVC matrix. The value of equilibrium elastic module E_e grows from 29 to 154 MPa when the filler content increases from 0.0004 to 0.0047. It is an evidence that the filler network becomes more rigid with increasing of filler concentration in it. The presence of inner stresses that are "frozen" in the composites with higher content of filler demonstrates the shape of TMA curves. The values of T_g, defined from TMA curves, decrease from 87 ^{0}C for pure PVC to 76 ^{0}C for composite with MWCNT content equal to 0.0047. It can evidence the creation of loose surface layer of PVC on the boundary polymer-filler with lower glass transition temperature. This loose layer is appeared as a result of strong interaction between PVC and MWCNT.

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Review and Improvement of a Method for Measuring Losses in the Dielectric Materials by Calorimetry

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The power loss plays a significant role in the design, implementation and use components in power electronics [1,2]. It is therefore important to be able to characterize them using techniques reliable and preferably in the nominal operating conditions. The calorimetric principle seems to be particularly suited to the full characterization of losses [3]. The calorimetric studied in this article was specifically designed to measure the losses in power capacitors. We offer a comprehensive analytical study heat exchange [4,5,6,7]. The surfaces of the device calorimetry are considered insulated, gray, opaque and perfectly diffusantes. The exterior wall is supposed adiabatic. The temperature gradients highlighted by this model and the response of the device in case tests show weaknesses in the system. The result is a degradation of measurement accuracy. This could, however, be improved by encouraging exchanges by radiation and using a single temperature. This is the subject of an ongoing study

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Conductive polymer composites based on metallic nanofiller and polymer matrix as smart materials for temperature sensors

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The presented work shows the analysis of percolation threshold in homo- and heterogeneous polymer matrix filled with silver nanoparticles. The characterisation of morphology and electrical properties of CPC obtained by the dispersion of filler in a polymer matrix have been studied from the point of their application as a material for temperature sensors. Two immiscible polymers were used to obtain samples: high density polyethylene (HDPE) and polybutylene terephthalate (PBT). As a conductive filler the silver powders with average diameter of 150 nm was used. Samples with different concentration of conductive nanoparticles were prepared by means of extrusion mixing and hot pressing.

The DC and AC conductivity measurements were performed on the investigated samples. It was found that both methods of the electrical characterisation are in consistence giving similar results. One can find that blends of immiscible polymers (HDPE/PBT) show lower percolation threshold than single components. It can be described by formation of co-continuous structure (phase separation). The obtained samples show high intensity of positive temperature (PTC) effect – resistivity increases by more than 10 orders of magnitude at commutation temperature. Additionally, the initial resistivity at room temperature is very low and stable, and the samples show very sharp transition from conducting to isolating state within very narrow temperature range. Moreover, the observed PTC effect is reproducible (see Fig.) with a potential for multiuse, as opposed to conventional fuses.

High performance of PTC effect for investigated polymer blends filled with metallic nanoparticles, such as low initial resistivity, high intensity of PTC effect, and high reproducibility, makes such composites promising for applications as materials for self-regulated elements (e.g. thermistor). Evaluated methods of processing of CPC can be used for preparation of smart materials.

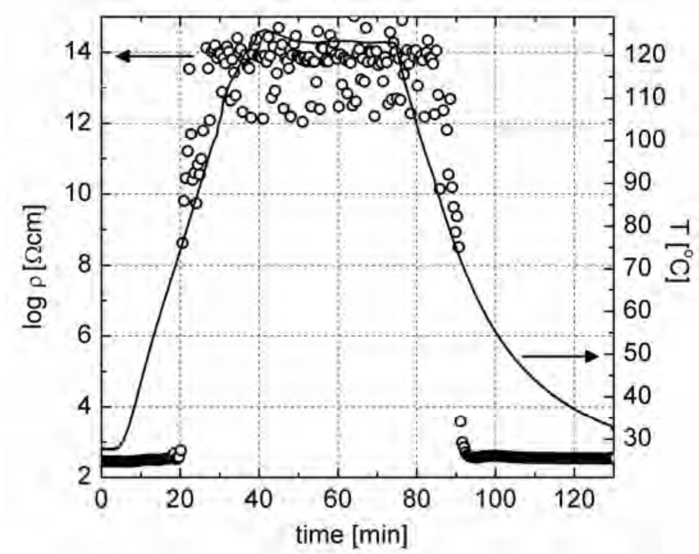

Fig. Stability of PTC device based on HDPE + 22 vol.% Ag. Left axis corresponds to logarithm of specific resistivity of the sample vs. time, whereas right axis shows evolution of sample's temperature.

Dielectric spectroscopy of a macroscopic epoxy/silica interface submitted to an hygrothermal conditioning.

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To investigate the effect of a hygrothermal conditioning on an epoxy/silica interface, a macroscopic experimental model of this interface has been built and characterized with dielectric spectroscopy. A quartz sheet with pulverized interdigitated electrodes has been moulded in an epoxy resin (see figure 1). The cell was conditioned at 80°C, above the Tg of the resin, and 80% RH. During the first days of conditioning, the spectra (Figure 2) exhibit a quasi-constant capacity, and a tan delta with a slope of –1 at low frequencies corresponding to the conduction in the resin. After about a week, the capacitance at low frequencies increased sharply and the tan delta began to decrease. This behaviour is discussed in terms of interfacial polarisation. The duration of the first phase is compared with the time of water diffusion throughout the resin.

Figure 1: photo of the test cell.

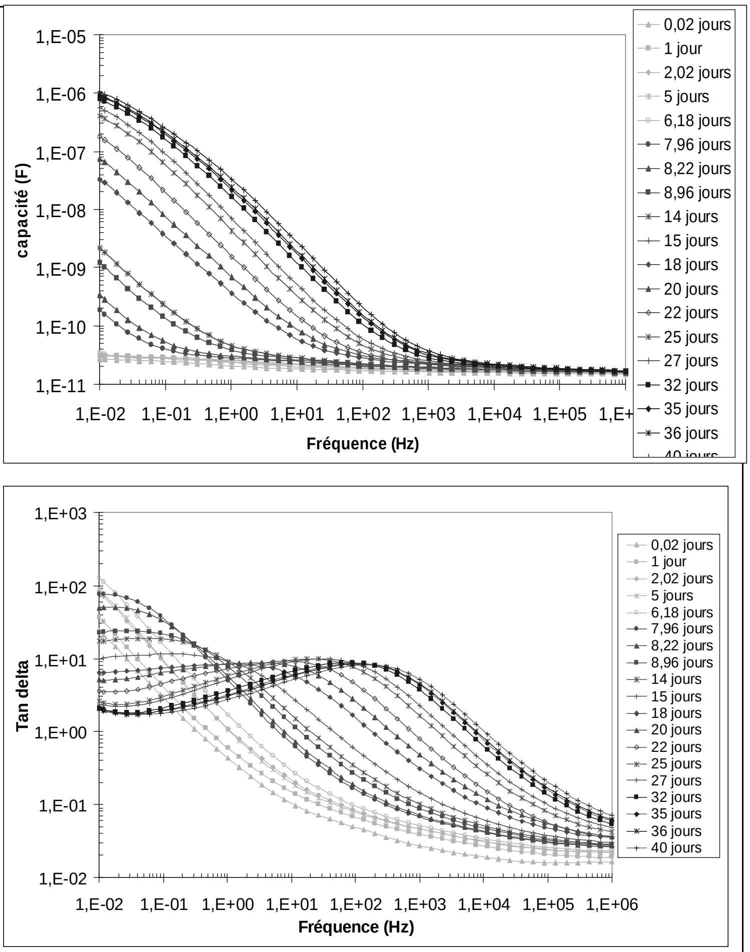

Figure 2: dielectric spectra.

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Back switching of ferroelectric polarization in PZT

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It was shown recently [1] that one can calculate the ferroelectric polarization switched back in a ferroelectric polymer after completion of poling (or switching) and followed short circuiting by processing displacement curves of two consecutive poling experiments using a special procedure. It has been found that the back-switched polarization in PVDF depended on the poling time and exhibited a maximum at a certain value of the latter.

In this work, the same method was applied to study the back switching phenomenon in PZT ceramics. Disk shaped samples 10 mm in diameter and 1 mm in thickness of a commercial lead zirconate titanate PIC-151 were used ($Pb_{0.99}[Zr_{0.45}Ti_{0.47}(Ni_{0.33}Sb_{0.67})_{0.08}]O_3$).

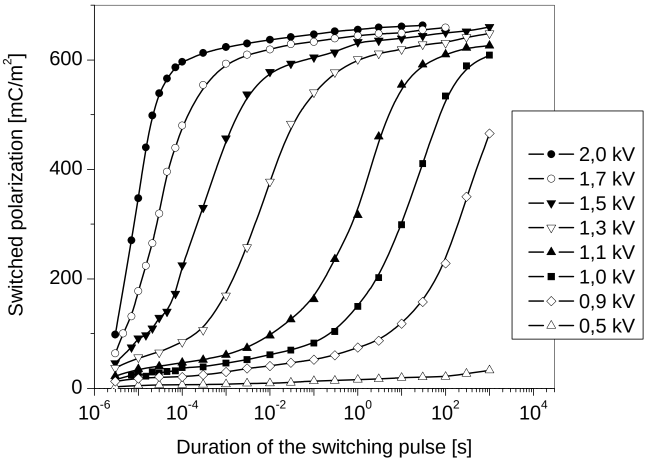

Fig. 1 Switched polarization as a function of ***V*** and ***t***.

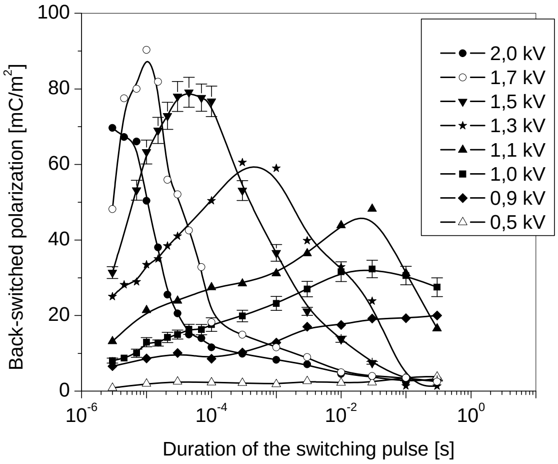

Fig. 2 Back switching of polarization in PZT.

All samples were electroded with silver fired into the surface at 720 °C. Each sample was conditioned by poling during 1000 s in the field of 2 kV/mm assuming that saturation was reached under these conditions. The same conditioning was made after each switching experiment. As one can see from Fig. 1, the value of the switched polarization is a function of the switching voltage (field) and the time of voltage application. However, a part of the already switched polarization, as shown in Fig. 2, returns back to its original state. The value of the back switched polarization is again a function of the applied voltage (field) and time.

Appearance of a maximum on the back switching curves can be explained by the effect of conductivity in formation of the compensating charge at the grains of PZT ceramics. If this field is not sufficiently neutralized (screened) by the trapped charges, as in the case of small times, then about 70 % of the switched polarization goes back, while at longer times and strong fields the back switched portion approaches zero. The obtained data are important both for understanding physics of the back switching and for selection of appropriate poling and switching conditions and parameters.

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Interrelation between conductivity and polarization phenomena in two-component ferroelectric polymers

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It is commonly believed that formation of polarization and its switching in ferroelectrics under high electric field strength is a fast process in the microsecond range.We have found, however, that in semicrystalline ferroelectric polymers like polyvinylidene fluoride (PVDF) containing both crystalline and amorphous phases, development of polarization continues during times 5 to 6 orders of magnitude longer than the estimated switching time. The controversy has been resolved by taking into account peculiarities of the depolarization field compensation in two-phase ferroelectrics and the effect of conductivity in such materials. Experiments were carried out on samples of 12.5 μm-thick biaxially stretched PVDF film from Kureha Co.

It has been shown that there are two components of the ferroelectric polarization, of which the first one is essentially field dependent and originates from a fast alignment of dipoles in crystalline regions, while the second slow component is controlled by the apparent conductivity of the material. Appropriate modeling revealed the importance of charge accumulated at the interfacial boundaries to form the slow ferroelectric polarization contribution. Good agreement of calculated and measured ferroelectric polarization has been observed for PVDF. Most probably the phenomenon is common for other two-phase ferroelectrics such as ceramics and ceramics-polymer composites.

After completing the charging, the sample is short circuited. If the polarization is not sufficiently compensated by charges trapped at the crystallite boundaries, some undesirable back switching of the formed polarization is possible. It has been shown by the example of PVDF that the back-switching of ferroelectric polarization in two-component systems like PVDF during short-circuiting after initial poling depends on the poling time and exhibits a maximum in samples poled for about 100 μs. The switched back polarization decreases to zero for poling times smaller than 1 μs and times exceeding 1 s. The phenomenon is explained on the basis of the same model proposed for polarization buildup in two-component ferroelectrics taking into account the role of conductivity induced interfacial charge accumulation at the boundaries between ferroelectric and non-ferroelectric components.

The influence of screening dynamics on polarization switching in PVDF has been also investigated experimentally and theoretically. The presented phenomenological model relates released screening charges to the formation of apparent conductivity modified by the partial charge recombination. The interplay of temporal screening charge release and reconstruction modeled through the temporal behavior of conductivity determines decisively the dynamics of polarization switching. Under the assumption that all screening charges are released instantaneously upon application of the switching field followed by recombination, a fit to experimental polarization switching data over 8 orders of magnitude in time is possible.

Thus, the effect of conductivity and the compensating charge accumulated at the cristallite boundaries due to conductivity on the dynamics of poling, short circuiting, and polarization switching in two-component ferroelectric polymers like PVDF has been clarified.

Dielectric Inspection of Biological Cells

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Technological innovations in dielectric cytometry and dielectric cell-assay on a chip are exciting challenges for newer applications of dielectric spectroscopy (DS) for biological systems [1]. In general, living cells exhibit large dielectric responses in the MHz region resulting from the relaxation of interfacial polarization that could be sensitive to cell geometries [2], cell types [3], and cell activities [3] and so on. Thus DS has higher potential for the cytometry and cell-assay. However, even though many DS studies have already been done for cell suspensions (mainly spherical cells and fewer biconcave erythrocytes), our knowledge is still limited. Thus, we studied the sensitivity of DS with morphological changes of cell, temporal variation, or cell differentiation.

Firstly, we prepared four different shapes of rabbit erythrocytes by precisely regulating the medium pH, i.e. discocytes (biconcave erythrocytes) at pH 8.5, echinocytes at pH 7.7, enlarged erythrocytes (expanded discocytes) at pH 5.6 and spherocytes at pH 5.3. Quantitative analysis of the observed spectra showed that the relaxation time and the Cole-Cole parameter specifically characterize the dielectric spectra from a certain type of erythrocyte. On the other hand, the accuracy of the analysis on the basis of the single-shell models (spherical or ellipsoidal model) is very high for the spherocyte but rather low for the other shaped erythrocytes. Here, numerical simulations on the basis of the three-dimensional finite difference method exhibited essential improvements of the accuracy.

Secondly, we monitored preserved rabbit blood for 37 days. Microscope observation showed that approximately 90% of the erythrocytes were echinocytes at the beginning of preservation and started to be transformed into microspherocytes around 20th day. The DS experiments showed the same critical point of 20th day, where the relaxation time and Cole-Cole parameter start to increase and decrease, respectively. The blood deterioration in the present study involved correlated morphological and electrical changes of erythrocytes, and DS successfully sensed the process.

Thirdly, cultured lymphocyte cell line (NB4) was used to monitor the cell reactions to the inducer of differentiation. DS responses clearly changed after 24h from the starting of the differentiation, where the relaxation time decreased significantly.

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Dielectric relaxation of low-molecular-weight molecular clusters in nanoscale confinement - MD study

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The properties of molecules in nanoscale confined geometries reveals effects not observed in bulk systems [1-2] and is of great interest to biology, geology and materials science. Using all atoms AMBER force field, we perform molecular dynamics simulation to study the effect of confinement on the properties of a number of low-molecular-weight molecular clusters.

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Approaching The Inverse Problem Of The Multi-Layer Skin System

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The problem of solving the electromagnetic inverse problem for skin (i.e. evaluation of the dielectric properties for various skin layers) is being investigated by comparing capacitive fringing field sensors of different geometry. The sensors are attached to the surface of the skin and therefore are relevant for non-invasive practical applications in healthcare. In contrast to coaxial probes typically used to determine the permittivity of biological materials, the shape of the capacitive fringing field sensors used in this project is thin circuit board (~3mm) so that it can easily be integrated into small portable devices. As a first approach, we have considered a two layer skin model. For the experimental investigation of the influence of the different model parameters on the measured signal we have built an artificial testing system with the ability to vary dielectric properties and thickness of the layers. In particular, the conductivity of the first layer is changed to test how the conductivity influences the prediction of the dielectric properties of the second layer that is kept constant.

In a future application relevant to the problem of non invasive in vivo glucose monitoring, we will be mainly interested in changes occurring in the deeper skin layers where the glucose-induced changes on the dielectric properties are occurring. However, these alterations can be obscured by dielectric changes in the upper layer and on the surface of the skin, (e.g. following sweating events). In the two layer systems we have therefore used solutions of water and sodium chloride with a concentration varying from 10 mmol/L to 100 mmol/L as a first layer. This range covers the normal range that are expected in the sweat of a healthy individual.

To separate the influence of the two layers we need a sensor with at least two different "penetration depths". We then use numerical simulations to predict the effective (mixture) permittivity and conductivity of the two layered medium by the different sensors. The effective bulk properties are predicted for a large number of combinations of dielectric properties of the two layers. The predicted values are collected in a four dimensional table for the various combinations of permittivity and conductivity of the two layers. This table can then be used as a look up table to determine the dielectric influence of the two layers separately by measuring the bulk at two different "penetration depths".

The results using the look up table were also compared with analytical formulas used to predict the permittivities of each of the two layers from a measurement of the effective bulk permittivities by two different sensors. These results will form an addition to the development of a dielectrics based algorithm applied to the experimental/clinical data for deriving continuous glucose related information.

Non Invasive Glucose Monitoring with a Dielectric Spectroscopy based Multi-Sensor Platform

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Solianis Monitoring AG is developing a multi-sensor device for non invasive continuous glucose monitoring (NI-CGM) in which one key element is the application of Dielectric Spectroscopy (DS). Changes in the dielectric properties of skin at various penetration depths have been investigated, and these changes will be shown to be correlated to the change in glucose concentration in patients during intravenously and orally induced glucose excursions within experimental clinical studies. A multi sensor approach is required since a number of extrinsic and intrinsic factors can affect the DS measurements. The multi-sensor concept includes fringing field capacitive sensors for broad band DS, optical, sweat/moisture, acceleration and temperature sensors to compensate for such factors. This work describes the current results of the ongoing technological development. It is shown that the concept is applicable, not only within strictly controlled clinical conditions using an intravenous glucose clamp technique, but also in more challenging environmental conditions where the patients experience conditions that are closer to “daily life” including the administration of glucose orally and controlled movements.

Eight patients with diabetes mellitus (4 T1DM, age 43±9 y; BMI 26.1±2.9 kg/m^2, duration of diabetes 22±14 y; HbA1c 7.4±0.9% and 4 T2DM patients, 66±2 y; 30.6±1.8 kg/m^2; 10±8 y; 6.9±0.3%) performed up to four study days. Glucose was administered orally to induce a hyperglycaemic excursion to a target level of 15 mmol/L. Euglycemia was re-established by s.c. insulin administration. In two of the four study days defined movements were introduced including sequences of cycling, walking around and regular deskwork. In the other two study days in addition to the movement blocks and the oral glucose administration, patients drank 3 litres of water. A multiple regression analysis was performed to establish a global model including all subjects and all study days. In a next step a personal model was established included the same parameters as the global one, but the coefficents were parameterised to each study subject to optimise the model performance. The models generated were tested for potential overfitting and demonstrated that an essential modeling parameter was the DS sensor that measured the change in dielectric properties deeper in the skin tissue. With the personal model glucose excursions could be tracked with an R^2 of 0.71 and an MARD of 17.9%, the global model yielded an R^2 of 0.6 and an MARD of 21.5% respectively.

These results demonstrate that glucose variations in patients can be monitored continuously by measuring changes in the dielectric properties of skin and underlying tissue. The multi-sensor approach is required to enable the dielectric properties of the skin at different penetration depths to be measured, and to compensate for perturbing effects that influence these measurements in closer to “daily life” conditions. Future steps will develop the data evaluation routines and algorithms to allow real time signal processing of the multi-sensor data and transformation into clinically relevant information for patients with diabetes in an outpatient setting.

The Dielectric Relaxation In New Leadless $A_2B'B''O_6$ Ceramic Materials

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A new group of leadless ferroic materials with general formula $Bi_2Me_{1,33}Sb_{0,67}O_6$, where Me = Li, Ni, Mg, Co and Zn has been synthesized using two-stage ceramic technology. As initial powders Bi_2O_3, Sb_2O_3, MgO, Ni_2O_3, Co_3O_4 and ZnO oxides, taken in stoichiometric ratio, have been used. The temperature of the solid-state synthesis measured by the differential thermal analysis was found to be ~810 °C. Optimum technological parameters (temperatures of synthesis and a baking, times of baking, heating and cooling rates, and a gas atmosphere) for manufacturing of single-phase samples with density 6.7 g/cm^3 were revealed. The X-ray diffraction analysis with use of Fe K_α radiation and Ni filter has shown that at room temperature the samples had pyrochlore structure with unit cell parameter $\boldsymbol{a}$ = 10.4951 A°.

Temperature dependences of the dielectric permittivity ε' and losses ε" at various frequency and a measuring field ~10 V/cm were studied in a temperature range of 300-800 K. Both a permittivity ε' and loss ε" are increased with temperature. It was observed the anomalous change of ε' and ε" for Ni, Mg, Co and Zn-containing materials at 765, 768, 570, and 780 K, which is related to structural phase transitions. The pronounced dielectric dispersion in a frequency range of 500 Hz - 1 MHz and temperature interval 300-800 K was found out. It is interesting that novel ceramic materials possess a huge value of $\varepsilon' \sim 10^4$ at low frequencies, which speaks the Maxwell-Wagner mechanism related to charge accumulation in grain boundaries. In high temperature region contributions to dielectric losses related to conductivity and low-frequency dielectric relaxation were divided. The diffused tgδ maximum observed in temperature dependence of losses has the relaxation thermally activated nature as it shifts to higher temperature as a frequency of a measuring field is increased. The computer analysis of the anomalous dielectric losses in frames of the Maxwell-Wagner relaxation model has revealed a good fit to experimental data.

The work has been executed at financial support of the Russian Foundation for Basic Research (grant # 06-02-96310) and CRDF (grant # PG 05-010-1).

Electrical Properties In Nanocomposites $Co_x(CaF_{2-\delta})_{(1-X)}$

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Nanocomposites $Co_X(CaF)_{100-X}$ were prepared by a method of ion beam sputtering of a composite target on a silicon substrate. The target represented cobalt plate in the size 280x80x10 mm^3, soldered to the water-cooled copper foundation on which surface hinge-plate of ceramics CaF a size 80x10x2 mm^3 nonuniformly fastened. The nanocomposite films of $Co_X(CaF_{2-\delta})_{100-X}$ (x ≈30 – 65 %) deposited on silicon substrate, were prepared during single work cycle and had a thickness near 5 µm. The Co concentration x was determined by x-ray electron-beam microprobe analysis from five measurements performed on different parts of the substrates with subsequent polynomial extrapolation of the content over the substrate length.

The samples were placed in a thermostat, where temperature was varied from +20 °C to +450 °C. The measurements of a capacitance (C) and a conductivity (g) were carried out in the frequency interval 10^2 - 10^6 Hz using a impedance analyzer E7-20.

Experiment has revealed increase of a capacitance and conductivity of composites samples with increase of a metal phase concentration. Anomalous increase C and g with increase x was observed at concentration Co corresponding to a percolation threshold when $x_c \approx 0{,}45$.

An experiment has shown that samples under studied materials at a room temperature possess high values of the low-frequency permitivity monotonously decreasing with increase of measuring frequency. It enables us to speak that the main contribution to the dielectric response is caused by polarization Maxwell – Wagner type induced by motion of the mobile charge carriers near to electrical inhomogeneities. The monotonic increase capacitance and electrical conductivities is observed as a temperature is approached to recrystallization temperature $T_{recr} \approx 340$ °C from below.

Obtained experimental results are discussed in the framework of model [1] considering correlated jumped motion of carriers due to Coulomb interaction.

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THE DIELECTRIC RESPONSE IN THE COMPOSITE $P(VDF_{60}/Tr_{40})$ - POROUS GLASS.

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It is known that the physical properties of ultradispersed solids differ essentially from those of the bulk materials. In particular size effects result in the drastic changes of the phase transition features, and one can expects that these effects to become especially significant if the characteristic size becomes comparable with correlation length of the order parameter critical fluctuation.

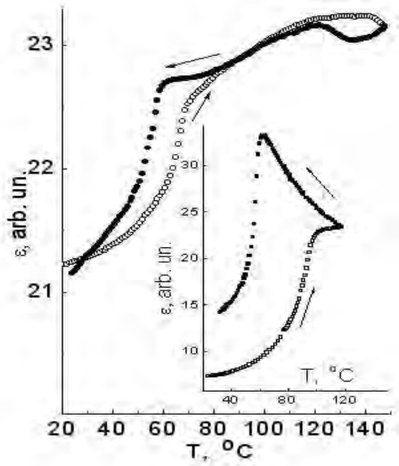
The purpose of the present work is the experimental study of the dielectric response in polar copolymer $P(VDF_{60}/Tr_{40})$, confined within porous glass matrix with pore sizes 320 nm in the vicinity of ferroelectric phase transition temperature.

Samples for experiment were prepared by immersing the preliminary vacuum-annealed porous glass in the saturated solution of copolymer in acetone for about 4 hours in a sealed quartz container.

Then the samples were annealing in vacuum during 6 hours at temperature of 150 ^{0}C for acetone removing.

Samples were in the form of rectangular plates 7x7x1 mm^3 clamped between aluminum electrodes. The measurements of dielectric permittivity ($\varepsilon^/$) and dielectric losses (tgδ) were carry out at heating and cooling regimes using impedance analyzer E7-20 at frequency range f = 25 Hz - 1 MHz.

The temperature dependences of $\varepsilon^/$, obtained at f = 1 kHz under experimental conditions are shown in figure. (Corresponded dependences of $\varepsilon^/(T)$ observed for the bulk $P(VDF_{60}/Tr_{40})$ are shown in insert.)



It was found, that the temperatures corresponding to paraelectric (PE) → ferroelectric (FE) phase transition practically are coincided in the both samples. However the FE→PE phase transition in confined $P(VDF_{60}/Tr_{40})$ is realized at lower temperatures in comparison with bulk sample.

The decreasing of FE phase transition thermal hysteresis wide in the confined copolymer is discussed in the framework of the model taking in account the interaction of polar phase boundaries with inside surface of pores.

This work was supported by Russian Foundation for Basic Research (Grants N 07-02-00228 and N 08-02-01089-a)

Broadband Dielectric Spectroscopy of Poly (2-ethoxyethyl methacrylate-co-2,3 dihydroxypropyl methacrylate) Membranes

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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. All polymers show complex dielectric relaxation spectra.

The spectra of the serie of membranes show almost three relaxation 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. 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. 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.

The activation energy of these processes has been calculated from the data by means of an Arrhenius plot and has been compared with that derived from molecular mechanics calculations.

Segmental Dynamics in Polysiloxane Blends

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The microscopic behaviour of polymer blends near to their glass transitions has been the subject of much research over the last decade or so due both to interest in developing a complete understanding of the glass forming process in a wide range of systems, and to the increasing importance of polymer blends in industrial products.

We present studies of blends of a polysiloxane with polystyrene and with polycyclohexylmethacrylate at a range of compositions. In both cases the two components have widely differing calorimetric Tg's (>150 °C) and results from broadband dielectric spectroscopy measurements are discussed in terms of dynamic heterogeneity in the miscible systems.

Most of the polymer blends of interest in industrial laboratories such as our own are not fully miscible. The polystyrene containing system is not miscible over all compositions, but shows the interesting property that, when annealed at certain temperatures, the polystyrene-rich phase passes through its glass transition before phase separation is complete. The resulting vitrified partially phase separated systems allow segmental dynamics during the phase separation process to be examined by broadband dielectric spectroscopy from the fully mixed through to the completely demixed states.

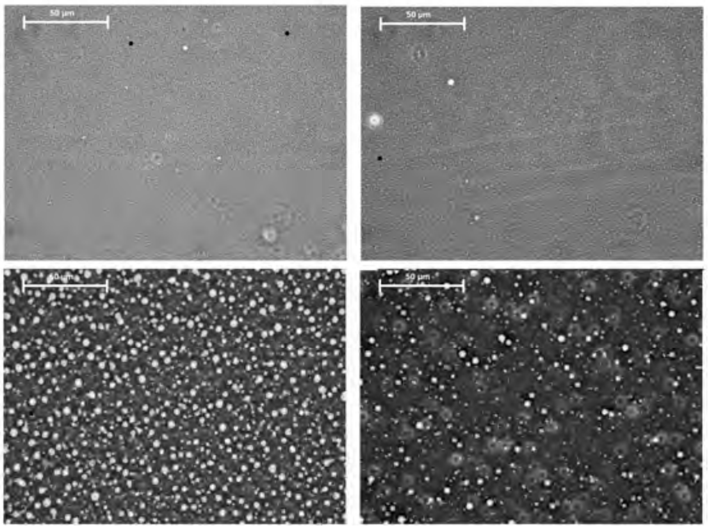

Figure 1 – Phase-contrast optical micrographs of a polysiloxane-polystyrene blend of a single composition annealed at increasing temperatures (top left to bottom right) demonstrating the ability to freeze the phase separation at various stages.

Non-Debye dielectric behaviour and near-field interactions in biological tissues: when structure meets function

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The Maxwell-Wagner theory (MWT) of interfacial polarization has been successfully used for decades to explain the frequency-dependent dielectric properties of dilute suspensions of particles [1]. The theory treats the suspended particles as systems of *independent induced dipoles* subjected to alternating fields, and therefore predicts simple Debye-type dispersion in which both permittivity and conductivity vary between low- and high-frequency plateaus. Unfortunately, MWT cannot replicate its own success when applied to more concentrated and structured (i.e., non-random) systems of cells such as tissues. The effective medium theory (EMT), devised [2] to incorporate contributions of the induced dipoles to the *average far-field*, brought some improvement, but the general behavior remained that of a simple Debye – in contrast with experimental data. Supracellular organization of tissues induces non-Debye behavior, as expressed by a dispersion function that includes the Debye-type and Jonscher's universal responses as its particular cases [3].

I will begin this talk by reviewing published data indicating that *near-field interactions* between neighboring cells induce deviations from the classical Debye behavior. Specifically, biological cells may perturb each other's electrical environment via *dipolar* (*multipolar*) fields induced by nearby polarized neighboring cells and via *conductance bridges* (such as pores and gap junctions) between cytoplasms and across cell membranes. Dipolar interactions explain the general features of the dielectric dispersion of percolation-like structures in liver [4], although further work is necessary to account for the absence of plateaus in the dispersion spectra. Dielectric behavior of tree-like (Cantorian) fractals (e.g., blood vessels in lungs) has been modeled as systems of branched transmission lines [5], although realistic microscopic models incorporating the cellular compartments are lacking. In the second part of the talk, I will discuss that blood represents an incredibly versatile experimental model for studying multipolar interactions in reversible structures of red blood cells (RBCs). Recent results from my laboratory revealed a wide variety of dielectric responses elicited by different structures generated by RBCs aggregation under various flow conditions and cell concentrations.

Results of numerical simulations for linear RBC aggregates (rouleaux) are encouraging [6], but more work remains to be done on percolation-like networks of cells. In a separate study, we observed that changes in the activity of brain have significant effects on the gap-junctional connectivity between cells, which in its turn induces changes in the brain dielectric properties. Conceivably, theoretical modeling of aggregated systems may face significant challenges. However, the expected benefits should offset the costs, especially if concerted efforts are devoted by the dielectric spectroscopy community to addressing such problems.

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A New Simulation Model For Dielectric Relaxation Based On Defect Diffusion Model And Waiting Time Problems

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We propose a new simulation model for dielectric relaxation based on defect diffusion process. The defect diffusion model (DDM) has been used to interpret dielectric relaxation and other relaxation phenomena [1-3]. The essential feature of the model is a cooperative interaction between the relaxing dipole and its nearest neighbors, containing defects, and the relaxation can only occur when a defect encounters of the dipole. In our model we have taken the motion of defect as a stochastic processes characterized by successive waiting time problem instead of classical random walk motion. Our system consists of point defect asuumed to be located at a distance l from a given dipole at $x = 0$ at time $t = 0$, and this defect arrives at the dipole first due to successive waiting time problem. We present computer simulation result of our study of such a simple model dipolar system and a dipole correlation function obtained from this new model under various physical conditions, appears in the form of a stretched exponential function $\phi(t) = \exp[-(t/\tau)^{\beta}]$, $0 < \beta < 1$.

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Molecular dynamics of n-ethylene glycol dimethacrylate followed by dielectric relaxation spectroscopy

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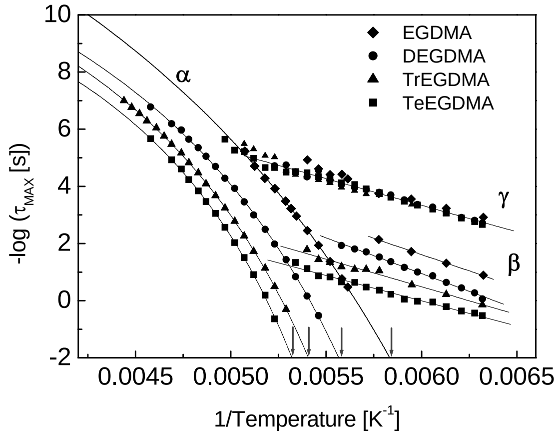
n-Ethyleneglycol dimethacrylate monomers due to its polyfunctionality have practical interest as precursors of cross linked polymers widely used in the production of coatings, information storage systems, spherical lenses and dental biomaterials and as matrixes for polymer dispersed liquid crystal devices [1,2].



A detailed dielectric characterization of n-ethylene glycol dimethacrylate monomers with n = 1 and 4 is provided. Besides the α-relaxation associated to the glass transition, two secondary relaxation processes were detected: the γ process assigned to the twisting motions within the ethylene glycol moiety, and the β process related with hindered rotations of carboxylic groups. While the relaxation time of the γ process is relatively independent of the size of the ethylene glycol group, the β process deviates to higher times with increasing n. At each temperature, the mobility of the cooperative process decreases with the increase of ethylene glycol moiety. The temperature dependence of the relaxation times obeys to the VFTH law for all the systems as usually found in fragile glass formers. The estimated glass transition temperature for τ=100 s increases with the increase, as also found from calorimetric analysis [3]. The fragility indexes estimated by both DSC and DRS techniques, increase with number of ethylene glycol units, *n*, suggesting a strong correlation between fragility (and also E^{eff}_{Tg}) and the glass transition temperature.

Acknowledgements: M.T. Viciosa and A.R. Brás acknowledge to Fundação para a Ciência e Tecnologia for PhD grants SFRH\BD\6661\2001 SFRH\BD\23829\2005 respectively.

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Monitoring the crystallization in a low molecular weight compound by Dielectric Relaxation Spectroscopy

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Ethylene glycol dimethacrylate (EGDMA) is a low molecular weight glass former that can be obtained as a nearly fully amorphous glass or in a nearly fully crystalline state depending on the thermal treatment to which it is subjected.

Its glass transition temperature, Tg , detected by DSC (mid point of the heat capacity increment) is -97.5 °C. The dielectric characterization was accomplished in the temperature range from –115 to 0 °C scanning frequencies between 0.1 and 106 MHz. The spectra of amorphous EGDMA show three relaxation processes: the α relaxation related to dynamic glass transition whose relaxation rate obeys to a VFTH law, and two secondary processes with Arrhenius temperature dependence. However,

In this work, isothermal cold-crystallization coming from below Tg was carried out at several temperatures, Tc (between -86 and -76 °C), and the dielectric spectra collected during crystallization were analyzed using the HN fitting procedure. The main observation concerns to the α relaxation, which depletes however without suffering any significant changes neither in position nor in shape. From the analysis of the evolution of the dielectric strength, $\Delta\varepsilon$ α , the crystallization degree, c χ , was estimated. Its Avrami's analysis allowed estimating the value of the characteristic parameter, n , between 2 and 2.8, indicating that this crystallization involves simultaneously nucleation and growth mechanisms [1].

When crystallization is carried out at Tc -80 °C a new process,α ' , arises at advanced states of crystallization in the low frequency side of the main α -relaxation. The molecular origin of this process is not totally clear but it can be related with a rigid amorphous phase formed by molecules either strongly bound to the crystalline fraction [2] or influenced by spatial confinement [3] or even originated by motions occurring in an orientationally disordered crystal phase [4].

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(FCT, Portugal)) through the project PTDC/CTM/64288/2006 is acknowledged. M. T. Viciosa acknowledges FCT for a PhD grant SFRH/ BD/6661/2001.

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Dielectric relaxation of Parylene C

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In the literature there are very few articles that describe precisely the dielectric properties of parylene. However these polymers are used in a large domain of applications. For some of them, it is necessary to precisely know these properties and their variation according to frequency and operating temperature. In our study, we investigate dielectric properties of Parylene C (Poly (mono chloro-para-xylylene)) thin films (5.8 µm) deposited by vapor deposition polymerization (VDP) from a di-chlorinated di-paraxylylene dimer. This polymer is integrated in liquid lens for auto-focus actuators with no moving parts. The optical power of the lens (*1/f*) is proportional to the dielectric constant of parylene and the reverse of its thickness. Dielectric properties were measured by a Novocontrol alpha-AN impedancemeter in large temperature and frequency ranges [-180°C – 140°C] [0.1 Hz to 1MHz].

The dielectric constant ε' is strongly frequency and temperature dependent as seen in figure.1. Three relaxation mechanisms (α, β, γ) are clearly identified in the loss factor (figure 2).

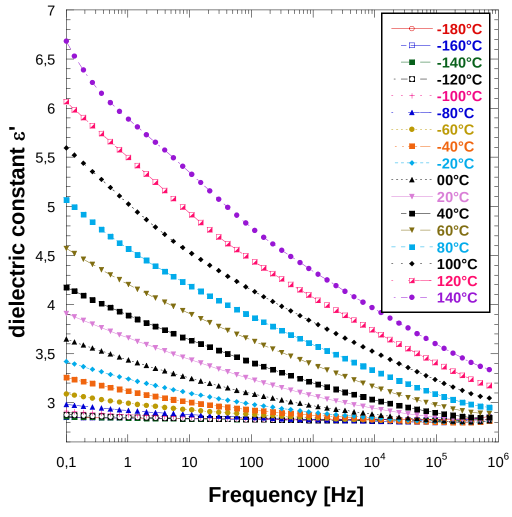

Figure 1 : *Dielectric constant against frequency*

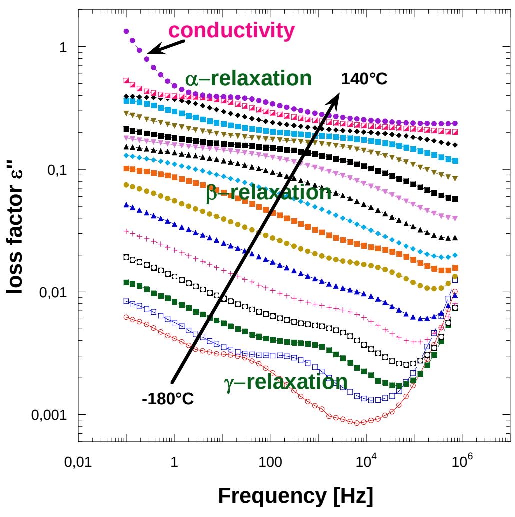

Figure 2 : *Loss factor against frequency*

Results will be focused on the origin concerning these three peaks. Particularly, explanations with regard to temperature dependence of α relaxation and the dielectric constant frequency shift are attempted.

Effect of Uniaxial Strain on the Dynamics of Elastomers

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The effect of chain orientation on the dynamics of polymer networks, chemically or physically crosslinked, is investigated using broadband dielectric spectroscopy. Measurements are performed in a conventional parallel-plate dielectric sample cell, custom-modified with a frame to which the sample is clamped and held at a constant strain. The direction of the applied electric field is perpendicular to the strain direction.

The local and segmental relaxations of polyurethane thermoplastic elastomers based on poly(tetrametylene oxide) soft segments and MDI-BDO hard segments are studied as a function of strain. Nanocomposites consisting of the same polyurethane containing clay nanoparticles are also studied. We attempt to correlate the effect of the nanoparticles on high-strain mechanical behavior with segmental dynamics at high strain observed using dielectric spectroscopy.

Flexible epoxy networks based on end-functional poly(propylene glycol)-diamine are also studied. The PPO chains in the networks are characterized by symmetrical dipole inversion, consisting of two uninverted dipole sequences originating at the midpoint of the chain. Therefore, they exhibit a normal mode relaxation even in the fully crosslinked state. This allows us to follow the effect of orientation on the dynamics at long length scales (length of the uninverted dipole sequence), in addition to segmental and local dynamics in these systems.

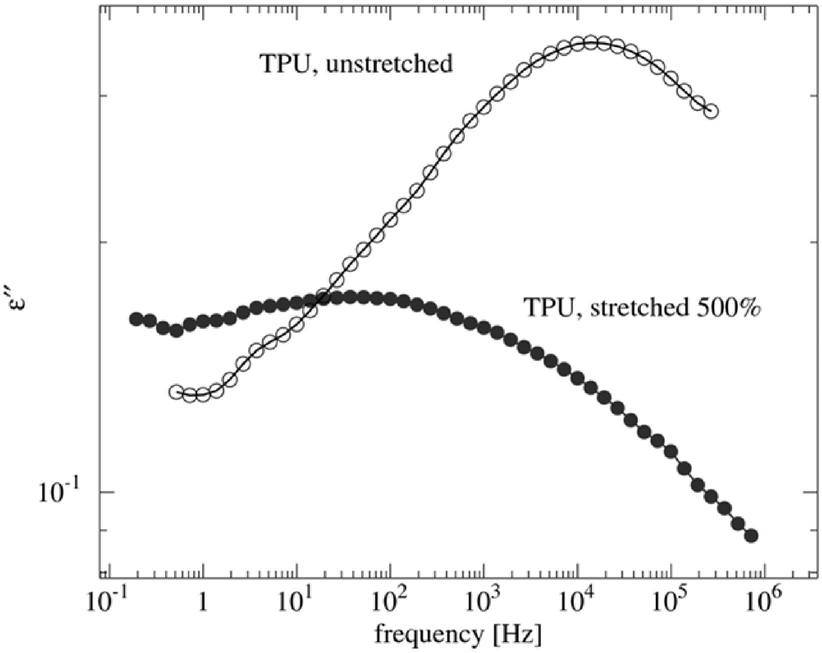

Figure 1: Dielectric loss spectra of unstretched and stretched thermoplastic elastomers, in the region of the segmental relaxation (273 K).

Preparation And Characterization Of Ferroelectrics Niobates Crystals With Tungstene-Bronze Structure

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The ferroelectric crystals deriving from tetragonal tungsten bronzes (TTB) family are of great interest because, on the one hand, their piezoelectric, pyroelectric and electronic performances, and on the other hand, of their use in the field of micro-electronics.

In the objective to amplify these physical properties, we proposed in this work to prepare monocrystal of the TTB type by the flux method, which can decrease the temperature of crystallization while limiting the departure of volatile oxides.

The temperature of solidification of these phases was determined by DTA. In addition, a thermogravimetry study showed that at this temperature, some starting products lose their weights. For this reason, it thus seemed us to use the method of crystalline growth by the flux method.

A series of preliminary experiments, led us to choose like flux, the carbonate of potassium (K_2CO_3). The mixture of oxides of niobium (Nb_2O_5), of gadolinium (Gd_2O_2), of lead (PbO), and of carbonate (K_2CO_3) crushed beforehand in the presence of flux (Flux/solution = 10%), is carried out in platinum crucible of 30 Cm^3 capacity on the temperature of 1200°C. After a stabilization of 4 hours at this temperature, crystallization is obtained by slow cooling (2°C/h) down to 950°C, and then to room temperature on the furnace inertia.

The study of physicochemical characterizations is in progress.

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Broadband Dielectric Spectroscopy of Multicomponent Polymer Systems: Crystalline and Associating Materials

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This paper reviews our recent studies of segmental and local dynamics of semi-crystalline polymer blends, as well as amorphous mixtures that exhibit strong intermolecular associations. In the latter area we will focus on broadband DRS results on solutions of poly(2-vinylpyridine) with low molecular weight phenols [1], and blends of poly(hexafluorostyrene-co-dimethylbutadiene) with amorphous polymers exhibiting various intermolecular H-bonding strengths. In both of these experimental systems we find that local glassy state processes are strongly suppressed due to the intermolecular interactions, similar to our recent findings for salt-containing P2VPy [2].

For semi-crystalline poly(ethylene oxide) blends with poly(vinyl acetate), a loss peak appears in the same location as the segmental process of neat PEO, indicating that relatively mobile amorphous regions with a large fraction of PEO exist even in blends with PVAc contents as high as 50%. In addition, the observed interfacial polarization process shifts significantly to lower frequencies with increasing PVAc content. These results are consistent with a morphology where the interlamellar regions are composed primarily of PEO and give rise to the α_{PEO} process in the blends, and most of the PVAc chains are located in the interfibrillar regions, which are responsible for the interfacial polarization processes.

This work was supported by the National Science Foundation, Polymers Program.

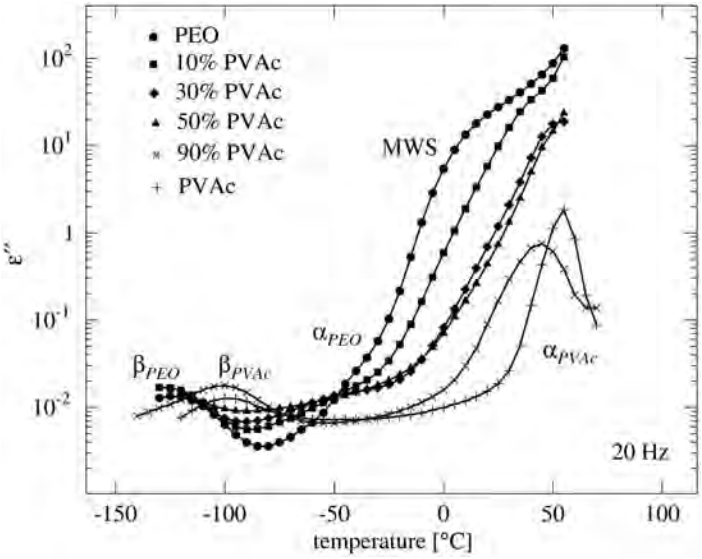

Figure 1. Dielectric loss vs. temperature (at 20 Hz) of PEO, PVAc. and PEO-PVAc blends (crystallized at 44 °C).

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Monitoring of polymer melt processing by dielectric spectroscopy

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For large-scale preparation of thermoplastic polymer composites, melt processing by extrusion or mold injection is mostly used in industrial process. For conductive polymer composites, it has been found that there is wide variation of electrical conductivity when the melt processing parameters were changed. This was well known for carbon black (CB) filled polymers and became recently evident for carbon nanotube-polymer composites. By several groups a tremendous influence of thermo-mechanical prehistory on the conductivity (and permittivity) has been reported [1-8]. Thus, both scientific interest to understand the origin of the conductivity changes during melt processing and technical interest to control conductivity and optimize processing condition arises. Except the interest on polymers with conductive fillers, there is also interest in in-line measurements of the dielectric permittivity of polymers with non-conductive fillers and polymer blends.

In order to study the influence of extrusion conditions on the (di)electric properties, in-line experiments have been performed in a slit die flanged to the outlet of a twin screw extruder. The measurement slit die contains two electrodes in plate-plate geometry [4,7]. AC conductivity and complex permittivity were measured in the frequency range from 20 to 10^6 Hz for different extrusion conditions (melt temperature, screw speed, throughput etc.) and after stopping the extruder. The investigations have been performed during melt processing of polypropylene, polyethylene, polycarbonate (PC), and polyamid-6 containing different amounts of multi walled carbon nanotubes (MWNT) [4,7]. It was found that the conductivities of all samples that during extrusion were in the order of magnitude of the matrix polymer. After the extruder was stopped, the conductivity showed a tremendous increase with time while we hold the melt at high temperature. The finding can be explained by the reorganization of the conducting network-like filler structure, which was (at least partially) destroyed under shear. The reformation of the conductive filler network is assumed to be partially due to (i) agglomeration [7,8] (e.g. by cluster aggregation in a percolating system) and (ii) CNT de-orientation under quiescent conditions.

More recently, we performed in-line measurements during mold injection of PC, polyamide-12 and composites of acrylonitrile-butadiene-styrene (ABS) and PC containing MWNT to evaluate the influence of melt temperature, injection velocity and mould temperature on the DC conductivity. A good correlation between in-line and off-line electrical conductivity was found.

In addition to composites containing conductive fillers (CB and CNT), we also applied the in-line dielectric spectroscopy to non-conductive polymer composites.

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Lithium conductivity and molecular mobility in poly(ethylene oxide)-based polyester ionomers

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As part of our continuing investigation of ion transport in model polymer electrolytes, we use broadband dielectric spectroscopy to investigate the dynamics of the polymer chains and lithium cations in a series of single-ion conducting polyester copolymers. The copolymers studied consist of PEO segments (of molecular weight 600) separated by Li-neutralized sulfonated isophthalate or neutral isophthalate groups (Figure 1). The total ion concentration is controlled by systematically varying the fraction of ionic isophthalate groups from 2.5% to 100%, corresponding to a ratio of ether oxygens to Li+ ions of 520:1 to 13:1 (EO:Li). Since the sulfonate anions are covalently connected to the polymer chains, the conductivity observed is associated solely with transport of Li+ cations.

Attachment of ionic groups to the polymer chain and complexation of PEO segments with Li+ ions causes a slowdown of segmental dynamics and an increase of glass transition temperature above a critical ion content, as well as the appearance of additional slow relaxation processes associated with short-range ion motion within ion pairs or aggregates. Conductivity is strongly coupled to the segmental polymer chain relaxation. At a fixed segmental relaxation frequency, molar conductivity increases with increasing ion content suggesting that a mechanism of ion transport involving exchange between associated species becomes active for small average ionic distances.

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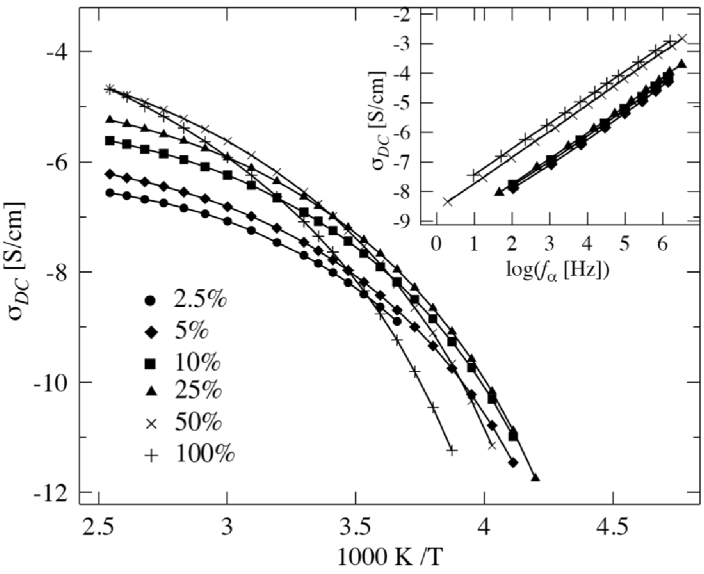

Figure 1. DC conductivity of the ionomers. The inset shows molar conductivity vs segmental (α) relaxation frequency.

Complex Nature Of The β Relaxation In Semi-Crystalline PLLA: Influence Of Crystallinity

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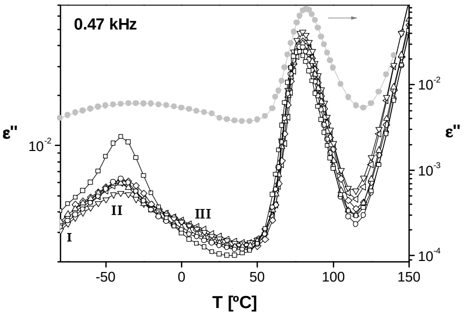
Despite the fact that polymer crystallization has been the object of intense research, this process is far from being fully understood. Moreover, most of the studies in literature deal with the crystallinity influence on the glass transition and not so much importance is given to secondary processes that usually are reported as not significantly affected.

In the present work, the β-relaxation is revealed as a probe for different morphologies attained by varying crystallization temperatures, T_c.

Poly(L-lactic acid), PLLA, was crystallized from the glassy state at different T_c (from 95 to 165 °C) to produce fully transformed semi-crystalline specimens exhibiting different crystallinity degrees, χ_c ($0.43 \leq \chi_c \leq 0.65$), determined by WAXS [2]. It was shown that the secondary β-relaxation process in semi-crystalline PLLA has a multi-component character as well illustrated in the figure (in gray is included the plot for the amorphous sample [1]). It becomes evident that the broad β-peak in the amorphous sample is decomposed in 3 secondary processes after crystallization. Dielectric spectroscopy proved to be a unique tool to reveal the complex nature of the β-process, which in semi-crystalline PLLA ($\chi_c > 0.40$) is reported for the first time. The detailed dielectric characterization is now provided.



The α-process was also investigated, shifting to higher frequencies/lower temperatures with the increase of T_c. From the VFT dependence of α-relaxation rates, the Vogel temperatures and T_g (τ=100s) were estimated, decreasing with T_c increasing. This result is quite compatible with the previous calorimetric and mechanical analysis studies [2, 3], rationalized [2] in terms of a 3-phase model where the rigid amorphous phase, whose thickness increases with T_c, reduces the constraints imposed by the crystalline wall on the chain motions inherent to the dynamic glass transition.

Acknowledgements: Financial support to Fundação para a Ciência e Tecnologia: PhD grant SFRH/BD/23829/2005 and project PTDC/CTM/64288/2006 is acknowledged.

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Dielectric Spectra Of Natural Cork And Derivatives

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Cork is a natural cellular material which has been used for centuries. Its unique mechanical, acoustical and thermal properties make cork and its derivative products ideal for many different types of applications [1,2]. Cork is a good electrical insulator and because of the cells filled with gas it might be possible to use it as a porous dielectric, which can be electrically charged and is able to retain this charge. So it could be of great interest to study the dielectric properties of these materials with the aim of finding possible new applications. For instance, to determine if it has piezoelectric properties that would make it suitable for use as smart sensors. Previous studies have already shown that the sample humidity greatly influences the electrical proprieties of cork products and consequently charge storage [3-5].

In this work samples from natural cork, commercial cork agglomerates and a composite of Cork/TetraPak® or Cork/TetraPak®/Paraffin were studied. In order to understand the water content samples could be or not dried prior to preparation and /or measurement. Measurements were performed using NovoControl-GmbH Alpha-N broadband impedance analyzer (frequency range was 10^{-1} Hz to 2 Mhz) and the temperature was controlled by a NovoControl-GmbH Quatro Criosystem BDS-1100 (temperature range used in measurements was –50°C to 120°C).

The results for the different types of cork samples were compared and also with previous published results for natural cork [3]. The influence of the drying was investigated in order to improve the ability of the materials to store space charge and consequently optimize preparation. A comparison was made with the results obtained by isothermal and thermally stimulated charging/discharging methods [4,5].

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The Analysis Of Isothermal Current In Terms Of Charge Injection Or Extraction At The Metal-Dielectric Contact

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The measured isothermal charging and discharging currents are analyzed either in terms of polarization mechanisms or in terms of charge injection/extraction at the metal-dielectric interface and the conduction current through the dielectric material. As long as we do not know the nature of the origin of the current it is not clear what information we can get by analyzing the experimental measured isothermal charging current and/or the isothermal discharging current. The analysis of the current-voltage behavior is unable to unravel detailed bulk/interface mechanisms, especially as the bulk features are equally undefined. There is a very general result that the measured current, the sum of particles and the displacement current, follows the empirical Curie-Von Schweidler law t^{-n} where t is a time after the application of the field and n is a constant often observed to be lower than 2.

We propose to measure the open-circuit isothermal charging and discharging currents just to overpass the difficulties related to the analysis of the conduction mechanisms through the dielectric materials. We demonstrate that besides a polarization current there is a current related with charge injection or extraction at the metal-dielectric contact and a reverse current related to the charge trapped into the superficial trap states of the dielectric and that can jump at the interface in a reverse way. It is proposed an analytical expression for the current. By fitting the experimental data to this analytical equation two important parameters can be determined (i) the highest value of the relaxation time for the polarization mechanisms still involved into the transient current and (ii) the height of the potential barrier W_0 at the metal-dielectric interface at the initial time when the step voltage is applied.

Dielectric Relaxation Study Of The Dynamics Of Sugars

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Carbohydrates are one of the most important families of compounds in nature. Huge number of members of this group and their variety causes that sugars play a key role in many processes occurring in living organisms. They can be building materials (chitin), a main source of energy (glucose). They can also act as a biological code in signaling and cell-recognition processes. Moreover, sugars have an important application in food science, medicine, pharmacy and cosmetics. It is enough to mention some representatives of this group like glucose, fructose, ribose, 2-deoxyribose, sucrose, lactose, trehalose, starch to understand how essential is to get as much as possible information about the structures and behavior of saccharides. That is why the study of the dynamics of carbohydrates is a very interesting topic.

In this presentation we would like to focus on the dynamics of the supercooled mono- and di- saccharides [1], [2]. Within these two subgroups we observed three relaxation processes, the structural (α-) and two secondary relaxations (β- and γ-). The relaxation process of monosugars, which we call β, is observed for the first time ever. We would like to discuss the possible molecular origin of these processes basing on our dielectrical data, theoretical calculations and existing models.

Moreover, in fructose, for the first time, we were able to observe dielectrically the mutarotation of the liquid sugar. We would like to discuss this phenomenon, how it reveals in the dielectrical spectra and what the consequences of it are for the future measurements of melting sugars and their mixtures.

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Identification Of The Molecular Motions Responsible For The Slower Secondary (β)-Relaxation In Sucrose

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Broadband isothermal dielectric relaxation measurements of anhydrous sucrose were made at ambient pressure in its liquid and glassy states. We found a new secondary relaxation that is slower than the one commonly observed in sugars. Additionally we carried out the dielectric measurements of the equimolar mixture of D-glucose and D-fructose in wide ranges of temperature and frequency. Comparison of the behavior of these two systems allowed us to make suggestions on the origin of the slower β-relaxation in sucrose. Computer simulations and coupling model calculation were performed to support our interpretation of the kind of molecular motions responsible for the slower secondary relaxation in the disaccharide considered.

Simultaneous dielectric, calorimetric and SAXS/WAXS experiments during polymer crystallization

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In order to understand nucleation; crystallization and other phase transitions in polymers, polymer based composites, or in liquid crystals simultaneous experiments with a combination of different methods are useful. Due to different sample geometry and thermal conditions it is usually difficult to compare the results of different individual experiments. As an important supplement to the classical techniques for studying crystallization like SAXS, WAXS, or differential scanning calorimetry, measurements which test molecular mobility like dielectric or mechanical spectroscopy are of interest during isothermal and non-isothermal crystallization. From such simultaneous experiments we can learn about the existence of pre-ordered structures before formation of crystals, as detected by DSC or X-ray scattering.

In this contribution we present the development of a device for simultaneous measurements of electrical properties and SAXS/WAXS intensities, which was extended to a microcalorimeter and allows measuring thermal properties like heat capacity and thermal conductivity additionally at the same time and at the same sample volume.

Thermally Stimulated Currents In The Electrospun Poly(Ethylene Terephtalate) Mats

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Electrically charged electrospun non-woven mats have the potential to find a wide variety of biomedical applications. Hence, their long-term charge stability at different corona - discharged conditions and environmental pressure would be very important.

In the present work electrospun poly(ethylene terephtalate) mats were prepared by two methods – electrospinning alone and electrospinning followed by corona discharge.

- PET mats onto stainless steel holders were obtained by electrospinning the PET solutions in trifluoroacetic acid (TFA)/ methylene chloride (MC) (50/50, v/v) at total polymer concentration of 13wt%, applied field strength (AFS) 1,7 kV/cm and feeding rate of syringe pump 1,6 ml/h.
- Samples of PET mats were charged in a point-to-plane three-electrode corona discharge system at 5 kV corona voltage and 1 kV grid voltage. Sample charging was performed in the course of 30 minutes at two different temperatures - 20°C and 140°C.

Some of the samples, together with their metal pads, were placed in a vacuum chamber and kept for 30 minutes under a 0.1 mbar low pressure.

For all of the samples, electret surface potential was measured by the method of the vibrating electrode with compensation, by which the estimated error was better than 5%.

Then, the thermally stimulated currents (TSC) in the temperature range (25°C-160°C) were measured using an electrometer VA-j-51 (RFT) in a linear temperature program controlled oven. The heating rate was 1.95 K/min. TSC spectra were recorded in open circuit conditions with two blocking electrodes.

A comparative study of the two kinds of the electrospun PET mats prepared by the different methods was carried out by the TSC measurements. For all of the samples the TSC curves showed two maxima: one close to 90°C and another in the 110°C region. The results presented here focused on the influence of the charging mode and the environmental pressure. The results obtained showed that the maximum position did not depend on two factors: the pressure, and the sample preparation methods at 20°C charging temperature. The TSC peaks shifted to the higher temperature values when charging temperature was 140°C. The intensity of the peaks for the corona charged PET mats was higher than that of the uncharged ones. A decrease of the peaks' intensity was observed for the samples kept 30 minutes under a 0.1 mbar low pressure.

Dielectric Spectroscopy On Ultra-Thin Polymer Films Having Free Surfaces – A Novel Approach

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Dielectric spectroscopy is a proven technique for the study of molecular and cooperative relaxation processes in ultrathin polymer films. Even on the nanometer scale, this technique provides, in fact, not only several sensitive experimental methodologies to assign the glass transition temperature [1,2] but also the possibility of accessing a broadband frequencies scenario of the changes induced by geometrical constraint and confinement to the segmental mobility [1,3], local secondary relaxations [3] and isothermal crystallization kinetics [1]. In the conventional parallel plate geometry the polymer layer is confined between the conductive surfaces of two solid electrodes. These samples are referred to as capped films or supported films without free surfaces. In this work we present a new experimental approach which allows probing the relaxation processes in ultrathin films having one free surface. The polymer is deposited by spin-coating on an interdigitated comb electrode (IDE) (Figure 1). In this geometry the polymer film has a surface in direct contact to the comb electrodes while the other surface forms an interface with the air/vacuum, which remains accessible for surface analysis techniques (SPM, ellipsometry) even during the dielectric experiment. Moreover, the well defined geometry (fixed electrode distance) allows a quantitative dielectric analysis yielding absolute information about the relaxation strength. Another important advantage of the IDE geometry with respect to the parallel plate geometry is the in-plane orientation of the electrical field that results in an equal representation of the specific (usually different) dynamic contributions from sub-layers of distinct dynamics in the dielectric response.

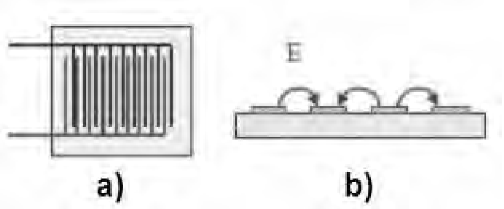

Figure 1: a) comb electrodes, the red and blue fingers are at opposite potential; b) electrical field vectors between the electrodes.

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Molecular Mobility Studies In PCN/PUMA Clay Nanocomposites

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Polycyanurate resins (PCNs) combine thermal and dimensional stability at solder temperatures, low outgassing, high adhesion to metals, low water absorptivity and low dielectric constant [1], and find many applications in electronics and aerospace industries. Despite their outstanding performance in many areas, their applications are limited because of their brittleness. Many efforts have been taken the last few years to modify the PCN network in a way that it would be less brittle keeping at the same time its outstanding physical properties [2,3]. In previous studies it was found that co-polymerization of cyanate esters with a flexible polymer such as polyoxytretramethylene glycol (PTMG) or polysulfone (PSF) lowers its brittleness but, at the same time, downgrades its mechanical properties. Studies are now moving forward in synthesis of hybrid clay nanocomposites where montmorillonite (MMT) is used as reinforcement material [4]. In the present work the results of molecular mobility studies in hybrid clay nanocomposites based on polycyanurate resins are presented in the frame of the structure-property relationships understanding.

Hybrid clay nanocomposites having as a matrix polycyanurate network modified though co-polymerization with 50%wt poly(oligo)-urethanemethacrylate (PUMA) and different clay content (Cloisite 30B) varying between 1 and 5wt% were prepared by two different ways. In one case MMT is mixed with PUMA using Brabender mixer and then introduced in a solution of the PCN monomer (BADCy), while in the other case MMT is introduced into a solution of BADCy and PUMA and homogenized either by stirring or using ultrasound.

Molecular mobility was investigated by means of thermally stimulated depolarization currents (TSDC) and broadband dielectric spectroscopy (DRS, 10^{-1}-10^{6}Hz) techniques in a broad temperature range (-150°C to 210°C). Differential scanning calorimetry (DSC), performed at a heating/cooling rate of 20K/min, was used in order to study the thermal transitions in the samples.

In all the samples two glass transitions are detected by DSC indicating a phase-separation of the PUMA and PCN components. The glass transition temperature of PUMA increases when it is co-polymerized with PCN. By DRS and TSDC techniques the secondary and the main α relaxations of PUMA and PCN are followed. The α-relaxation of PUMA in the hybrid PCN network is detected at lower frequencies/higher temperatures as compared to that in the bulk. Meanwhile the γ-relaxation of PUMA in hybrid materials has a reduced activation energy and lower intensity as compared to the pure PUMA.

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Dynamics of a nematic mixture confined to molecular sieves studied by broadband dielectric spectroscopy

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Broadband dielectric spectroscopy (10^{-2} to 10^{9} Hz) was employed to investigate the molecular dynamics of the liquid crystalline mixture E7 confined to the cylindrical pores of the molecular sieves MCM-41 and SBA-15, with pore diameters of 3.7 and 6.8 nm respectively. Because E7 does not crystallize it was possible to cover a temperature range of more than 200 K providing an exhaustive dielectric characterization of that confined liquid crystal for the first time. Thermogravimetric analysis gives a LC filling degree of 100% in MCM-41 and of 94% in SBA-15.

Dielectric measurements revealed that the isotropic to nematic phase transition of bulk E7 cannot be detected for the molecules confined in both molecular sieves. Moreover a new slow relaxational process over the whole temperature range was detected. This process is present neither in the bulk LC [1] nor in the pure hosts. This slow relaxation process is assigned to the molecular fluctuations of the molecules of E7 in interaction with the pore wall. Indeed the existence of E7 molecules strongly interacting with the pore walls by hydrogen bonds between the LC cyano groups and the hydroxyl groups of the matrix was put in evidence by FTIR measurements.

The temperature dependence of the surface process found in both systems obeys to a Vogel-Fulcher-Tamman law as also observed for the temperature dependence of the relaxation rate for other confined liquid crystals [2]. The pore size dependence is discussed in detail.

Acknowledgements: Financial support to Fundação para a Ciência e Tecnologia: PhD grant SFRH/BD/23829/2005 and project PTDC/CTM/64288/2006 is acknowledged.

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Time- And Frequency-Domain Polarization Imaging On Poly(Vinylidenefluoride-Co-Trifluoroethylene) Films

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Two non-destructive thermal methods for three-dimensional (3D) tomography of space-charge and polarization distributions in dielectric materials are presented and compared. The two methods, Thermal-Pulse Tomography (TPT) and Focused Laser-Intensity Modulation Method (FLIMM), are very useful tools for the investigation of new dielectrics. FLIMM is implemented in the frequency domain [1], while TPT [2] works in the time domain. In an effort to further increase the lateral resolution while minimizing the thermal stress on the sample, 3D polarization images of poly(vinylidenefluoride-co-trifluoroethylene) P(VDF-TrFE) films poled with a well-defined grid-pattern electrode were obtained. In low-resolution scans, the details of the grid electrode are very well reproduced, while at high resolution both techniques reveal a gradual transition between poled and unpoled regions on a length scale of 250 μm. These results will be compared with simulations taking into account the 3D heat flow.

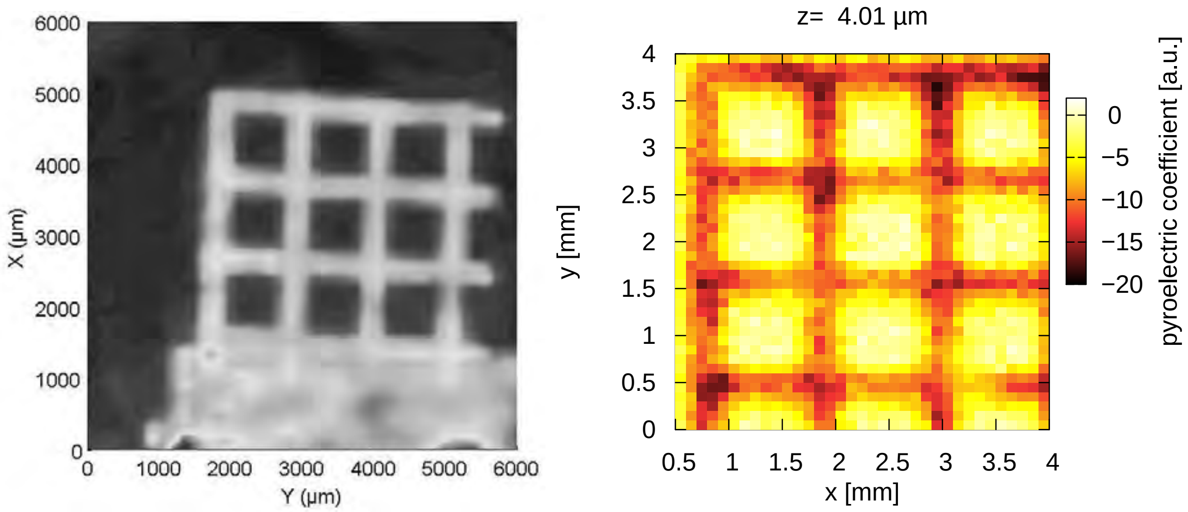

Figure 1. Maps of polarization in a 12 μm P(VDF-TrFE) film showing inhomogeneities after a low-resolution scanning with FLIMM (left) and TPT (right).

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Effect of low frequency dielectric dispersion on Photoconductivity decay in gase layered crystals

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Low frequency dielectric relaxation in charge carrier systems is mainly caused by "horizontal" transitions of charge carriers, involving relatively small change of energy. On the contrary, the decay of photoconductivity in semiconductors is connected with "vertical" transitions, involving relatively large change of energy. Therefore, the comparison of relaxation dynamic of the two different processes allows one to study the possible mechanisms of the effect of low frequency dispersion on trapping-detrapping dynamic of charge carriers in semiconductors.

In this work, the correlation of low frequency dielectric dispersion and decay of photoconductivity has been studied by comparison of kinetic shapes of the both processes. The photoconductivity relaxation has been measured by direct method in the time domain from 1 to 3600 s and by intensity modulated photoconductivity in a frequency range of 20-10^3 Hz. The sinusoidal light intensity modulation was realised using light emitting diode with radiation maximum on 600 nm, what approximately corresponds to the band edge energy of GaSe crystals.

The time dependence of the photoconductivity after termination of light illumination good fits to power dependence with the exponent close to 0.15-0.2. The spectral shape of intensity modulated photoconductivity shows maximum at about 200 Hz on imaginary part of photocurrent with strong broadening from Debye shape corresponding to $1\text{-}n = 0.25\text{-}0.3$. The observed shape characteristic of the photoconductivity kinetic correlates to exponent of $1\text{-}n \approx 0.23$ obtained from the low-frequency dielectric spectra caused by charge hopping movement in high-resistivity GaSe crystals.

The following possible mechanisms of the effect of dielectric dispersion on kinetic of the photoconductivity are considered, namely:

1) the direct dispersive transport of localized carriers; but in low frequency region of the dielectric spectra the dominating mechanism of the photoconductivity is a non-dispersive dc current. Besides, the dependence of the dispersive conductivity according to the dielectric spectra corresponds to stronger frequency dependence proportional to $\omega^{0.8}$;

2) the dispersive character of carriers transport to localization or recombination center with following trapping, what could lead to time dependence of trapping-detrapping time. In this case the carrier flow has to be the prevailing processes to determining the rate of trapping. But the prevailing carrier flow process according to the dielectric spectra is a non-dispersive dc current;

3) the change of trap parameters (energy position, cross section) with time of carriers localization on level in the forbidden gap.

The change of energy level of carrier trap during the carrier occupation time is considered as the most probable mechanism of the effect. In this case the carriers trapped shortly are placed on higher energy level and have shorter time of releasing in comparison with carriers occupied for long time, what is caused by slow screening via the hopping medium.

Dielectric and Thermal Properties of Some Supercooled Alkyl Halides

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The dielectric permittivity and relaxation times of 1-bromo-2-ethyl pentane (3-(bromomethyl) pentane) are compared with the permittivity and relaxation data on 3-bromopentane. The loci of permittivity data in the complex plane can be fitted to a single Cole-Davison skewed arc as with neat 3-bromopentane. Glass transition temperatures (T_g) from complementary thermal data on both compounds are compared with those obtained from viscosity measurements. Thermal areas of "cold crystallization" of these alkyl halides, as observed from thermal data, are compared with previously reported crystallization temperatures from dielectric and viscosity data. Additionally, melting points of these compounds determined by the abrupt change in dielectric and viscosity response at the solid-liquid transition are compared with those obtained from thermal data.

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Comparison of dielectric and mechanical relaxations in different poly(vinylidene fluoride - hexafluoropropylene) films

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Poly(vinylidene fluoride - hexafluoropropylene) (P(VDF-HFP)) is a random copolymer of the PVDF family that attracted attention during the past decade because of its electrostrictive properties [1,2]. However, there are open questions about its possible ferroelectric nature and the origin of its electromechanical activity. In particular, the effect of the relatively low elastic modulus (about 500 MPa) and the role of mobile charges as well as their possible interaction with fluorine-containing dipolar groups are still a matter of discussion [3,4].

In this contribution, we discuss the influence of dipole concentration, molecular-chain orientation and crystallinity on mechanical and dielectric properties. Films of different molar composition (two types of P(VDF-HFP) 85/15 with different molecular weight from Solvay and P(VDF-HFP) 95.3/4.7 from Shanghai Fluoro-Materials Institute) are investigated. All films were solvent-casted from polymer powder, selected films were stretched at 90 °C with a ratio of 4:1. DRS combined with dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC) and infrared absorption are employed in order to investigate dielectric and mechanical relaxation in relation to the above-mentioned structural parameters.

The temperature dependence of the elastic modulus at 10 Hz shows two well-separated steps (at the glass transition around -50 °C and at +50 °C) which are present in the non-stretched as well as in the stretched film. Stretching at 90 °C increases the modulus below the glass transition by a factor of about two. Two distinct relaxation regions are also visible in the temperature dependence of the dielectric relaxation time: the low-temperature relaxation with a Vogel-Fulcher-Tammann temperature dependence that is related to the glass transition, and the high-temperature relaxation with an Arrhenius-like temperature dependence which is considered to originate from space charges. Both relaxation processes are markedly affected by film composition, film preparation and mechanical treatment (stretching), but the relations between mechanical and dielectric relaxation are still not obvious. The investigation of these phenomena provides a key for a better understanding of the contributions of dipoles and space charges to the electric polarisation and their interactions which seem to determine the ferroelectric and electromechanical properties and particularly their temperature dependence which is important for possible applications.

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Dielectric Relaxation In Freeze-Dried Disaccharides And The Potential Significance To The Moisture Buffering Of Freeze-Dried Products

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Objectives A variety of excipients (including various dissacarides) are used routinely in lyophilised product formulation, to provide for a moisture buffering environment and thereby sustain shelf life. Our previous work [1] provided insight into the structure-activity relationships of four disaccharides (lactose, sucrose, trehalose and maltose) in relation to the mechanisms and moisture sensitivity of two principal sub-T_g relaxations observed for these materials. In this paper we examine the potential significance of the relaxation behaviour of one of the sub-T_g relaxations in relation to the potential moisture buffering effects of the disaccharide excipients.

Methods Disaccharides (lactose, trehalose, sucrose and maltose) were freeze-dried to moisture contents in the region of ~2% to ~4%, and measured using a Solartron 1296 dielectric interface connected to a Solartron 1255 frequency response analyser, in the frequency and temperature ranges of 0.1Hz to 1MHz and –100 to 0°C.

Results All four disaccharides revealed two sub-Tg processes. The faster of the two relaxation processes was singled out for further analysis by fitting the Havriliak-Negami function to spectra measured in the temperature range -90 to -15 °C and ascribed to the rotation of the pendant hydroxyl-methyl group [1]. The temperature dependency of the fit parameters ($\Delta\varepsilon$, τ, ε_∞ and α), the temperature dependence of the Fröhlich parameter B(T) along with values of activation energy ΔH were used to speculate as to the potential moisture buffering effects of the four disaccharides. The magnitude of B(T) for the fast relaxation process follows the trend: trehalose > sucrose > maltose > lactose. Charge screening of dipole-dipole interactions, associated with a tendency for the dipoles to orientate in an anti-parallel arrangement, was used to explain the observed trends in the B(T) parameter. The sensitivity of this parameter to moisture was also considered, and B(T) found to increase to a greater extent for trehalose than for maltose or sucrose, and finally with lactose, displaying the least sensitivity to moisture. These trends correlate with earlier findings that moisture sensitive drugs (similar in structure to ATP) are more stable when freeze-dried with either pure lactose, followed by pure sucrose and finally pure trehalose [2]. The activation energies for the series follow a similar rank order to that for the B(T) parameter, with trehalose having the highest activation energy. One might infer that high activation energies confer greater stability to the system, and lead one to expect that trehalose would protect an active drug molecule from hydrolysis to a greater extent than lactose. However, this was not the case and lactose provided greater protection.

Conclusions The magnitude and the temperature dependency of the B(T) are key parameters which reflect the degree of molecular mobility, which in turn underpins the diffusion rate of the trace amounts of water within a freeze-dried product. The diffusion of water molecules through the freeze-dried matrix impacts the extent of hydrolysis of a moisture sensitive additive (e.g. drug) and so dielectric measurements may provide a useful means of scoring the relative stabilising effects of a variety of excipients which are assumed to act as moisture buffers.

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Dielectric Relaxation In Aqueous Solution At Millimeter Diapazone

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The development of the relaxation model of the aqueous solution need the carrying out of a number of experimental investigations of dielectric properties of these subjects in the wide diapasone of wavelength, temperatures, and salinity. The measurement of temperature and concentration dependencies of real and imaginary part of dielectric permittivity of distillated water and of a number of mono- and poly-elecrolyte water systems at frequencies 35 – 75 GHz and temperature interval from 271 – 353 K were carried out at experimental test bench. The experimental methodic is based on study of reflection coefficients of microwave power from the liquid surface and the moveable piston during changing of the height of the liquid between its reflecting surface and the piston.

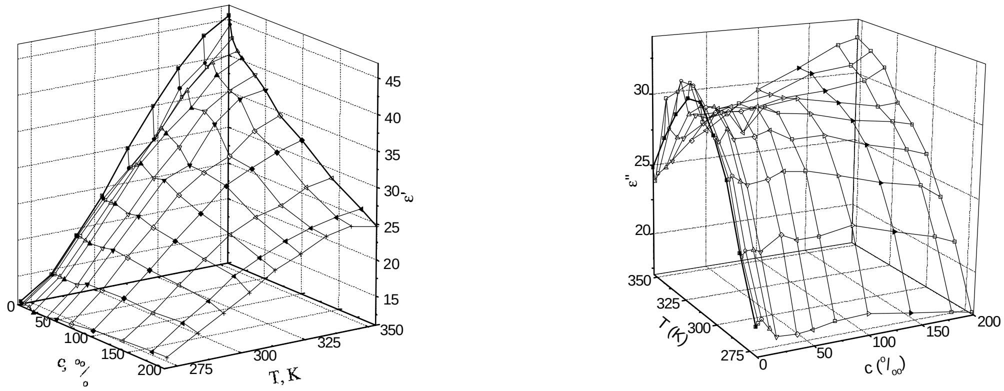

Fig.1 Temperature and concentration (0-200 °/oo) dependence of real (left) and imaginary (right) part of complex dielectric permittivity of NaCl in water at frequency 35.5 GHz.

The complex permittivity of distilled water, poly- and monoelectrolytes was measured within systematic error of 0.7% of ε' and 1.5% of ε'' and unbiased error (95% confidence limit) of 0.5% of ε' and 1% of ε''. It was found that both the permittivity and loss of polyelectrolytes exhibit a dependence on concentration with strong temperatures dependences. As an example Fig.1 show temperature and concentration (0-200 °/oo) dependence of real (left) and imaginary (right) part of complex dielectric permittivity of NaCl in water at frequency 35.5 GHz.

Peculiarities Of The δ–And α-Relaxations In Polymers With Cyanobiphenyl Liquid Crystalline Side Chains Of Different Lengths

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A recent observation of the multistage dielectric relaxation in cyanobipenyl polyacrylates (CBPA) with six methylene groups in the side chain[1] was the motivation for the present investigation of CBPA with long side chains of different lengths. In this research the dielectric relaxation of CBPA polymers with 8, 9 and 11 methylene groups in the side chain have been investigated in the temperature range of 100K-470K.

It is found that an increase of side chain length results in an increase of the thermodynamic stability of the nematic phase just below the izotropic one. At low temperatures, in the $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ spectra, anomalies corresponding to rotational motion (β-relaxation) of mesogenic cyanobiphenyl groups have been observed. Above T_g the sequence of δ- and α- relaxation processes are observed in the loss spectra. In all CBPA compounds the amplitude of δ-relaxation loss peak dominate the α- relaxation one, which pointed out to preferential parallel ordering of the long axis of the side chain. Using the proportionality of $\log(\omega_\alpha/\omega_\delta)$ to the retardation factor $g(S)$, the temperature dependence of order parameter $\Delta S(T)$ has been obtained. In the frame of Martin-Saupe mean-field theory a power law behavior of

$$S(T)-S(T_i)\sim\left[(T_i-T)/T_i\right]^{\gamma}$$

is analyzed. Here T_i is the isotropisation temperature. A power law behavior of $\Delta S(T)$ is clearly observed. The γ exponent turned out not to be universal, increasing with side chain length from 0.73 to 1.3.

In the isotropic phase the δ-relaxation mode obeys VFT relation for all long side chain CBPA samples. The activation VFT parameter A increases with decreasing side chain length. Fits show that the VFT temperatures of δ-relaxation in the isotropic phase are approximately 15K below isotropisation temperatures for CBPA with long side chains. The obtained VFT temperatures are in a good agreement with DSC data.

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Bulk And Interfacial Dynamics Of Pdms/Titania Nanocomposites

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We present results of a study on the molecular dynamics of poly(dimethylsiloxane) (PDMS), a crosslinked semicrystalline polymer, with inclusions of titania nanoparticles. The nanoparticles were prepared in situ using the sol-gel method.

The aim was to investigate the degree to which the dynamics of the polymer are affected by the nanoparticles, as well as the mechanism through which this take place. This study follows up on a previous study by our group on PDMS/silica nanocomposites, which showed that near the surface of the nanoparticles an interfacial layer with modified dynamics is formed [1-3].

The Thermally Stimulated Depolarization Currents (TSDC) technique due to its high resolving power has proven to allow the separation of relaxations that have similar frequencies. In particular, it allows the discrimination of the dynamics of the bulk polymer from those of the interfacial layer. Furthermore, it allows the separation of the α relaxation connected with the glass transition in the amorphous regions and the α_c relaxation attributed to the dynamics of polymer chains in the crystalline regions.

Dynamic Relaxation Spectroscopy on the other hand provides information on the molecular mobility over a large frequency range and the temperature dependence of the dynamics.

Differential scanning calorimetry (DSC) was used complementarily in order to obtain information on the thermal properties of the samples and importantly on the state of the samples (crystallinity degree, quality of the crystals) depending on the thermal protocol used for the dynamic measurements.

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Inertial effects in anomalous dielectric relaxation

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The role played by inertial effects in anomalous relaxation of various generalizations of kinetic equations to anomalous diffusion is discussing. In order to give a physically meaningful description of the anomalous dielectric behavior at high-frequencies (especially in the far-infrared region), inertial effects must be included just as in normal relaxation. The omission of inertial effects in the relaxation process gives rise, in the context of dielectric relaxation, to the phenomenon of infinite dielectric absorption at high frequencies. Inclusion of them, on the other hand, yields the return to transparency at high frequencies. In practice, models of the inertial rotational Brownian motion are frequently used in studying orientational relaxation in liquids in order to compare spectra obtained by various probe techniques such as dielectric relaxation, infrared absorption, Raman scattering, etc. with the corresponding theoretical spectra. In the context of Brownian motion, inertial effects may be included by either averaging the inertial Langevin equation or by constructing a kinetic equation for the evolution of the probability density function in phase space. The starting point of the inclusion of the inertial effects in anomalous dielectric relaxation is a generalization of the Klein-Kramers equation to fractional dynamics. Various generalizations of the Klein-Kramers equation for the translational motion have been proposed, e.g., in Refs. [1-3]. Furthermore, Coffey *et al.* [4,5] have recently shown how inertial effects may be included in the fractional dynamics of an assembly of dipoles (rotating either in a plane or in space) just as in normal relaxation. They have also demonstrated one how are particular generalized fractional Klein-Kramers equations for the rotational motion can reproduce nonexponential (Cole-Cole type) anomalous dielectric relaxation behavior at low frequencies, and how the unphysical high-frequency behavior of the absorption coefficient due to the neglect of inertia may be removed in fractional relaxation as in inertia corrected Debye relaxation. The inclusion of inertial effects in the fractional dynamics just as in the conventional Brownian dynamics thus ensures the desired return to optical transparency at high frequencies. Moreover, Gordon's sum rule for the integral dipolar absorption is satisfied.

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KWW-type electrode polarization effects in glass

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In ionic crystals, the DC conductivity is proportional to the mobility and to the number density of the mobile point defects. In the case of ion-conducting glasses, the cations provided by the network modifier are usually regarded as the mobile charge carriers. The alternative perception of effectively charged vacant sites (which interact with each other) as mobile charge carriers is, however, also feasible. It has the further advantage of being consistent with new simulation results.

The value of the ionic conductivity at low frequencies does not provide information on the value of the number density of the mobile charge carriers, unless their mobility is known. In glasses, the absence of polarization due to grain boundaries provides the possibility to measure the effect of electrode polarization in a sample cell with blocking electrodes. Indeed, at least in principle, such measurements offer a challenging route towards determining the number density of the mobile charge carriers. Here, the simplest view is to assume that the relaxation process at the electrodes is of the Debye type. In this case, it should be possible to use the (very high) values of the dielectric function at low frequencies in order to find the number density of the mobile charge carriers.

However, inspection of the dielectric function at low frequencies clearly proves that the relaxation is non-Debye. Rather, it is suitably described in terms of a Kohlrausch-Williams-Watts-type stretched exponential function. Such a function may be interpreted as a superposition of elementary relaxation processes with different relaxation times and is thus indicative of dynamic heterogeneities. As expected, the low-frequency limiting values of the permittivity are extremely high. Within experimental error it is, however, not easy to decide whether the resulting number densities should be interpreted as pertaining to the modifier cations or to the vacant sites.

The systems under study have been sodium borate and sodium metaphosphate glasses, both being archetypal glassy electrolytes. In addition to the well-known dispersion of the complex conductivity, the polarization effect can be precisely seen at low frequencies. The evaluation of our data shows clear evidence for the existence of dynamic heterogeneities in glass.

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Phase Transformations In Confined Solid Solutions $NaNO_2$ – KNO_2.

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These contribution is devoted to the study of phase transformations observed in confined solid solutions (1-x)$NaNO_2$ – (x)KNO_2 at x=0, 0.05 and 0.1. 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. As host matrices we have used porous glasses (3D random dendrite pore network with average pores diameters 320, 24, 20, 7 and 3 nm), artificial opals (3D regular pore network with cavity sizes 45 and 60 nm) and chrysotile asbestos – quasy-1D system of parallel channels with diameter about 6 nm. The samples were prepared by immersing of the preliminary annealed matrices in the melted KNO_2-$NaNO_2$ mixture with different concentration. Temperature evolution of structure was studied by neutron diffraction and small-angular neutron scattering (SANS), dielectric properties of these nanocomposite materials (NCM) were studied at the frequency diapason 1 Hz – 2.5 MHz. All measurements including conductivity, internal friction and shear elastic modulus were performed in the temperature interval 293 K – 550 K, i.e. in the ferroelectric and paraelectric phases. It is shown that there is a critical "diffraction size" (close to 50 nm) for confined sodium nitrite where the crossover of the ferroelectric PT from the first order to the second one is observed. Decrease of average nanoparticles sizes leads to a suppression of incommensurate PT. The temperature dependences of order parameter are presented on Fig. 1.

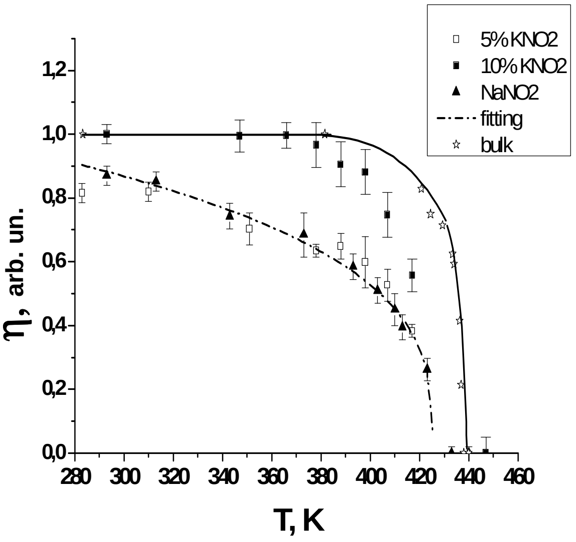

Fig. 1

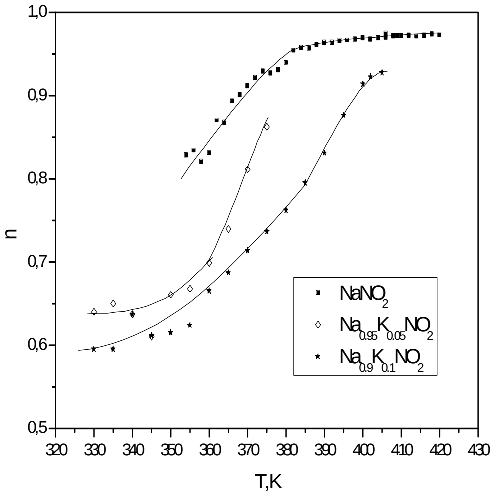

Fig. 2

In our frequency and temperature ranges the shape of the dielectric loss spectrum can be well enough described by the sum of two components - the $\mathbf{1/\omega^n}$ term related to the conductivity, and the Cole-Cole type term, related to the relaxation contribution. With increase of temperature the parameter **n** grows from 0.7 up to 0.9 and tends to 1 (Fig. 2). That is to a slope which we would have in case of through conductivity. Such behavior is in agreement with the assumption about the formation of a premelting state above 380K [1-3] for NCM within small pores. It is shown that for confined $NaNO_2$ in the region of anomalous high values of ε tgδ can be more than 10, however the introduction of potassium has reduced considerably this value demonstrating (as diffraction patterns) a “hardening” of lattice.

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Chain Dynamics of Transformed Cassava Starch Using Dielectric Spectroscopy

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Cassava is a source of starch available in Latin America, Asia and Africa and it has potential applications in food and packaging industry and drilling muds for oil wells. It is a natural polymer made of 70% of branched amylopectin chains and 30% of amylose which is linear. In the granular state the biopolymer is semicrystalline with type A structure. The transformed samples were made by heating a well dispersed mixture of starch with 25 wt % water to 140° C and moulding it in 30mm disks with an average 600 µm thickness. The final moisture content was 15 wt%. The Dielectric Spectroscopy runs were carried from 133 to 383 K and then back to 133 K, by 5 K steps, in a frequency range $10^{-2} < \nu < 3.2 \times 10^{6}$ Hz. During the heating run the spectrum showed important features due to the moisture content. A relaxation peak whose position is frequency independent is present in the vicinity of 370 K and is attributed to the presence of clustered water molecules. The cooling run represented in Fig. 1(a) corresponds to a dry starch and gives a less complex spectrum. At low temperatures two secondary relaxations, γ and β, were clearly observed either in ε'' or M'' domains. They are originated by short range molecular motions or rotations, most probably caused by localised chain motions or the methylol group present in the anhydroglucose units.[1] The secondary modes follow Arrhenius behaviours with activation energies E_γ =0.54 eV and E_β =0.69 eV in very good agreement with previous determinations on starches of different biological origins.[1, 2] The high temperature range is better resolved in the dielectric modulus domain due to the intense contribution of the conductivity, see (Fig (1(b)).

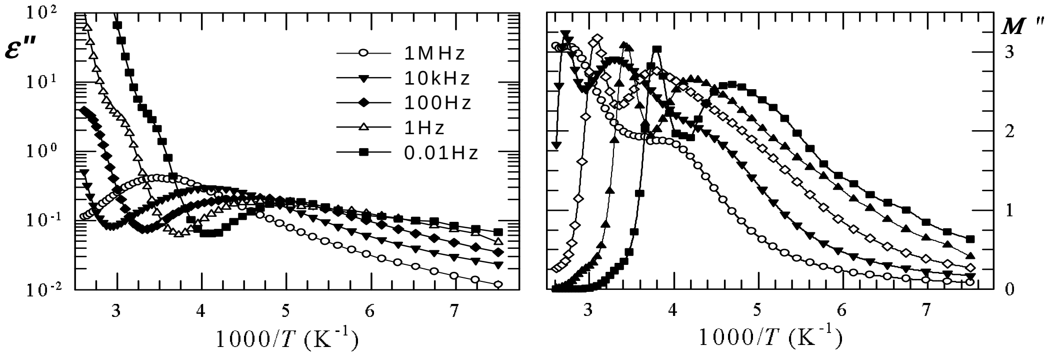

Fig. 1 Isochrones of dry Cassava Starch, cooling run: (a) $\varepsilon''(10^3/T)$, (b) $M''(10^3/T)$

An α mode is identified in a temperature range which corresponds better to the temperature range where the glass transition has been identified by other techniques but it is strongly overlapped by the conductivity. The relaxation time variation is Arrhenius, with an activation energy of E_α =1.09 eV, which implies a reduced cooperativity. The remaining relaxation parameters of the Havriliak-Ngami distributions are calculated.

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Dielectric Relaxations and Moisture Effect in Native and Transformed Cassava Starch

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Broad Band Dielectric spectroscopy in starch from different biological origins has been widely used and the results have lead to different interpretations as to the molecular origin of the observed modes [1]. The increasing applicability of the these renewable, biocompatible materials for medical, tissue engineering, drilling materials in oil wells, packing industry, is linked to the understanding of the effect of water on the properties of these materials. Thermally stimulated depolarization currents technique, TSDC, is a powerful tool to observe, isolate, and quantitatively analyse the different relaxation modes of the dipolar entities. Its equivalent frequency is in the mHz range. Granular Cassava starch is a semicrystalline polymer with 70% and 30% of amylopectine and amylose chains, respectively. The crystalline order is the type A monoclinic structure [2] most common in cereals, and the degree of crystallinity is 28 % as determined by WAXS. The protocol of the TSDC technique [3] implies that successive runs on the same sample will record the drying process of the material due to the necessary evacuation of the cell when the gas interchange is performed, the temperature reached in the preceding run and the chosen polarization temperature. The TSDC results for native starch show drastic changes due to the continuous variation of the water content. The transformed samples were made by heating a well dispersed mixture of starch with 25 wt% water to 140° C and moulding it in 20mm disks with an average 600 μm thickness. The transformed starch is completely amorphous but a strong retrogradation effect was observed when the sample was equilibrated in an atmosphere of K_2SO_4 saturated solution, which results in a water content $h= 35$ wt%. When comparing the 16 successive runs performed on a transformed sample, one observes the huge effect on the secondary relaxations of the water loss; the β local mode widens, and shifts to higher temperature as the water concentration, h, decreases. The γ relaxation which corresponds to the shortest range movements is not affected by the h variation. The main peak presents a bimodal distribution and as h decreases the two modes shift 80 K and 100K, respectively. The results of the same experiment performed on a transformed sample that was previously thoroughly dried at 130°C show the perfect reproducibility of the local relaxations and the primary mode, as well as the bimodal profile of the latter. The similarity and differences of this mode with those obtained after drying the sample in the cell, will be discussed. The deconvolution of this mode with the SADSA procedure allows to extract the relaxation parameters distribution for each mode. The huge plasticization effect of water in amorphous cassava starch has been demonstrated by the changes presented in both the local and the bimodal cooperative modes identified in the TSDC spectra.

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Single Cell Analysis Using A Scanning Dielectric Microscope

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The electric properties of biological cells can be obtained by analysing the dielectric relaxation of the cell suspensions, which is due to interfacial polarization or the Maxwell-Wagner effect. The analysis is usually carried out by assuming a population of uniform cells, although there is more or less variation of cells in the cell division stage, metabolic state, morphology and so on. The estimated electric parameters of cells are, therefore, 'average' ones, and their interpretations require careful considerations, especially in studying the responses of cells to external stimuli. The problem can be resolved by measuring single cells instead of a mass of cells. Recently, techniques for single cell measurement have been developed, namely ac electrokinetic methods including electrorotation and dielectrophoresis [1] and single cell dielectric spectroscopy using microfluidic systems [2]. The techniques are applicable to suspended cells like blood cells but not to cells attached on a substrate in tissue culture. Alternatively, the scanning dielectric microscope (SDM) that has been developed for imaging fine particles by dielectric spectroscopy [3] is favourable for studying the attached cells. This paper describes some examples of the dielectric spectra and dielectric images of single cultured cells obtained using SDM and discusses their theoretical analysis.

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Activated-hopping and Free-diffusion Dynamics in the Glass-forming Liquids

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One of the most wide used theories of the glass forming liquids is the theory of Adam and Gibbs. An extension of this theory at the molecular level has been suggested by the author [1]. Two equivalent equations for the measuring the size of the cooperatively rearranging region have been obtained, one from the kinetic and the second from the thermodynamic properties of the liquids. By measuring the size of the cooperatively rearranging region the number of configurations of the range can be estimated. Obtained number of configurations is lager than in the solid-like Adam-Gibbs cooperatively rearranging region with two configurations, and is a specific constant for every liquid. From this fact it follows, that the cooperatively rearranging region is a units with internal dynamics. The rearrangement of the molecular units, witch have been identified as thermodynamic "beads" is found to be: activated hopping over the potentials barriers and non-activated, free-diffusion ones. On rising the temperature above the glass transition temperature the activated hopping rearrangements are transformed in free-diffusion ones. The activated hopping rearrangements produce a solid-like component, wile free-diffusion ones a second specific liquid component in the liquid dynamics. In this way the glass-transition appear as specific melting of the solid-like dynamics. The rate of the transformation of the activated-hopping into free-diffusion dynamics have been found to increase with increasing the fragility of the liquids, and in fragile liquids 35 K above the glass-transition temperature nearly half of the total dynamics is free diffusion one. The observed dielectric relaxations in the polymer and low-molecular weight supercooled liquids are discussed from the point of view of the theory.

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Effects of SiO_2 Nanoparticles on Dielectric Properties and Thermal Stability of LDPE

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In the last five years many groups of research in the field of dielectrics from all over the world have been focused their energies and resources toward a new topic called nanodielectrics [1-3]. These newly born materials are polymer nanocomposites with dielectric and electrical insulating properties which are increasingly becoming popular due to significant improved behaviour compared to the traditional polymer microcomposites. Until now several methods for processing and characterization have been tested, and some theories and models have been proposed for these materials having a huge nanofiller-polymer interface area which seems to be the main responsible for their unique properties. Despite the encouraging advances in this field we are still far from understanding and controlling the phenomena in these materials.

In the present work two dielectric properties – permittivity and tan delta – are analyzed by dielectric spectroscopy over a frequency range of 1 mHz – 10 MHz for nanocomposites obtained from low density polyethylene (LDPE) filled with nanoparticles of SiO_2. The dielectric properties are compared with data concerning material morphology as resulting from X-ray diffraction measurements as well as with thermal stability tests performed by chemiluminescence analysis. The influence of the filler concentration (between 2 and 10wt %) on the dielectric behaviour of the nanocomposites is also discussed in connection with structure and thermal stability modifications.

The preliminary results obtained at room temperature emphasize different dielectric behaviours of the nanocomposites, depending on the frequency and on the filler concentration. In the case of the permittivity, values smaller than those for the base polymer are observed for 2 % and 5 % concentrations of SiO_2 particles especially for high frequencies. Regarding the tan delta the values are smaller than in the unfilled polymer for all the filler concentrations, but this lowering is only at very small frequencies. The influence of the temperature on the dielectric behaviour is also presented in the full paper.

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Boundary-element calculations for effects of low-frequency electric fields in a doublet-shaped biological cell

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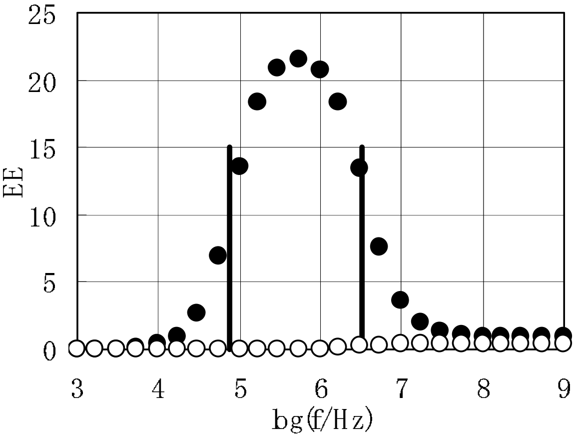
Biological cell suspensions are characterized by their electrically inhomogeneous structure consisting of conductive cytoplasm and outer medium and the thin insulating cell membrane surrounding the cytoplasm. When the cells are placed in external electric fields, the inhomogeneous structure causes discontinuities in the electric fields producing several effects, such as the transmembrane potential (TMP), and the Maxwell stress tensor (MST) at the outer and the inner surfaces of the cell membrane. The insulating cell membrane causes the decrease in the field strength in the cytoplasm against that in the outer medium. These field-effects have been utilized for cell-manipulations and -analyses, and are possible mechanisms of physiological effects of the electric fields.

In the present study, amplitude of TMP, normal stress and outward force density on the cell membrane, and filed strength in the cytoplasm were evaluated numerically for doublet shaped cell models relevant to *Saccharomyces cerevisiae* with the boundary-element method based on the interfacial polarization mechanism.

Fig. 1 shows the frequency-dependence of the square of the field intensity (EE) at the centres of the junction and the mother cell. This figure shows that EE at the junction is increased in the frequency region between the two characteristic frequencies determined from the previous calculations of the dielectric spectrum of the model [1]. The maximum value in EE increased with the decrease in the radius of the junction. This suggests that ac fields of specific frequencies cause intensive Joule heat at the junction and its intensity increases as the progress of the cell division. Calculations of other parameters under other electrical and morphological conditions showed that the ac fields of specific frequencies cause enhanced effects at specific positions in the cells.

Fig. 1. Frequency-dependence of the square of the field intensity (EE) at the centres of the junction (●) and the mother cell (○) for a model in which the radius of the junction is 1/10 of that of the mother cell and the conductivity of the outer medium equals that of the cytoplasm, under the condition that the external field is directed along the long axis of the model. Vertical bars show the characteristic frequencies for the dielectric spectrum of the model.



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Dielectric properties of liquid crystals in the millimeter and sub-millimeter or THz frequency range

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To date, the dielectric properties of liquid crystals (LCs) in the millimeter and sub-millimeter (or terahertz, 1 THz = 10^{12} Hz) frequency range were relatively unexplored. These data are, however, important both for understanding the mechanisms of interaction between MM waves and LCs, especially near the phase transition points, and for the practical application of LCs in this frequency range, for example, in phase-shifters and polarizers. In the present study, we employed coherent time-domain spectroscopic (THz-TDS) and reflection-type broadband dielectric spectroscopic techniques to determine the optical constants of nematic 5CB and 8CB. These are two imprtant members of alkylcyanobiphenyl group LCs with various lengths of the mobile alkyl chain C_nH_{2n+1} (n = 5 and 8) in the sub-millimeter and millimeter wave range, respectively.

At 60 GHz and 115 GHz, we find the extraordinary and ordinary refractive indices of 5CB (8CB) are n_e = 1.651 (1.619), n_o = 1.624 (1.579) and n_e = 1.665 (1.656), n_o = 1.600 (1.615), respectively. For the range of 250 – 280 GHz, the corresponding indices for 5CB (8CB) are n_e = 1.68 (1.61), n_o = 1.64 (1.56). The imaginary indices of 5CB (8CB), k, are in the range of 0.010 – 0.015 and 0.040 – 0.045 at these frequencies. THz-TDS studies reveal that n_e = 1.77, n_o = 1.58 from 0.2 to 0.9 THz for 5CB or a birefringence of 0.20 ± 0.02, comparable to that of the visible range. On the other hand, the birefringence of 8CB is much smaller, 0.02~ 0.09 in the THz range. For example, we find the real indices of 8CB are n_e ~1.76 and n_o ~1.66 at 0.4 THz. The difference in refractive indices at 60-120 GHz and at 400 GHz can be due to dispersion region in the MM wave range for LC. The temperature dependence of the indices of refraction for 5CB at 60 GHz and 500 GHz or 0. 5 THz are shown in Fig. 1(a) and (b) below.

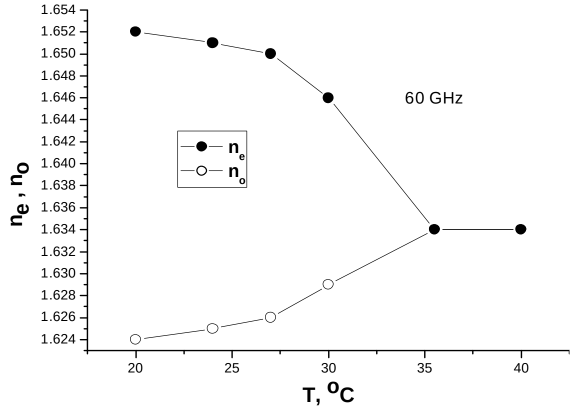

Fig. 1(a)

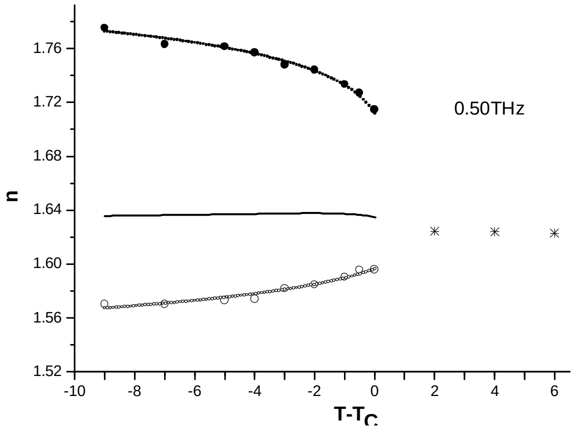

Fig. 1(b)

Real-time dielectric spectroscopy on ultra-thin layers of H-bondings liquids tuned by organic molecular beam deposition.

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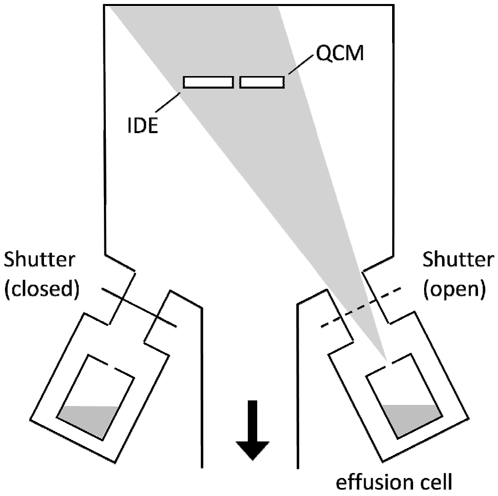
Real-time dielectric relaxation spectroscopy on a molecular beam deposited glass forming liquids is proposed as a novel approach to study the dynamic glass transition under geometric confinement. To reach highest sensitivity for small capacitance changes in a wide frequency range (0.1 Hz – 10^6 Hz) and an open electrode configuration, we have employed µm spaced interdigitated comb electrodes (IDE) at ultrahigh vacuum conditions (UHV, $p < 10^{-8}$ mbar).

Evaporation experiments using an effusion cell (Knudsen cell) show a great linearity between the electrical capacitance and the layer thickness as monitored by a quartz crystal microbalance (QCM). On the other hand, after ceasing the deposition, slow decreases in the dielectric response yield a precise measurement of the film evaporation rate, which was found to slow down when the film approaches a residual thickness below 2 nm.



In this presentation a detailed description of the theory and instrumentation of the new approach is given. First results on sorbitol and glycerol will be discussed.

Dielectric studies of hydrogen bonds in pure and diluted monohydroxy alcohols

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Glass forming monohydroxy alcohols exhibit not only a structural relaxation but also a slower, single-exponential Debye-type relaxation process which freezes in already in the liquid phase. Using dielectric spectroscopy we study how these relaxations evolve when the aprotic alkyl halide n-bromobutane is added to n-butanol, thereby diluting the hydrogen-bond network [1]. The structural relaxation times vary smoothly over the concentration range of this completely miscible binary system. The Debye process remains unaffected by the dilution of the OH groups up to n-bromobutane mole fractions of about 50%. For larger hydroxy dilutions the Debye-like process turns rather abruptly into a feature which develops significant spectral broadening, becomes faster, and decouples strongly from the primary relaxation. In the dilute limit the decoupling between the time scales of the structural and Debye-type relaxations amounts to almost 6 decades when extrapolated to the glass transition temperature. This relatively large, strongly concentration dependent decoupling is interpreted in analogy to normal modes in polymers. The present results indicate that the structural and the Debye-like responses of monohydroxy alcohols are unrelated.

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Broadband dielectric measurements of anhydrous and hydrated connective tissue

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The study of hydrated proteins is important from various points of view. On the one hand, the dynamics of water in the hydration shell of proteins is crucial for their biological function. On the other hand, water confined in that shell does not crystallize and, unlike bulk water, can be easily supercooled. However, when the motion of the hydration water comes to rest upon cooling, then also the conformational changes of the protein must cease. This may be phrased by saying that the bio-macromolecules are the slaves of water. In order to study the water-protein interplay in detail we studied several proteins for different hydration levels.

In this contribution we focus on nominally dry and on hydrated elastin and collagen which are responsible for the elasticity and the tensile strength, respectively, of the connective tissue of vertebrates. We carried out broadband dielectric measurements to identify the contributions of the hydration water as well as of other dipolar and conductivity degrees of freedom. We discuss our results in relation to recent nuclear magnetic resonance experiments.

Broadband dielectric study on fructose-water mixtures from liquid to glass as a function of concentration

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The dielectric studies on various materials from a liquid to glass have been performed as a function of temperature. Usually the glass transition temperatures of sugars locate in the vicinity of room temperature so that the sugar water mixtures with high sugar contents are in the glassy states near the room temperature. Therefore, the concentration variation from pure water to pure sugar can be utilized for the investigation of the dynamics of aqueous systems from liquid to glass as a function of concentration isothermally.

Broadband dielectric measurements for fructose-water mixtures with various fructose concentrations in the range of 5 wt% - 94.6 wt% were carried out in the frequency range of 2 mHz - 20 GHz at 25 °C, in order to make clear the dynamics of water and sugar molecules in sugar-water mixtures from liquid to glass states as a function of fructose concentration.

For the mixtures with fructose concentrations, C_f, below 55 wt%, the relaxation process i.e., the β process was observed. While in the fructose concentration C_f above 55wt%, two relaxation processes can be recognized. The relaxation process i.e., the α process appears in the frequency lower a decade than that of the β process. The α process results from the cooperative motion of two components and the β process is dominated by the local motion of water molecules.

Figure 1 shows plots of the relaxation times of the α and β processes, τ_α and τ_β, as a function of C_f at 25°C. In $C_\mathrm{f} < 55$ wt%, τ_β increases slightly with C_f. In $C_\mathrm{f} > 55$ wt%, the τ_β increases with C_f clearly. In 55 wt% $< C_\mathrm{f} <$ 90 wt%, τ_α shows the increasing behavior similar with τ_β. In $C_\mathrm{f} > 90$ wt%, τ_α observed for $C_\mathrm{f} = 90$ wt% fructose is ca. 100 ns and it increases steeply, then it reaches at ca. 1 s for pure fructose which is in close vicinity of the glassy state, at which τ_α is 100s-1000s.

For $C_\mathrm{f} > 55$wt% which corresponds to the number of water molecules is less than 8 for one fructose molecule, the α process results from the cooperative motion of components appeared. At $C_\mathrm{f} = 90$wt% which corresponds to the number of water molecules is less than 1 for one fructose molecule, and the temperature dependence of τ_α is extremely large in $C_\mathrm{f} \geqq 90$ wt%. Therefore, two characteristic concentrations were observed at which the dynamics of the fructose-water mixture changes from liquid to glass.

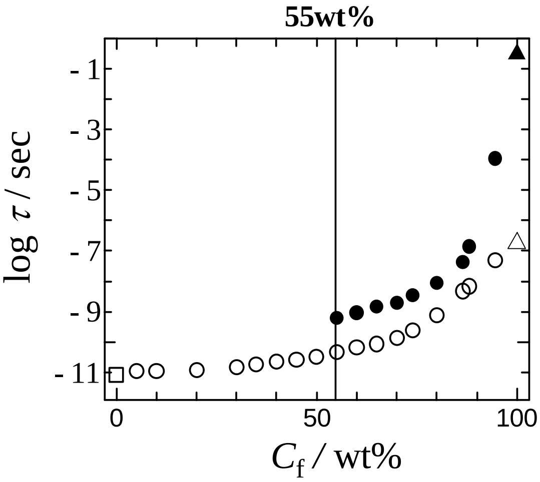

FIGURE 1. Concentration dependences of relaxation times τ for the α process (closed circle) and the β process (open circle) at 25 °C. The plots of pure fructose at 24°C (triangles) and pure water at 25 °C (squares) were quoted from the literatures [1] and [2], respectively.

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Quantifying the deviations from bulk behaviour in ultrathin polymer films

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The thickness dependence of the cooperative dynamics of ultrathin films of atactic poly(2-vinylpyridine) [1] capped between aluminum layers (model nanocomposites geometry) [2] has been investigated in a wide range of frequencies and temperatures by means of broadband dielectric spectroscopy. Due to specific hydrogen bond interactions the polymer layers at the very interface show a reduced mobility compared to the bulk [3, 4]. By treating the influence of an absorbing substrate as a small perturbation in the activation energy of the relaxation modes related to the dynamic glass transition, we proposed that the deviations from bulk behavior derive from the balance of such a perturbation and the thermal energy [1]. A thickness dependent Vogel-Fulcher-Tammann equation allowed us to demonstrate that the deviations from bulk behavior are sensitive to the time scale of the experiment [5] and vanish at sufficiently high temperatures [5, 6]. In addition to that, we introduce an analytical tool being able to quantify the temperature dependence of the deviations from bulk behavior and the lenghtscale of the interfacial interactions based on measurable quantities. Finally, we discuss on the limitations of dielectric spectroscopy for the investigation of polymer layers next to an attractive interface.

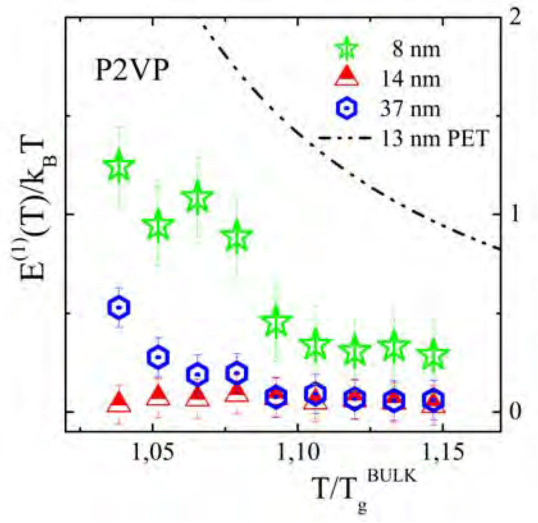

Figure
Thickness dependence of the correction factor to the activation of the structural relaxation process for ultrathin films of P2VP (symbols) and PET (dashed line), as extrapolated from Ref [3].

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Coupling Between the α Process and Boson Peak in Glycerol-Water Mixtures

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Understanding the liquid-glass transition and its related dynamics is one of the most important and challenging problems in modern condensed matter physics. Glycerol and its mixtures with water are hydrogen-bonded (H-bonded) liquids, which are widely used as models to study the cooperative dynamics and also glass transition phenomena in complex liquids.

The typical dielectric spectra of glycerol-water mixtures display dielectric dispersion in an extremely broad frequency range. The α process that reflects the slow cooperative relaxations, excess wing and the high frequency Boson Peak (BP), corresponding to an excess of the vibration density of states at frequencies around $\omega_{BP} \approx 1\,\mathrm{THz}$. In general, the link between BP and oscillators at frequencies $\omega > \omega_{BP}$ has been investigated in detail [1-3]. Meanwhile, relation of the BP to the relaxation processes at low frequencies, $\omega << \omega_{BP}$, has been less studied. An attempt to establish such a link between the α process and the BP was undertaken both theoretically [4] and experimentally [5].

Recently a new phenomenological relationship for complex dielectric permittivity was proposed in order to provide a comprehensive fitting of our experimental data both for conductivity, main process and excess wing [6, 7]. In turn a phenomenological description of the BP can be provided in terms of a damping oscillator. We propose here the coupling between the slow structural rearrangement (α process) and the modulation of the oscillator altitude (BP). The broadening of the BP obtained by the model is in qualitative agreement with the experimental data.

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A Monte Carlo study of an XY-model of TTB materials

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Abstract:

Different phases of TTB system has been studied by using XY-model and Monte Carlo simulations. The investigation of critical temperature (T_c) of the system in the (T_c, J_y) plane, show three different regions. The first one is observed when the exchange interaction J_y is less than 2.0 and greater than 0.7 and called a morphotropic phase in which the polarizations are $P_x \neq 0$ and $P_y \neq 0$. In the second zone where $0 < J_y < 0.7$ only the polarization of x-axe is present ($P_x \neq 0$ and $P_y = 0$). The third part of phase diagram (T_c, J_y) concern the case where $J_y > 2.0$. In this phase and contrary to second one only the polarization of y-axe is not zero and the critical temperature increases linearly when the exchange interaction J_y increases.

Dynamics of poly (propyleneoxide) amines confined in clay

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The dynamics of poly (propyleneoxide) amines intercalated in montmorillonite clays, have been investigated by Dielectric Spectroscopy. The amines of interest were the commercially available α, ω-diamines known as Jeffamine D-series amines with molecular weights in the range 400 – 4000. 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 20 – 46 Å [1].

The polymeric chain motions are restricted between the clay platelets, thus giving a true 2D confined system. This system is well suited for the investigation of confinement effects on chain dynamics since we were able to vary gallery height (i.e. the available space for chain motion) by using Jeffamines of different chain length and to affect interfacial properties by interacting protonated diamines with the negatively charged surface of the clay platelets. Jeffamines exhibit the dielectric normal mode due to the fluctuation of the end-to-end vector as well as the segmental mode due to local, segmental fluctuations. Dielectric Spectroscopy, thus, can provide information on the chain dynamics monitoring all the possible motions of the macromolecules, from local chain motions up to global chain translational and rotational motions

Our results indicate that for low MW (MW ~ 400) intercalated PPO chains, which are oriented parallel to the silica sheets when they adopt a lateral bilayer configuration, the segmental and global chain motions are strongly suppressed. For PPO chains of higher MW acceleration of segmental dynamics is observed when relatively high diamine loadings are combined with lower basal spacings (ca. 20 Å).

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Relation between the Distributed Nature of Processes in Polymer Materials and their Electrical Ageing Process

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Abstract: This paper aims to incorporate the distributed nature of processes at play in polymer insulators into the description of their electrical ageing process. Indeed, organic insulators are semi-crystalline disordered systems showing a spatially varying morphology. Their amorphous phase is an active system in which the chain segments are continuously undergoing conformational changes characterized by different relaxation processes each with a characteristic relaxation time. This phenomenon is called "Physical ageing" and is largely affected by the application of an electrical field. Consequently, processes occurring in these materials do not have a characteristic Debye response and the parameters affecting the electrical ageing process are distributed. In a first treatment, we have considered the instantaneous state of the material on a local scale to analyze the ageing process and the different parameter variations which probably contribute to this phenomenon. These variations were then taken into consideration for the elaboration of the ageing model, first to yield an insight into the way the material ageing evolves over time and subsequently to produce a statistical description of a sample lifetime.

Dynamical Properties of Functionalized Polymers: Specific Chain Dynamics versus Matrix Plastification

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Functionalized polymers, i.e. polymers modified with one or several chemical groups are interesting from both a technological and fundamental point of view. Being sensitive to the dipole moment fluctuations, Broad Band Dielectric Spectroscopy (BDS) offers possibilities as a selective tool where components having stronger dipole moments, i.e. polar groups, can be studied in detail. It was envisioned that it might be possible to determine motions of specific parts of the chain by "labelling" a polymer with covalently bound polar groups in specific positions. This requires functionalizing a polymer by placing polar group at the end of the chain (end-chain functionalization) or in the chain (in-chain functionalization) such that relationships and correlations of individual fluctuations of the chain can be resolved. In contrast to traditional approaches involving small molecular probes; functionalized polymers offers a direct way to evaluate the polymer dynamics simply because the probe is more or less directly "slaved" to the chain dynamics. However, this approach requires complete control of the polymer synthesis such that the functional group can be varied but leaving all other structural characteristics of the polymer constant. Secondly, the polar group as a selective but "soft" probe must be evaluated; thus other effects such as changes in the overall polymer matrix properties must be carefully evaluated and, if necessary, deconvoluted.

In this work we study the dielectric and rheological properties of a series of end-chain and in-chain functionalized polystyrenes (PS) having a wide range of functional groups.

While rheology gives information about the overall dynamical properties of the whole matrix, BDS here gives more specific information about the contributions of the functional groups to the dynamics. By systematically varying the chemical groups BDS show that the dynamics of end-chain functionalized polymers is considerable faster than the pure PS polymer- as a result of an extra contribution at high frequencies. Comparing these results with the rheological response and the thermal behaviour from Differential Scanning Calorimetry (DSC), we see that this is likely to be an effect of matrix plasticization whenever the chemical group is relatively large. However, for cyano-functionalized polymers we found that this smaller chemical group has negligible influence of the overall properties - i.e. CN can be used as selective probe to study the dynamics. Thus by combining results from the end-chain and in-chain functionalized polymers we are able to extract information about specific fluctuations of the polymer chain - i.e. end-chain and main-chain fluctuations.

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Dielectric relaxation processes in liquid, supercooled and glassy states of a pharmaceutical drug: Ibuprofen

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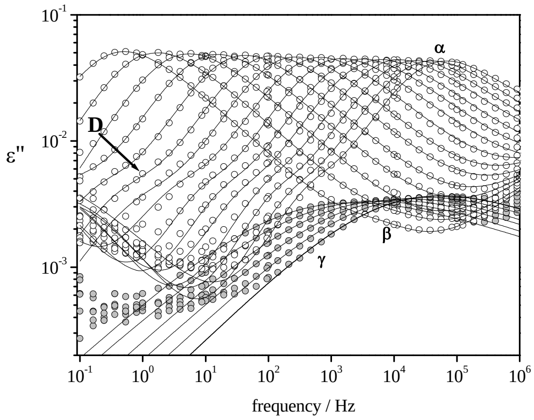

Broadband Dielectric Relaxation Spectroscopy (DRS) offers very interesting possibilities to probe the molecular dynamics in the supercooled and glassy states [1] and was recently introduced to pharmaceutical sciences [2,3]. Ibuprofen is a worldwide used pharmaceutical drug, showing analgesic, antipyretic and anti-inflammatory properties. It easily avoids crystallization so that no phase transition interferes with the continuous slowing down of molecular mobility upon cooling within the supercooled regime, allowing probing molecular dynamics over an extended frequency/temperature range.

In this work DRS (10^{-1}–10^{9} Hz) is used in order to get relevant information regarding the different modes of motion, from molten down to the glassy state, present in Ibuprofen. Four different relaxational processes identified as α, β, γ, and D (see Figure) were detected and characterized. MD simulations allowed inferring a great ability of ibuprofen to form hydrogen bonding aggregates such as dimers and trimers either cyclic or linear, which seem to be in the origin of the particular dynamic behaviour of ibuprofen.

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Dielectric study of cured epoxy resin with mesogenic unit

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The aim of this work was to study dielectric relaxation processes in crosslinked epoxy materials in a wide range of frequencies and temperatures. Four selected epoxy compounds undergo a transition to a liquid crystalline phase at elevated temperatures (above 60°C) due to the presence of a mesogen in their molecular structure: a rigid core formed by two aromatic rings connected through either an ester or an azoxy group. Aliphatic chains are attached symmetrically to both ends of the core, yielding two pairs of homologues differing in the length of each tail (2 or 8 carbon atoms). The monomers were cured using standard amines as curing agents. The obtained solid products were analysed using dielectric spectroscopy in the temperature range of -50°C to 150°C. The Havriliak-Negami formula was fitted to the data and characteristic parameters of the observed and analyzed relaxation processes were compared in detail. The results were also compared to the dielectric response of pure monomers and complemented with calorimetric data (DSC) recorded for the studied mixtures. Relaxation data for the cured products obtained from pairs of homologous compounds were studied in order to find out whether the different length of the chains of the monomers has any effect on the dielectric properties of the resulting network.

Acknowledgment

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New mixing rule of composite systems

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The paper studies dielectric properties of elastomer filled with Ni spherical particles of different sizes within the range 35 – 115 µm. The experimental analysis is followed by the examination permittivity/conductivity mixing rules. A new mixing formula for the composite system consisting of spherical metallic particles and polymer matrix is presented. This formula includes both Ni particle content and Ni particle size as two independent variables.

Keywords: composites, polymer, permittivity, mixing rule, rules of mixture

Introduction

Composite materials with metallic fillers represent a two-component or multi-component system, whose properties are affected by the properties of polymeric matrix [1], properties of metallic filler and by their mutual interaction at the filler-polymer interface. Composites are often a subject of the current material research, yet only a little attention is paid to the impact of the particle size. This topic becomes increasingly important with the advance of nanocomposites. This work was focused toward experimental studies and numerical analysis of the impact of Ni filler size on the dielectric properties of the whole composite, even if the total Ni content remains constant. Based on experimental findings, a formula for the permittivity (dielectric constant) of a composite, accounting for both concentration and size of metallic filler particles, is developed.

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Relaxation Study of PETg/Montmorillonite nanocomposites by dielectric spectroscopy

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In this work, we focused on relaxation phenomenon modifications by varying the amount of nanofiller in a PETg matrix. The PETg was chosen because it is unable to crystallize (copolymer of terephtalic acid, ethylene glycol and 1,4-cyclohexane dimethanol) and Montmorillonite (MMT) was chosen as modifier because of its important specific surface.

Microstructure was identified by X-Ray diffraction. We identified the intercalated structure and two different samples series with different basal spacing values (3.31 and 3.48 nm). One other structure characterisation has been conducted by EDX on Silicium. It shows that the nanofiller seems to agglomerate for contents upper than 3% (w/w).

Structural relaxation behaviours were characterized by mean of Dielectric Relaxation Spectroscopy and Differential Scanning Calorimetry. Main α Relaxation was characterized using the glass transition temperature T_g, fragility index m, Kauzmann temperature T_k and relaxation time at T_g $\tau(T_g)$. The secondary β relaxation was characterized using the apparent activation energy E_a.

Anomalous Dielectric Relaxation in Binary Mixtures of Mesogenic Solvent / Non-mesogenic Solute

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Dielectric relaxation studies of binary mixtures of strongly polar and mesogenic n-heptylcyanobiphenyl (7CB), with nonpolar and non-mesogenic compounds: n-heptil-cyanophenyl (7CP) and carbon tetrachloride (CCl_4), were performed. Measurements of dielectric permittivity are performed by means of concentration value in isotropic (I) and nematic (N) phase of binary mixtures with different mole fraction in solution (x_{max} = 0,17). Experimental results present the temperature behaviour of dielectric permittivity for different binary mixtures. Analysis particularly concern the transition from the isotropic to nematic phase going trough the two-phase (isotropic + nematic) region. Pretransitional effects could be clearly observed in the temperature region close to the transition point, as consequence of the reminiscent second-order behavior [1]. The results confirm the expectations on the relation between an extension of the anomaly in the rotational diffusion and the degree of the liquid heterogenity on the molecular level. An increase of the concentration of the non-mesogenic and non-polar solute in the mixture with mesogenic and strongly polar compound leads to increasement of this heterogeneity {2}. As a result, the determined value of the anomalous rotational diffusion exponent α decreases and in the dielectric relaxation experiment one observes the broadening of the absorption band {3}. Correlation between the non-mesogenic admixture concentration and the anomalous diffusion exponent was found.

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Self-assembly, molecular dynamics and kinetics of structure formation in dipole functionalized discotic liquid crystals

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The self-assembly, the molecular dynamics and the kinetics of structure formation are studied in a series of dipole-functionalized hexabenzocoronene (HBC) derivatives with applications as electronic materials [1,2]. Dipole substitution was found to destabilize the crystalline phase except for the dimethoxy- and mono-ethynyl substituted HBCs that undergo a reversible transformation to the crystalline phase. The disc dynamics are studied by dielectric spectroscopy and site-specific NMR techniques that provide both the time-scale and geometry of motion. Application of pressure results in the thermodynamic phase diagram that shows increasing stability of the crystalline phase at elevated pressures. Long-lived metastability was found during the transformation between the two phases. These results suggest new thermodynamic and kinetic pathways that favor the phase with the highest charge carrier mobility (crystalline phase).

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Peculiarities of high-temperature dielectric relaxation in vinylidene fluoride – hexafluoropropylene copolymers

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An intensive dielectric relaxation process in the vicinity of melting point was observed earlier in polyvinylidene fluoride PVDF [1] and its copolymers with hexafluoropropylene HFP [2]. The process is related to the space charge manifestation, and the aim of the present investigation is to find additional arguments in favor of this hypothesis.

According to the theory [3], the peak frequency of dielectric loss, f_m, follows the relation

$$f_m = \frac{\pi}{d^2}\frac{D}{2}, \qquad (1)$$

where D is the diffusion coefficient and d is the film thickness. In order to check influence of thickness on the relaxation process, we studied extruded VDF/HFP 93/7 films (d=130 and 40 mkm) with evaporated Ag electrodes. According to (1), for the specified thicknesses, f_m should change up to order of magnitude. However, our experiments showed that, for example, at 100°C f_m changes for more than two orders of magnitude. This means that it is influenced not only by thickness, but by other factors as well.

The system under study is more complex than studied in [3]. If the relaxation process appears at temperatures when part of crystals are melting, then the film is at least a two phase system. It means that quasi-free charge carriers will form double electric layer on the phase boundaries between the melt and the electrode and between the melt and the crystal. This heterogeneity of the system, when only a part of crystals melted, can affect the diffusion coefficient D in (1). This can explain quantitative contradictions between the experiment and the theory.

The other problem to be solved in this paper is to check the study the role of specific interactions on the polymer-metal boundary. The theory developed in [3] proceeds from the supposition that there are no such interactions. In fluorine containing polymers studied, in case of evaporated Al electrodes there are signs of chemical interactions [4-6]. Their influence on the relaxation process was checked in this paper. For this we have studied films with the same thickness ($d \approx$ 60mkm) and evaporated Al and Ag electrodes. The analysis showed that the peak frequencies of imaginary part of electric modulus, for example, at 100°C, differ in 25 times. In case of films with Al, this frequency is lower. So, chemical interactions of fluorine atoms with evaporated Al electrode significantly increase the relaxation time of the space charge relaxation.

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Sol–gel processing, Structural and dielectric properties of Ce, La-doped Lead Titanate ceramics

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The aim of this work has been the preparation and characterization of sol-gel derived Ce,La-doped PbTiO3 ceramics. Ce,La doped lead titanate bulk powders of perovskite type were prepared by a sol gel process. An excess of lead (10%) was added in order to compensate the Pb losses during the annealing process. The effect of temperature on the evolution of the powders was studied using Fourier Transform Infrared (FTIR) spectroscopy, thermal Gravimetric Analysis (TGA), Differential Thermal Analysis (DTA), RAMAN and X-Ray Diffraction (XRD). The effect of Ce,La doping concentration on the crystal structure was also investigated. The La,Ce doped lead titanate bulk powders (PLCeT) annealed crystallize in a pervskite phase.

Dielectric measurements have benn also realized. Optimization of the sintering time and temperature enabled us to give a more convenient interpretation of the results obtained.

Terahertz Time-Domain Spectroscopy of Hydrogen-bonding Liquids : Primary and Secondary Alcohols

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Hydrogen-bonding liquids have been studied extensively in many scientific fields. Recently, special attention have been paid to the functions of hydrogen bond from the view point of life process as well as physical and chemical processes. Dielectric spectroscopy is one of the most effective methods to study the hydrogen-bonding liquids since the hydroxyl group is polar and the dynamics of this bonding is essential to the function. However, the dynamics has not been well understood because of lack of the frequency range in terahertz region. Recent developments in dielectric spectroscopy have made it possible to measure the complex permittivity of liquids in terahertz frequency range. In this study, we employed a terahertz time-domain spectroscopy to study the dynamics of the hydrogen bonding in primary and secondary alcohols.

Complex permittivity measurements have been performed precisely on some monohydric alcohols in the frequency range between 0.2 and 2.5THz at temperatures from –20 to 50C. Systematic comparison of the terahertz dielectric response was made on methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol and 2-methyl-1-propanol. We found that there are three characteristic features commonly recognized for all the alcohols measured in this frequency range : (1) Effect of the lower frequency relaxation process usually so called primary relaxation. (2) Dielectric loss peak around 1.2THz. (3) Effect of the vibrational mode existing in the higher frequency range above 2.5THz. Strength of the loss peak around 1.2THz for the secondary alcohols is larger than that for the primary alcohols. Discussion will be made on the origins of the dielectric dispersions observed in the terahertz frequency range. In this case, the values of complex permittivity measured at frequencies between 10MHz and 25GHz are also used together with the terahertz response.

Investigation of interfacial polymer-clays properties through dielectric spectroscopy

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The great interest in polymer nanocomposites having the inorganic component dispersed to a nanometer scale, is due to the dramatic improvement of physical properties of the material with respect to polymer matrix (and traditional composite) reached by just dispersing very low amount of nanofiller [1]. Moreover, they are also interesting system for the investigation of polymer dynamics at interfaces. In particular, the dynamic behaviour of the polymer at the interface with the clay can be at the origin of the modification of the gas transport properties [2,3,4]. We present an investigation of grafted random copolymers of ethylene and propylene (EPR) mixed with montmorillonite at different percentages [5]. The copolymer was grafted with polar groups that act both as compatibilizer and as probe for the dielectric spectroscopy. The modification of the relaxation properties was studied upon the addition of clay at different concentration. In order to investigate the dynamic properties of the polymer strictly interacting with the clay, samples were prepared by washing the nanocomposite with a solvent of the pure polymer. The residue material, which mainly consists of the clay particles and the polymer interacting with them, still presents a dielectric signal where only the secondary relaxation is visible and the structural relaxation is disappeared. By the analysis of the overal set of data, for the case of EPR grafted diethylmaleate we can estimate that at maximum 30% of the dipolar groups are immobilized on the clay surface. Support from 'Nanopack' FIRB 2003 D. D. 2186 grant RBNE03R78E is acknowledged.

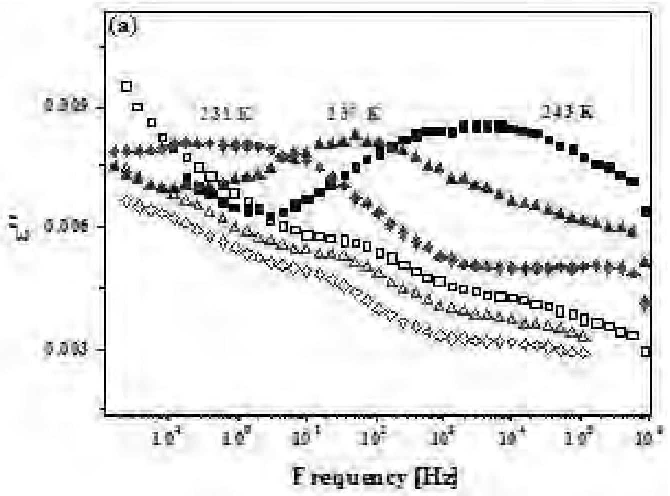

Fig. 1. Dielectric loss spectra above Tg of EPR-DEM (closed symbols) and the residue sample (open stmbols) of a 20% MMT nanocomposite.

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Dielectric Spectroscopy of Lead-Free $NaNbO_3$-Based Relaxor-Like Ceramics

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Dielectric spectra of ceramic $NaNbO_3$-$Sr_{0.5}NbO_3$-$LiNbO_3$ (NSLN) solid solution compositions exhibiting the diffuse phase transitions [1,2], have been studied in the wide frequency (10^0-10^9 Hz) and temperature (100-600 K) ranges. In the temperature dependences of dielectric permittivity the peak with a strong frequency dispersion and the maximum temperature T_m obeying the Vogel-Fulcher law characteristic of relaxors is observed. At $T >> T_m$ the reciprocal dielectric constant and the thermal dilatation of ceramics follow the linear temperature dependence, however, below the temperature $T_d >> T_m$ the deviation from linearity is observed. Such kind of deviation in classical relaxors, such as $PbMg_{1/3}Nb_{2/3}O_3$, is usually believed to be the result of formation of polar clusters which constitute the essential ingredient of relaxor structure.

By means of deconvolution of dielectric spectra we show that alongside relaxational dielectric response, strong frequency-independent dielectric contribution is observed at all temperatures, which can be attributed to the phonon polarization. In contrast to classical perovskite relaxors where the phonon contribution to the permittivity in the range of T_m is usually negligible, in NSLN it amounts to significant portion (~50%) of the total low-frequency dielectric permittivity. In classical relaxors due to cooperative interactions among polar clusters the characteristic relaxation time (τ) increases upon cooling much faster than the Arrhenius law predicts. The Vogel-Fulcher law, $\lg\tau \propto (T-T_f)^{-1}$, is usually believed to correspond to the transformation into nonergodic relaxor state (assumed to be a kind of dipole glass) below a freezing temperature T_f . In NSLN we observe the Arrhenius behaviour of τ which means that cooperative interactions are insignificant and glassy freezing of the dielectric spectrum is absent.

The results obtained demonstrate that large diffuse and dispersive permittivity peak which is apparently similar in all relaxors may have very different origin in different materials.

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Electrical and electro-optical properties of $BaTiO_3/SrTiO_3$ superlattices

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By using a microscopic model taking into account a quantum mechanical method based upon the orbital approximation and the dipole-dipole interaction due to the local electric field acting on the constituent ions, we calculated the electrical and electro-optical properties of $BaTiO_3$ (BT)/$SrTiO_3$ (ST) superlattices at room temperature. The calculations show that the spontaneous polarization and linear electro-optic coefficients of the superlattices increase with their richness in BT while their relative dielectric constant decreases with it, indicating that important is the spontaneous polarization of a unit cell less is its dielectric response which is in accordance with the experimental measurements [1, 2]. In addition, as shown by Shimuta *et al.*, the magnitude of the spontaneous polarization of the BT/ST superlattices, particularly that of the 3/3 and 10/3 structures, exceeds the measured value of the polarization of BT single phase film prepared using the same preparation conditions as those of the superlattices (0.07 C/m^2) [3]. The highest value of the calculated spontaneous polarization, which is 0.1955 C/m^2, is as large as that measured by Sarkar *et al.* [4] (P^{spn} = 0.184 C/m^2) for a symmetric BT/ST superlattices with a stacking periodicity of 6.4 nm. With regard to the relative dielectric constant, the superlattice with a stacking periodicity of 3/10 has an average ε_{33} of 259.97. This value, which is as large as those measured for BT ($\varepsilon_{33} = 260$) and ST ($\varepsilon_{33} = 230$) single phase films [3], agrees well with that measured by Shimuta *et al.* [3] ($\varepsilon_{33} = 270$) for the same superlattice structure and also with that reported by Sarkar *et al.* [4] ($\varepsilon_{33} = 260$) for a symmetric BT/ST superlattices having a stacking periodicity of 8 nm. Finally, we have shown that significant enhancement of the linear electro-optic coefficients can be achieved in BT/ST superlattices. This enhancement, which concerns also the ST layers, arises from the combined effects of strain, induced in the BT layers by the epitaxial growth, and internal polarizing electric field originating in the BT layers and acting on the electronic clouds of the polarizable constituent ions of the system. The significant electro-optic effect observed here complements a recent experimental work in which Hiltunen *et al.* [5] show that the superlattice structure clearly provides an enhancement of the linear electro-optic effect. It is expected that the superlattice structure provides also an enhancement of the optical second harmonic generation (SHG) coefficients being seen that the SHG effect of the oxygen-octahedra ferroelectrics is strongly correlated to the linear electro-optic effect as stated by Wang [6].

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Dielectric Spectroscopy of $LiNbO_3$:Tm Nanocrystals Embedded in a SiO_2 Glass Matrix

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In this paper we present the preparation, by the sol-gel method, of a transparent SiO_2:Li_2O:Nb_2O_5 gel doped with Tm^{3+}. The dried gel was heat treated (HT), in air, at temperatures between 500°C and 800°C.

The glasses and glass-ceramics were studied by differential thermal analysis (DTA), X-ray power diffraction (XRD), scanning electron microscopy (SEM), dc conductivity (σ_{dc}), ac conductivity (σ_{ac}), thermally stimulated depolarization current (TSDC) measurements and the dielectric properties in function of frequency and temperature.

The X-ray diffraction patterns show that SiO_2 and $LiNbO_3$ crystal phases are present in the sample treated at temperatures above 650°C. Besides the SiO_2 and $LiNbO_3$, $NbTmO_4$ crystal phase was detected in the sample treated above 750°C. The XRD and SEM analysis show that the particles size and number increases with the rise of the HT temperature. The electrical and dielectrical properties were related with the glass and glass-ceramics microstructure.

Dielectric Properties Study of $xLiFe_5O_8$-(1-x) $LiNbO_3$ Composites Processed Using Microwave Energy

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The electroceramics with high dielectric constants have been in increasing demand due to the miniaturization of electronic devices. In particular, the lithium niobate ($LiNbO_3$) owing their remarkable pyroelectrical, piezoelectrical and photorefractive properties is interesting, presenting a large variety of applications in technology. The cubic lithium ferrite ($LiFe_5O_8$) in the ceramic form is actually used in microwave and memory core applications, high-density magnetic recording devices, magnetocaloric refrigeration, magnetic resonance imaging (MRI) enhancement and magnetically guided drug delivery (ferrofluid technology). $LiFe_5O_8$ is an interesting ferromagnetic material due to its square hysteresis loop and high Curie temperature.

In this work we present the preparation and properties analysis of the x-$LiFe_5O_8$-(1-x)$LiNbO_3$ di-phasic composite, where the x is between 0 and 100% (% wt). The composites were sintered, using microwave radiation, through the use of commercial microwave oven.

The influence of treatment parameters in the structural and electrical properties of theses composites were investigated using XRD, SEM and impedance spectroscopy measurements.

Dielectric properties of $NaNO_3$ in porous glasses

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Recently, many studies have been carried out on the physical properties of materials in confined geometry, especially for ferroelectrics, where finite-size effects are of fundamental interest in thin film ferroelectric memories, microcomposites [1-3]. Introducing ferroelectric materials into a porous glasses matrix is one of the methods of preparing nano–size ferroelectrics, but publications on physical properties and phase transition on porous glasses filled with ferroelectrics are few. The aim of the present work was to develop a method of introducing of $NaNO_3$ into the porous glasses and to study the impact of the method and pore size on physical properties and phase transition of embedded nanocrystals. The results of dielectric and dilatometric measurements of porous glasses filled with $NaNO_3$ from water solution and from the melt are presented. The relation between phase transition temperatures versus average values of pore dimensions was determined.

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Dielectric Properties of SiO_2-$LiFe_5O_8$ Glass-Ceramics by Sol-Gel Processing

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The lithium ferrite ($LiFe_5O_8$) is a very interesting ferromagnetic compound due to its square hysteresis loop and high Curie temperature. It has attracted the attention of scientists and engineers for a long time with regard to their application as a low-cost substitute of garnet ferrites in several devices like high-density magnetic recording, magnetic fluids, ferrofluid technology, magnetocaloric refrigeration, magnetic resonance imaging (MRI) enhancement and magnetically guided drug delivery.

In this work we present the first studies of the (x)SiO_2-(1-x)[$Li_2O.5Fe_2O_3$] (% mol) glass and glass-ceramic, with x between 88 and 97%, prepared by the sol-gel method. $LiFe_5O_8$ ceramic was also prepared by the conventional solid-state method.

The influence of the heat-treatment parameters, in the glass and glass-ceramics structure, was investigated through the XRD, FT-IR, Raman, SEM and Impedance Spectroscopy measurements. The samples structural and dielectrical properties were related and compared to those of the $LiFe_5O_8$ ceramic.

Dielectric properties of $CaCu_3Ti_4O_{12}$ (CCTO) doped with GeO_2

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$CaCu_3Ti_4O_{12}$ (CCTO) is a compound with perovskite structure that displays interesting dielectric properties. In particular, the polycrystalline CCTO was reported to exhibit an extraordinarily high dielectric constant (ε_r) of about 10^4–10^5 at room temperature, and good temperature stability over a wide range from 100 to 600 K.

Some researchers suggested that this dielectric behaviour is intrinsic, while others have attributed this behaviour to extrinsic effects. Among the last ones, the barrier layer capacitor model (BLC) is, by now, commonly accepted.

The preparation method and doping has a great influence on the microstructure and dielectric properties of this material.

In this work, the samples were prepared by solid state conventional technique using stoichiometric amounts of CuO, TiO_2, $CaCO_3$. The obtained material was doped with GeO_2 with concentrations from 2% up to 14% by weight, and sintered at two different temperatures, 1050 and 1100 °C, during 12 hours.

The samples have been studied by X-ray diffraction (XRD), scanning electronic microscopy (SEM) and dielectric measurements.

The composition of the grains, grain boundaries, and the second phases have been determined using X-ray diffraction, scanning electronic microscopy and energy dispersive X-ray spectroscopy (EDX). AC impedance spectroscopy measurements, in the frequency range 10^2 – 10^7 Hz, at room temperature, have been performed. The results show an increase of ε_r for all doped samples relatively to undoped CCTO, arising a maximum for the 6% doped one, where is observed the segregation of Cu-rich phase. The effects of sintering conditions and GeO_2 doping on the segregation phase are studied and correlated with the relaxation parameters calculated using the Cole-Cole model.

Dielectric relaxation in diepoxy nematics at elevated temperatures

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Relaxation processes in four low molecular weight liquid crystalline materials were studied. All the investigated compounds form a nematic phase at temperatures above 60°C, in one case a smectic A phase also appears. The investigated materials have rigid cores built from two aromatic rings connected through either an ester group or an azoxy one. Two aliphatic chains with terminal epoxy groups are attached symmetrically at both ends of the core. Two compounds containing eight carbon atoms in the tails were compared with their homologues having two carbon atoms in a chain. The length of the aliphatic chain usually affects the temperature range of the mesophase, which is also observed in our case. The dielectric response was investigated in the high frequency range from 10^4 to 10^9 Hz. The monomers were placed between gold-plated electrodes. Dielectric spectra of nematics often have a complex structure, depending on the alignment of the molecules with respect to the direction of the probing electric field. In non-aligned materials two relaxation bands with characteristic frequencies of the order of 10^6 and 10^9 Hz are most likely to appear, as a result of overlapping of different relaxation processes due to different weighted sums of four underlying relaxation modes depending on the macroscopic orientation of the sample [1]. In our studies, a relaxation process related to molecular motions was clearly visible in each of the materials, in both the liquid crystalline and the isotropic state, though its characteristics were different for the particular cases. All the observed relaxation processes were analyzed by fitting the Havriliak-Negami formula to the data. The obtained characteristic parameters were compared in detail.

As the investigated monomers have epoxy groups at both ends, they can be used to synthesize larger structures [2]. The elevated temperature range routinely used in the standard curing procedure for such materials includes such values of temperature at which the studied compounds are in mesophase range. Therefore, the presented results for the monomers may also become helpful for a further analysis of these compounds, during and after crosslinking.

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Mutual Dependence of Primary and Johari-Goldstein Secondary Relaxations in Glass-Forming Systems

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We report evidences from broadband dielectric spectroscopy (1 mHz-10 GHz) that the dynamics of the primary α- and the secondary Johari-Goldstein (JG) β- processes are strongly correlated in different glass-forming systems over a wide temperature T and pressure P range, in contrast with the widespread opinion of statistical independence of these processes. The experimental study was carried out on several polar molecules both as a component in binary mixtures and in neat systems [1]. The α-β mutual dependence is quantitatively confirmed by: a) the overall superposition of spectra measured at different T-P combinations but with an invariant α- relaxation time (see Fig.1); b) the contemporary scaling of the isothermal-pressure and isobaric-temperature dependences of the α-and β- relaxation times as plotted versus the reduced variable $T_g(P)/T$, where T_g is when $\tau_\alpha(T_g)=10^2$s; c) the change of dynamics in the Arrhenius behaviour of JG relaxation time always occurring on crossing the T_g-P_g line, both isobarically and isothermally. These novel and model-independent evidences indicate the fundamental role played by the JG relaxation in glass transition, often overlooked by most current theories. On the other hand, the whole phenomenology can be rationalised in the framework of Coupling Model [2] and confirms a recent NMR study [3] showing a strong correlation of α-β dynamics.

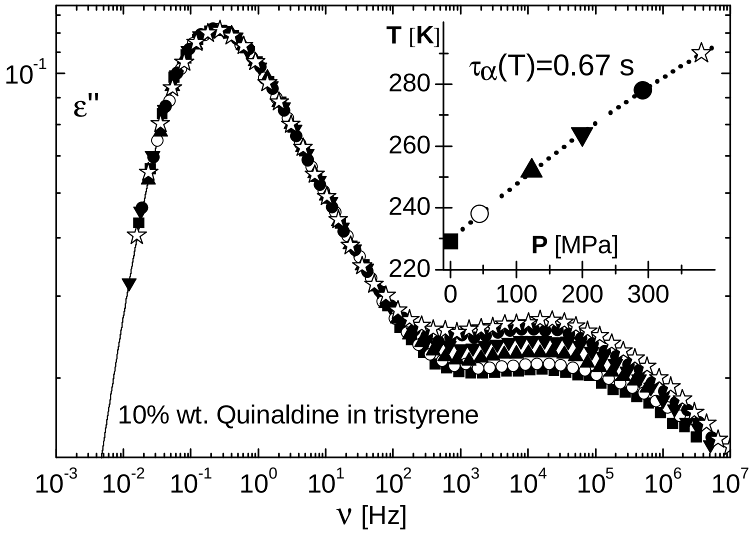

Fig.1 –Loss Spectra with τ_α=0.67 s obtained for different T and P in a binary mixture.

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Influence of uniaxial stretching on dielectric response of miscible polymer blends

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To gain new insight into the component segmental dynamics of polymer blends, we are performing dielectric relaxation experiments on samples subjected uniaxial stretching deformation, below and above the average glass transition temperature, T_g , with high stretching speed. In this context, one model system, polystyrene/poly (vinyl methyl ether) (PS/PVME) blends in miscible state, is studied in PS high concentration range (50-80 wt% of PS). Those compositions were chosen due to the confinement effect on molecular motions of the dielectrically active component caused by high-T_g component. By means of dielectric spectroscopy in a frequency range 10^{-1} – 10^{7}Hz, the dynamics of PVME units in the blends has been selectively investigated. The temperature range investigated is from 175 to 385 K. The main relaxation process observed in these ranges of frequency and temperature is the relaxation of the PVME segments constrained by the much less mobile PS chains. Our results evidence that for those compositions the effect on the dielectric relaxation process observed can be related with the degree of orientation of the polymer chains.

Microwave dielectric properties and conductivity of aqueous solutions of polydiallylmethylammonium and diallylmethylammonium trifluoracetates

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Solutions of polyelectrolytes find wide application in various fields of a science and techniques. In particular aqueous solutions of the polydiallylammonium salts have a high biological activity and are used in medicine. The information on hydration and transport properties of solutions is necessary for their optimum application.

In order to establish the features of molecular-kinetic hydration of polyelectrolyte, the microwave dielectric properties of aqueous solutions of polydiallylmethylammonium (poly(DAMA)) and diallylmethylammonium (DAMA) trifluoroacetates have been studied in temperatures interval 288-308K. Complex dielectric permittivity was measured by a method of thin dielectric rod in the wave-guide at frequencies 7.5, 10.0, 13, 16, 18.9, 22 and 25 GHz (in the region of maximum of dispersion of dielectric permittivity of water). The values of dielectric relaxation time τ were found. They characterize the changes of the water molecules mobility in the hydration shells of ions. The activation enthalpy $\Delta H_\varepsilon^{++}$, free energy $\Delta G_\varepsilon^{++}$ and entropy $\Delta S_\varepsilon^{++}$ of dielectric relaxation processes were calculated using the temperature dependences of the dielectric relaxation time. The growth values of τ and $\Delta H_\varepsilon^{++}$ was observed for poly(DAMA) and DAMA trifluoroacetates aqueous solutions. It indicates on the structure-making influence of ions on the tetrahedral hydrogen bond net of water. The concentration dependences of τ and $\Delta H_\varepsilon^{++}$ exhibit an opposite behaviour to that of the electrolyte solutions with typical hydrophilic hydration (KCl, etc.). Thus for the first time the hydrophobic hydration of polydiallylmethylammonium is established.

The conductivity of aqueous solutions of trifluoroacetic acid, poly(DAMA) and (DAMA) trifluoroacetates was investigated in a wide area of concentration, (including solutions with a high degree of dilution) for the establishment of features of ionic transport. Measurements are executed in temperature interval 288-308K. It is revealed, that the equivalent conductivity of poly(DAMA) and (DAMA) trifluoroacetates solutions follows the linear dependence $\lambda=\lambda_\infty- Ac^{1/2}$ (where λ - equivalent conductivity, c – molarity) up to 0,1 M in contrast to the cases of other polyelectrolytes and weak electrolytes. The limiting ionic mobility λ_∞ for the trifluoroacetate, diallylmethylammonium and polydiallyl-methylammonium ions is found. It is shown, that process of charge transfer in the polydiallylmethylammonium aqueous solutions is realized, mainly, due to the migration of trifluoracetate -ion.

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Elementary process of the α relaxation of polyhydric alcohols : dielectric study from 10μHz to 2.5THz

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Polyhydric alcohols such as sugar alcohols undergo glass transition through their supercooled state easily without special treatment. This fact seems to be a major reason that sorbitol, glycerol and so on have often been used in studying the glass transition phenomena. It has been considered that the hydrogen bonding network is responsible for such characteristics of polyhydric alcohols. However, relation between the network and the dielectric relaxation processes has not been understood very well.

We have performed complex permittivity measurements on liquid sugar alcohol system in the frequency range from 10μHz up to 10GHz [1-4]. The system includes different samples composed not only of pure sugar alcohols but also of their mixtures and of materials with small amount of water. Experimental results for all the samples show two dielectric relaxation processes which are attributed to the structural α process and the Johari-Goldstein β process. The α process follows the non-Arrhenius VFT manner and the β process follows the Arrhenius manner. The α-β bifurcation is also observed as usual. It is noted that the relaxation frequencies for the α and the β processes depend not only on T but also other parameters characterizing the samples such as mixing ratio (average number of carbons Nc) and sugar fraction (X) in samples containing water. Surprising finding is that plots of log fm with Nc and X on the horizontal axis show the similar feature as is seen in the usual relaxation map for $1/T$. This multivariate feature for the α and β process was recognized for the first time. This feature suggests that the elementary process of the α process doesn't originate from one molecule but a part of the network.

We have examined this concept by using more simple alcohols such as n-alcohols (1-propanol, 1-butanol and 1-pentanol) and diols (1,3-propanediol, 1,4-butanediol and 1,5-pentanediol). In this case, complex permittivity measurements have been carefully performed in the frequency range between 10MHz and 25GHz at temperatures higher than their melting points to avoid unwanted complexity such as cooperativity. We also performed viscosity measurements. It was found that the corresponding n-alcohol and diol give quite different values of viscosity although the main relaxation frequencies are very similar. This suggests that the origin of the main relaxation process for the alcohols is a dipolar relaxation process due to switching of one hydrogen bond. The larger values of viscosity for the diols is understood as a result of forming the hydrogen bonding networks unlike the n-alcohols. Such difference between n-alcohols and diols is also suggested from dielectric measurements up to 2.5THz. Finally, the switching of one hydrogen bond is supposed to be the elementary process of the α relaxation in polyhydric alcohols from the continuity at melting point.

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Improving determination of relaxation spectrum by artificial neural networks

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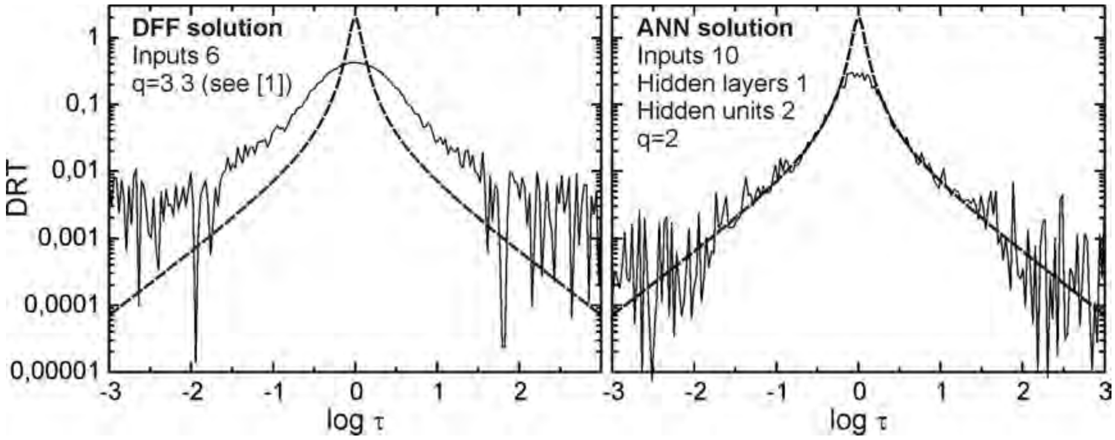
In the previous conference (BDS 2006), *digital functional filters* (DFFs) [1] operating with equally spaced data on a logarithmic scale (geometrically spaced data on linear scale) have been demonstrated as efficient linear algorithms for recovering the *distribution of relaxation times* (DRT) from a wide variety of the time- and frequency-domain functions. The provided tests have shown that there are no problems to determine relatively broad and moderately asymmetric distributions; however, a single linear algorithm does not ensure good solutions for discrete, narrow and essentially asymmetric relaxation spectra.

In the presented contribution, improvement of DRT recovery is discussed by adapting ideas from *artificial neural networks* (ANNs) [2]. Attempts to employ standard ANN strategies did not succeed. One of reasons for this was incompatibility of commonly used activation functions [2] with specific DRT normalization by the constant area under the curve leading to uncontrolled variation of spectrum amplitude for narrow and line spectra.

The innovations have been made by converting DFF into ANN. For this, the hidden units are incorporated in a filter maintaining its moving (sliding) principle. One of the fundamental findings of this research is the *square activation function* to be very advantageous for DRT recovery in that it: (i) enhances the resolution due to a high gain for large signals lengthening the narrow spectra, (ii) ensures the non-negativity for the recovered spectra due to squaring the signals, (iii) reduces significantly the sensitivity to noise due to a small gain for small signals, i.e. input noise.

As an example, bellow in Fig., DFF and ANN solutions are demonstrated for DRT recovery from the dielectric permittivity (Cole-Cole model, $\alpha = 0.95$) distorted by additive random noise within interval [-0.01, 0.01]. As seen, ANN provides considerably higher accuracy.



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Glass Transitions and Dielectric Relaxations Observed in Partially Crystallized Protein-Water Mixtures

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According to an adiabatic calorimetry measurements of heat capacities and enthalpy relaxation rates of a 20 % (w/w) aqueous solution of bovine serum albumin (BSA) in a temperature range from 80 to 300 K, two enthalpy relaxation effects related to a glass transitions at around 110K and that over a wide temperature range (120-190K) were observed for a quenched sample from 300K down to 80K and three separated relaxation effects at 110K, 135K, and above 180K were observed for a sample annealed in 200-240K after the quenching [1]. To investigate the relationships between the thermal glass transitions and dynamics observed by the adiabatic calorimetry, broadband dielectric measurements of BSA-water mixtures with various BSA concentrations were preformed in a frequency range of 2mHz - 20GHz and temperatures in a range between 300K and 80K.

Three relaxation processes could be detected. The relaxation times of the three processes are 100 s at approximately 110K, 130K, and 200K. Therefore, these relaxation processes are related to the glass transitions observed by the adiabatic calorimetry [1]. The relaxation process whose relaxation time is 100 s at ca. 200K can be interpreted to be due to a local chain fluctuation of protein. The relaxation process whose relaxation time is 100 s at ca. 130 K is due to ice. The relaxation process whose relaxation time is 100 s at ca. 110K is due to the molecular motion of uncrystallized water (UCW).

The temperature dependence of the relaxation time of the UCW changes at approximately 200K, i.e. the glass transition temperature of protein in the mixture. At temperatures below 200K, the temperature dependence of the relaxation time is smaller than that above 200K, and obeys the Arrhenius type. This behaviour of the UCW in BSA-water mixtures is similar to that found in the β relaxation of water in protein-glycerol-water mixture [2], aqueous mixtures of various molecular liquids and polymer [3, 4], nano-confined water [3], and mixtures of two van der Waals glass formers [3, 5] when crossing the glass transition temperature of the mixture. Based on these similarities, theoretical interpretation of dynamics in hydrated proteins is given.

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Observation of Polymer Crystallization through Ion Motion: Low Density Polyethylene

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In a previous study of ionic conduction for low density polyethylene(LDPE),[1] it was found that the dispersion curve of the frequency response functions in a low frequency region is broader than that of the single conductivity relaxation time[2] dispersion curve. Furthermore, the breadth of the dispersion curve and dc conductivity depends on the thermal treatment time of a sample. Additionally, a differential scanning calorimetry (DSC) curve changed from a simple fusion curve to a complex one which reflects a formation of inhomogeneous structure. The experimental result in that study suggests that the ionic motion in LDPE is affected by the inhomogeneous structure of polymer solid which was generated by thermal treatment. In the present study, the thermal effect on the ionic motion is investigated more accurately under the well-controlled temperature condition with the aim of precise examination for the relation between the ionic motion and the structure in polymer solid.

Films of LDPE were obtained by vaporizing the solvent after pellets of LDPE had been dissolved in toluene at about 120 °C. After the vaporization, the films were cooled to a room temperature. The films thus obtained were treated thermally. At first, all samples were heated up to 120 °C, kept for 10min at this temperature and cooled down to designated temperatures for example 100 °C. Electrical measurement was made at this temperature by the apparatus of TA Instruments DEA2970. Electrode of the interdigital sensor[3] was employed in order to make accurate experiment.

From the time development of the permittivity and the conductivity measured just after the sample was cooled down to a designated temperature, it is found that the permittivity and the conductivity at several frequencies increase initially but after some time passed these quantities decrease. These two different tendencies against the time seem to reflect the ion motion related to different morphology in crystal growth. In order to confirm this point, the Avrami analysis was applied to these electrical data. The Avrami index was estimated as 2.3±0.1 or 2.5±0.1 for the earlier process and 3.7±0.5 or 3.9±0.6 for the later process. These values indicate that the earlier process reflects the two dimensional crystal growth and the later process reflects the three dimensional crystal growth, although the values for the later process are a little large.

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Theoretical Approach for Characterization of Dielectric Properties of Metal Containing Nano-Composites

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A new theoretical approach has been developed for the characterization of dielectric properties of composite materials based on a dielectric matrix containing metal/semiconductor nano-particles. In equilibrium, an electron can be released from the metal nano-cluster and hop between traps inside the dielectric matrix around the cluster. The electron and the cluster are bounded by Coulombic and polarization forces and consequently form an elementary dipole. The number and strength of such equilibrium dipoles depends on temperature. The solution of the derived integral equation for the time dependent dipole relaxation function depends on the dielectric characteristics of the matrix and nano-particles size distribution that can be easily obtained experimentally. The characteristic time of the electron tunnelling jumps between neighbouring traps is a function of the same parameters. The unknown quantities are the electron bound energy in the trap and the traps density in the matrix.

Porous non-organic silica glasses with controlled pores sizes, containing 4-6 mass% of Pd nano-particles were used as test materials. They were characterized by SEM (Scanning Electron Microscope) and EDS (energy dispersive X-ray spectroscopy) methods in order to obtain pores size distribution and sample composition. A corresponding average radius of metal clusters inside the porous dielectric matrix was obtained by a small angle X-ray diffraction method. The dielectric properties of the samples were investigated using a Broad Band Dielectric Spectrometer (NOVOCONTROL BDS 80) in wide frequency (0.1 Hz - 10^5 Hz) and temperature (-120 – 300 ^{0}C) ranges. The experimental dielectric data has then been fitted with theoretically calculated complex dielectric permittivity value. The model coincides with the experimental results and shows reasonable values of the fitting parameters.

To show the universality of the theoretical approach another well-studied [1] metal containing polymer system will be tested.

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Rotational and translational diffusion of glass formic liquids in 2D confinement

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Broadband Dielectric Spectroscopy is employed to investigate the molecular dynamics of glass forming materials in the bulk as well as under conditions of two dimensional confinement (in nano-pores-Figure 1). This experimental method has the unique advantage of being able to characterize – in a single experiment – both the rotational and the translational component of the glassy dynamics. While the first component corresponds to the alpha relaxation process, the latter one is related to the macroscopic conductivity. The present study has a twofold motivation: (i) to systematically investigate the correlation between the rotational and the translational diffusion of organic glass forming materials in the bulk; (ii) to examine how 2D confinement impacts this correlation.

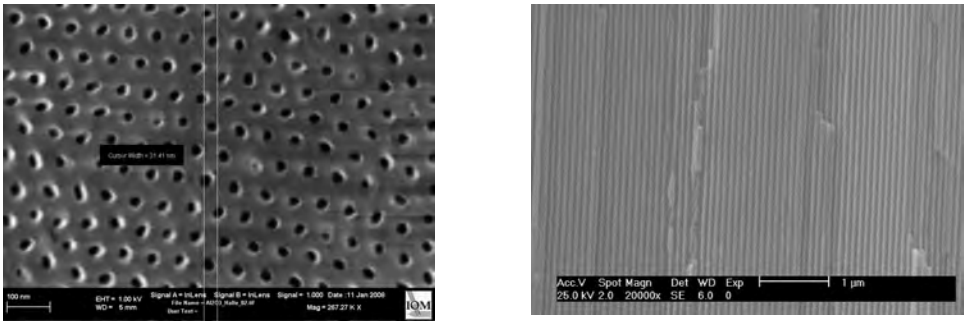

Figure 1. a) SEM images of the porous alumina host membranes (top view),
b) the corresponding cross section (pore size 16 nm)

Influence of confinement on molecular and director reorientational dynamics of liquid crystals

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Broadband dielectric spectroscopy and photon correlation spectroscopy have been applied for investigations of the dynamic behavior of liquid crystals (5CB and 8CB) confined in porous matrices with random pores. We observed deep supercooling of liquid crystals in random pores. The relaxation times of the process due to the molecular rotations (investigated by dielectric spectroscopy) in deeply supercooled state were slower than at the temperatures corresponding to nematic phase by a factor of 10^6. This slowing down was accompanied by anomalous broadening of the dielectric spectra. The mode (reorientation of molecules around their short axes), that was molecular in the bulk liquid crystals, transformed to collective one in confined material under deep supercooling. We assign this qualitative change in dynamics to coupling of molecules to the pore walls and among themselves via molecule-wall interactions.

The dynamics of director orientation fluctuations was investigated by photon correlation spectroscopy. In nematic phase of bulk liquid crystals the relaxation process due to director orientation fluctuations is single exponential. The dynamics of this process was also drastically modified by random confinement. The slow relaxation process which does not exist in the bulk liquid crystals and a broad spectrum of relaxation times appear for confined 5CB and 8CB. The temperature dependencies of relaxation times of director reorientations and molecular reorientations at temperatures bellow bulk crystallization temperature were in agreement with the Vogel-Fulcher formula. The results on the influence of confinement on properties of liquid crystals obtained by dielectric and photon correlation spectroscopy were compared with the results of Differential Scanning Calorimetry experiments.

The Adam-Gibbs approach and the dielectric alpha-relaxation of polymer systems

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In this talk I will summarize the recent progress obtained by our group in the application of the Adam-Gibbs (AG) approach, relating the dynamic and thermodynamic behaviours, to the dielectric relaxation of polymer materials. First, the applicability of the AG approach for the segmental relaxation of a wide variety of polymers, including both the equilibrium and the non-equilibrium range around the glass transition, will be presented [1-3]. In the second part I will discuss the extension of the AG approach to experiments above atmospheric pressure (up to 300MPa) on standard polymers [4,5]. In the last part, I will show how the AG approach combined with the self concentration concept has given rise to a predictive model for the component dynamics of multicomponent polymer systems, namely, athermal polymer-polymer blends [6-9] and concentrated polymer solutions[10]. The same approach has been found to be valid for pressure experiments on the multicomponent polymer systems[11]. Finally, the implications of all these results on the nature of the polymer segmental dynamics[12,13] will be highlighted.

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Impedance spectroscopy study of $Pb_{2(1-x)}K_{1+x}Gd_xNb_5O_{15}$ samples

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The $Pb_{2(1-x)}K_{1+x}Gd_xNb_5O_{15}$ (PKGN) phase having the tetragonal Tungsten Bronze (TTB) structure form one of the largest and yet purely studied families of ferroelectric materials [1-3]. PKGN powder is elaborated by solid state reaction technique and compressed in pellets form for dielectric measurements. X-ray characterization, performed at room temperature, was showed a structural correlation versus lead concentration. SEM images show a good crystalline morphology of the samples. The complex impedance spectroscopy (CIS) technique was used to study electrical properties of the samples, which was showed the strongly change of transition temperature with the lead composition. The Cole-Cole diagrams at different temperatures are also reported.

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Time-resolved Nonlinear Dielectric Responses in Molecular Systems

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Impedance measurements in the 0.1 Hz to 50 kHz range are performed beyond the linear response regime, reaching fields as high as 450 kV/cm. Saturation of the steady state dielectric constant is observed, but our main focus is on the effects of the energy that is transferred irreversibly from the external field to a molecular glass-forming liquid. Because the slow degrees of freedom absorb this energy, their heterogeneous configurational temperatures are increased before the heat is transfered to the phonons on the time scale of structural relaxation [1]. This allows us to assess the configurational contribution $C_{\mathrm{p,cfg}}$ to the total excess heat capacity $C_{\mathrm{p,exc}}$, which varies systematically with fragility between 45 % and 85 % [2].

More recently, we have devised a time resolved variant of high field impedance spectroscopy, where the harmonic field is applied for few cycles at a low field, followed by several high field cycles. Fourier analysis of the resulting signals provides a period by period time resolved picture for the response of the configurational temperature with a 5 mK resolution, resulting from a sensitivity on the 5×10^{-5} level for $\tan\delta$. It turns out that this heating is responsible for an extremely pronounced non-linearity in the electric field, with the changes in the dielectric loss easily exceeding 20%. The experiments provide detailed insight into the nanoscopic heat flow in liquids and to non-linear dielectric effects in general.

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Properties and nature of the secondary relaxations in ethylcyclohexane and related materials at low and high temperatures

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The comparative use of high resolution dielectric spectroscopy and mechanical spectroscopy at ultrasonic frequencies represents a powerful method to investigate the dynamical properties of glass forming liquids having weakly polar character and very low dc conductivity. In the case of ethylcyclohexane, this approach has allowed us to reveal the existence of a beta relaxation process in the supercooled and glassy state, and of multiple secondary relaxation processes, slower than the alpha-relaxation, in the high temperature liquid. The observed relaxation processes appear with very similar activation parameters at low- and at high temperatures, above and below the glass transition temperature T_g, in different materials having structural similarities with the ethylcyclohexane molecule. Also on this basis, a possible intramolecular origin of the processes has been proposed.

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Structural and Dynamical Aspects of the Cold Crystallization of a Flexible Polymer as seen by Time Resolved Neutron Scattering and Broadband Dielectric Spectroscopy

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Polymers that possess a certain molecular symmetry around its backbone have a natural tendency to crystallize into highly ordered domains. However, given the connectivity between segments, the dynamics of polymers is inherently slow which often kinetically counteracts the formation of crystals. As a result the structure of polymers is most often only partially or non-crystalline (amorphous).

In order to understand the mechanism governing the crystallization in polymers it is important to understand both the polymer dynamics and the structure and how they are interrelated. Polydimethylsiloxane (PDMS) belongs to a rather peculiar class of extremely flexible polymers which exhibits a very small energy barrier for rotations around their backbone. In view of this, PDMS represents a natural model system possessing very fast dynamics where the mobility of the chains can be directly related to the crystallization process.

Here we present a complete study of the structural and dynamical aspects of the crystal formation of PDMS starting from a fully amorphous glass state at low temperatures. Using time resolved wide angle neutron scattering (WANS) and small angle neutron scattering (SANS) we are studying the structural aspects of the crystallization over a wide range of length scales of approximately 5000 – 2 Å. This is combined with a real time analysis of the segmental dynamics by using broadband dielectric spectroscopy (BDS) and the overall thermodynamical properties employing differential scanning calorimetry (DSC).

In this communication we will concentrate on the kinetic results obtained using the different techniques which will be compared and analyzed with particular emphasize on the interplay between the structural and dynamical properties. A particular emphasis is made on crystallization mechanism and the potential role of mesomorphic phases acting as precursors in the transition from the amorphous to crystalline state.

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Resolving Interfacial Fluctuations and its Effect on the Segmental Dynamics in Nano-segregated Block Copolymer Melts

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Block copolymers spontaneously self-assemble into well defined structures with variable geometry (spherical, cylindrical, lamellar etc) depending on the chemical details (molecular structure, composition etc) and external conditions such as temperature and pressure. It is of significant interest to understand how this structure formation, typical in the range of some tenths to hundreds of nanometer, affects the polymer chain dynamics.

For this purpose, poly(isoprene)-poly(dimethyl siloxane) block copolymer melts are ideal as a model system as the both polymers exhibit a low glass transition temperature, strong mutual repulsion ($\chi \sim 0.17$) and well-separated dynamics. Consequently PI-PDMS spontaneously self-assemble to well-defined equilibrium structures. Most importantly in the context of dynamics, cis-PI exhibits a net dipole both parallel and perpendicular to its backbone. This makes it an ideal candidate to investigate both the global dynamics (normal mode) as well as the local segmental alpha-relaxation using Broadband Dielectric Spectroscopy (BDS). By comparing the dynamics of the corresponding pure PI homopolymers, the effect of confinement on the dynamics can be directly deduced.

We will present results of a study of various PI-PDMS block copolymer melts where the PI part varies between 5 000 to 10 000 g/mole. Using small angle x-ray scattering (SAXS), we deduce the detailed structural properties (sizes) and the ordering behaviour (crystal structure) of the system. Dielectric spectroscopic measurements show that the confinement induces a faster and broadened normal as well as local segmental relaxation process having an extra fast relaxing component in the high frequency side of the dielectric loss peak.

In this communication we show that by properly taking into account chain connectivity (self-concentration) and interfacial fluctuation effects, we can construct a simple model capable to quantitatively explain both the broadening and acceleration of the alpha-relaxation. The extracted width parameters of the interface were found to be in the range of the estimated values based on thermodynamical and capillary wave dynamics arguments. The results do not only demonstrate the importance of fluctuations effects on the local alpha-relaxation, but also how BDS can complement scattering techniques to give highly detailed structural information.

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Control of Uniformity of Nanoparticles Distribution in Polymer Matrix - Using BDS

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Nanoparticles have very high surface energy and exhibit a tendency to aggregation. It is very hard to separate them and introduce to polymer matrix uniformly. Aggregation of nanoparticles results in a loss of unique properties of nanocomposites. All present methods of control nanoparticles distribution in polymer matrix need expensive equipment.

Our task has been to investigate the possibility of determination of uniformity of nanoparticles distribution in polymer matrix using broadband dielectric spectroscopy.

The composites based on nylon 6 and polypropylene were investigated. Laminated silicates and multiwall nanotubes were used as filler. Complex dielectric constant $\varepsilon^* = \varepsilon' - \varepsilon''$ in the frequency range $10^{-4} – 10^{7}$ Hz was measured using BDS40 (Novocontrol). These data were expanded by the measurements of ε* in frequency range 3-40 GHz using panoramic standing-wave factor gauges and in optical region using spectral ellipsometer "Elf".

It was shown that the most prospective methods to control the uniformity of conductive nanoparticles distribution in polymer are the next:

a) measurement of slope angle (α) of increasing part on frequency dependence of alternating current conductivity $\sigma_{ac}(f)$ in log-log coordinates. The value of tgα is different for the cases of samples with uniform and non uniform distribution of filler in polymer matrix. Furthermore distortion of form of σ_{ac} spectra can be observed in the last case.

b) measurement of dispersion of local electrical properties in microwave region over the entire sample.

Mapping of optical properties of the sample surface is prospective for the determination of local filler concentration scattering for the composites based on laminated silicates. The diameter of light beam was about 200 μm. This diameter is enough to introduce a concept of local optical properties and local concentration of laminated silicates particles. Precision of measurements of optical properties using spectral ellipsometer is sufficient to analyze scattering of local filler concentration.

Temperature dependencies of **ε*** in microwave region were measured for the composites nylon 6 + laminated silicates. The temperature changes from 20 to 190^{0}C. It was shown that ε' of composites increase with the temperature especially at $T > 100$ °C. The dielectric losses remains practically constant. This increase of ε' results in variation of reflection coefficient of electromagnetic waves from the composites surface. These results show that one can carry out remote control of the surface temperature of nanocomposites by means of millimeter waves. The control is possible even through a flame.

High Pressure Segmental Dynamics in Polymer/Plasticizer Binary Mixtures

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Plasticizers are usually added to polymers to give them the desired flexibility and processability by changing the dynamical properties of the polymer chains. Plasticizers work by embedding themselves between the chains of polymer, increasing the free volume, and thus significantly lowering the glass transition temperature of the polymer. It is therefore very important to have an appropriated framework to give a quantitative description about how the dynamic behaviour of a given polymer is modified by the incorporation of a second component. We present in this work an Adam-Gibbs (AG) based model, combined with the concept of the self concentration, to describe the temperature-pressure dependence of the component segmental dynamics in miscible binary mixtures at any concentration. In order to test the model we have analyzed by means of dielectric spectroscopy the component segmental dynamics in different polymer/plasticizer binary mixtures at several concentrations for a wide range of pressure and temperature. In particular we have studied mixtures of poly(*o*-chlorine styrene) (PoClS) with 1,1-´bis-(p-methoxyphenyl)cyclohexane (BMPC) and poly(vinyl acetate) (PVAc) with diethyl phthalate (DEP). We found that the temperature-pressure dependence of the component segmental relaxation time is very well described by the here presented model by means of only one fitting parameter once the neat components are fully characterized. The good agreement between calculated and experimental relaxation times shows the plausibility of the model. We also analyze in this work the pressure dependence of the glass transition as well as the fragility of the polymers at different concentrations.

Dynamical properties of trans-Poly(isoprene) and its copolymers with styrene

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Poly(isoprene) (PI) has been the subject of extensive experimental investigation by using different techniques such as dielectric and mechanical spectroscopy, nuclear magnetic resonance (NMR), neutron scattering and molecular dynamic simulations. It has also been deeply studied as a component in block copolymers or in polymeric blends. As it can be synthesised with different microstructures (1,4-*cis*, 1,4-*trans* and 3,4 conformations) and molecular weights, it has a wide range of applications from tire to textile industries. However, most of the experimental and theoretical effort was focused on *cis*-PI. Nevertheless, in spite of the fact that 1,4-*trans* poly(isoprene) is included in several formulations of industrial materials, to our knowledge, there are not yet extensively experimental measurements on the *trans* conformer.

In this work, dielectric spectroscopy measurements were performed on trans-poly(isoprene) and trans-isoprene-styrene copolymers in a wide range of temperature ~Tg-70K to Tg + 130K and frequencies (10-2 to 106 Hz). For the homopolymer (avoiding crystallization by quenching) three dielectric processes (global chain motions, segmental and local relaxations) were observed in order of decreasing temperature. Both the segmental and local relaxations of the here studied trans-PI, were found to be markedly different compared with the corresponding process in cis-PI. In contrast the temperature dependence of the relaxation times related to the normal mode was independent of the chain conformation but its intensity is one order of magnitude lower in trans-PI indicating a lower dipole moment in trans- configuration. Finally, we will analyse the dynamic of copolymers of trans-isoprene and styrene recent developed [1] with different styrene contents. For the copolymers, no crystallization on cooling was observed and, as in the case of the homopolymers, three dielectric processes were founded.

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Charge Transport of Conjugated Polymer Coated Core-Shell Nanoparticles

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Conjugated polymer[1] coated latex particles have found intense interest since they have first been reported in 1987.[2] A conventional nonconducting core polymer renders the composite film-forming ability and the formed film transparency and flexibility, while a thin conjugated polymer shell is required to obtain particles with useful electrical features. We have synthesized redispersible polypyrrole (PPy) core-shell nanoparticles with a nonconductive polymer core and a polystyrene sulfonate (PSS) shell loaded with PPy and investigated their application as hole injection layers in PLEDs.[3] I-V-L plots of the PLED device reveals comparable performance with the one from the Poly(3,4-ethylenedioxythiophene) PEDOT/PSS. As such, conjugated polymer coated core-shell nanoparticles could be a promising candidate for printable electronics.

Morphology and charge transport of the PPy embedded in our core-shell nanoparticles are of paramount importance to understand and improve the performances of devices based on our core shell nanoparticles. Therefore, we characterized our newly synthesized redispersible polypyrrole core shell nanoparticles in terms of charge transport, using mainly broadband dielectric spectroscopy.[4,5] Using temperature-frequency-voltage dependent conductivity data we experimentally proved different charge transport mechanisms i.e. hopping and fluctuation-induced tunneling mechanisms[6] in the core shell nanoparticles. Furthermore, electrode and interfacial polarization processes were observed. The results were compared with data based on the corresponding bulk counterparts. Complementary experimental techniques have been used in order to study and understand the relationship between morphology and charge transport.

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Orientational and phase change dynamics of 4-iodo-4'- studied by broadband dielectric spectroscopy

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Noncentrosymmetric polar organic materials play an important role in pyroelectric thermosensing and other applications emerging [1]. However, the presence of possible phase transitions and relaxation effects [2] in the crystalline state prove crucial to the applicability of such materials for technological use. Thus, molecular dynamic studies are an important means to gain knowledge on relaxations and the existence of possible phase transitions in a material. In this work, the molecular dynamics of polar 4-iodo-4'-nitrobiphenyl (INBP) (P2/c and Fdd2 symmetry [3]) studied by broadband dielectric spectroscopy (BDS) is presented. The material was investigated in the frequency range from 0.1 Hz to 10 MHz and at temperatures between 150 K and 450 K. In the entire temperature range, only one dielectrically active process was observed. At freezing temperatures, the process can well be described by an Arrhenius-type dependence of the relaxation time and a rather low activation energy of 13.6 kJ/mol. With increasing temperature, the Arrhenius-type dynamics merges into a Vogel-Fulcher-Tamman (VFT)-type glass transition dynamics. The dielectric results are discussed in the context of a possible presence of a phase transition(s), being supported by X-ray and crystallographic studies [4].

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Dielectric relaxation of Polyethyleneoxide in porous alumina

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Under ordinary conditions (below 340K) Polyethyleneoxide (PEO) is a semicrystalline polymer which due to its simple structure is very difficult to obtain in a fully amorphous state. As a consequence, and in spite of its numerous applications and significance among polymers, the characterisation of the molecular motions of glassy PEO is not complete.

As in most cases the crystalline phase of polymers is regarded as immobile, the dielectric response of semicrystalline polymers has frequently been used for the characterisation of molecular relaxations in the amorphous phase. The study of the dielectric relaxation of semicrystalline polymers, however, is often challenging due to several reasons. On the one hand, a high degree of crystallinity implies low fraction of amorphous phase, and therefore, low amplitude for the signal of interest. On the other hand, the existence of multiple crystallite-amorphous phase boundaries favours the occurrence of charge polarisation effects, which often hide relaxation processes. Finally, it is possible that some dielectric relaxation within the crystalline phase also contribute to the overall signal observed.

In particular, in the case of PEO the charge polarisation contribution is very high and overlaps other underlying dipolar reorientational processes, which make difficult a proper and isolated observation of the segmental α-relaxation of amorphous PEO. In the present work we show a route to overcome some of these drawbacks, namely, by introducing PEO into pore-structured (20 to 100 nm diameter) alumina matrixes. At these pore sizes no "confinement" effects are expected on the dynamical behaviour of the α-relaxation of PEO, but there are apparent changes in the crystallization (growth, fraction, size and shape of crystallites) and charge transport behaviour.

Dielectric properties of oxides coated fabrics for advanced shielding materials

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Increasing number electromagnetic radiations (EMR) of wide frequency range cause electromagnetic compatibility and radioecology problems. This radiation differs from natural electromagnetic background and introduces complex influence on electronic and biological object reactions.

Ability of materials to reflect or absorb electromagnetic radiation energy in given frequency range is used for development of electromagnetic shields and radio wave absorbers that is one of the most effective means for EMR suppression. Modern shields and electromagnetic wave absorbing structures employ different kind of materials from simplest metallic shields to complex composite structures or conductive polymers. Since absorption of electromagnetic energy happens due to magnetic, dielectric and conductive loss the shielding properties are defined by complex dielectric constant, magnetic permeability and conductivity of material that has to be maximized for maximum shielding efficiency.

In this paper the dielectric properties of coated fabrics for shielding materials was investigated.

Space charges in solid electrolytes detected by the scanning Kelvin probe

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Thin films of the ion conducting polymer polyethylene oxide (PEO) show a dielectric behaviour which can be attributed to a space charge polarization of internal mobile charges. With a three-dimensional discrete hopping model, it is possible to describe the dielectric properties of such systems. The mobile charges can fluctuate thermally activated over barriers in a multiwell energy structure. By considering all electrostatic interactions in the system, especially the attracting interactions between the ions and their image charges in the electrodes, it is found that effects at the electrodes play an important role. It has been shown that these electrode effects are responsible for the Kohlrausch behaviour of the polarization current in the long time range as well as for the increase of the dielectric permittivity at low frequencies [1].

The space charge distribution, predicted by simulations with the hopping model, can be determined by measurements of the surface potential with a scanning Kelvin probe contactless. A tip oscillates driven by an electromagnetic system above the sample. The potential difference between the tip and the surface results in influenced charges in the tip giving rise to an alternating current which is measured by a lock-in amplifier. This current vanishes if the surface potential is equal to the tip potential. By adjusting the tip potential with an external voltage source, the surface potential can be determined.

In the steady state a large potential drop is found at the negative electrode due to the existence of space charges (Fig. 1). This potential increase is the steeper the higher the density of ions in the sample is. A comparison of the measurements and the simulations yields negative mobile charges and positive stationary charges. Furthermore, the temporal development of the surface potential after application of a voltage step is observed. It shows that for Al electrodes, which form a thick blocking oxide, charge injection is negligible. However, for Cu electrodes (Fig. 2) the surface potential near the negative electrode has a pronounced maximum in time indicating the build-up of positive intrinsic ionic space charges and subsequent the injection of negative electrons.

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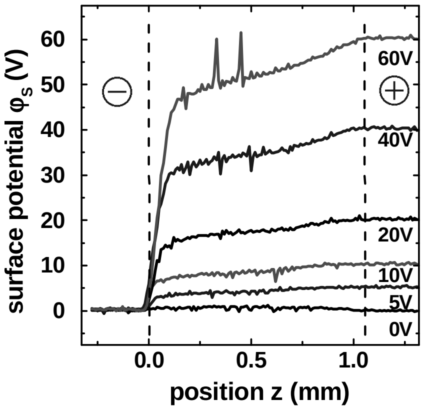

Fig. 1: Surface potential in the steady state (Cu electrodes).

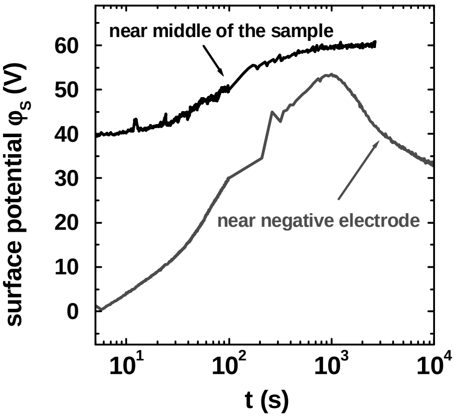

Fig. 2: Temporal development of the surface potential after a voltage step (Cu electrodes).

Analysing dielectric interphases and particle properties in polymer-based nano- and micro-composites

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Charge transport in a composite material containing conductive particles induces polarisation processes at interfaces reflecting the microstructure. In general, its details are unknown and thus an analysis of measured effective properties fails or is subject to large uncertainties. However, according to Bergman's theorem the quasi-static permittivity comprises integral structural information. We show in which cases and how this information can be used to analyze broadband dielectric and/or magnetic spectra of composite materials [1]. Even without any *a priori* knowledge of the microstructure, the properties of the constituents can be determined in an unambiguous way.

We have investigated composites consisting of magnetite particles (Fe_3O_4) in a polymer matrix (an epoxy resin). Especially, we compare systems containing nano-particles (diameters between 20 and 30 nm) and micro-particles (diameters between 0.5 and 5 µm). Temperature-dependent broadband dielectric spectroscopy in a frequency range between 50 Hz and 1 GHz reveals a relaxation process of the polymer matrix. The presence of micro-particles does not affect the permittivity of the matrix, while the dispersion of nano-particles yields a significant change. We discuss the results in terms of modified interactions at the surface of the particles as well as of their surface-to-volume-ratio.

Combining the integral structural information obtained from the dielectric spectra with the results of magnetic spectroscopy (10 MHz - 5 GHz) we are able to evaluate the permeability of the dispersed particles. Once again, micro- and nano-particles show different properties.

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Dielectric properties of ionic liquids

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Broadband dielectric and terahertz spectroscopy (10^{-2} Hz to 10^{+12} Hz) are combined with Pulsed Field Gradient Nuclear Magnetic Resonance (PFG-NMR), Rheology and photon correlation spectroscopy to explore charge transport and translational diffusion in selected ionic liquids. The dielectric spectra are interpreted as superposition of high-frequency relaxation processes associated with dipolar librations and a conductivity contribution. The latter originates from hopping of charge carriers on a random spatially varying potential landscape and fits quantitatively the observed frequency and temperature-dependence of the spectra. A further analysis delivers the hopping rate and enables one to deduce – using the Einstein-Smoluchowski equation – the translational diffusion coefficient of the charge carriers in quantitative agreement with PFG-NMR measurements. By that, the mobility is determined and separated from the charge carrier density; for the former a Vogel-Fulcher-Tammann (VFT) and for the latter an Arrhenius temperature dependence is obtained. There is no indication of a mode arising from the reorientation of stable ion pairs.

Dielectric relaxation in microemulsions with and without triblock copolymer

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Water-in-oil microemulsions are thermodynamically stable mixtures of water droplets in a continuous oil phase. The droplets are stabilized by a monomolecular surfactant layer. The surfactant molecules have a polar, hydrophilic head group and an apolar, lipophilic tail. The investigated microemulsion consists of water and decane with sodium bis(2-ethylhexyl)sulfosuccinate (AOT) as surfactant. The structure of this system is well characterized by small-angle-X-ray and small-angle-neutron scattering. The conductivity of such systems shows a steep increase when volume fraction or temperature increase over a certain critical value. This behavior can be understood as dynamic percolation.[1] In the dielectric spectrum of a microemulsion, as a heterogeneous system, an interface polarization, known as Maxwell-Wagner-Sillars, can be observed. In the high frequency regime a relaxation can be observed, which is attributed to a reorientation of the AOT molecules in the shell.[2]

Adding the amphiphiliic triblock copolymer PEO-PI-PEO to such a microemulsion leads either to decorated micelles or to an interconnection of droplets and thus to a transient network. This depends on polymer chain length and droplet density. Here we will present dielectric spectra and conductivity of pure and polymer containing microemulsions. We performed frequency and temperature dependent measurements in a range of -20°C to 50°C and 10^{-1} Hz to 10^{9} Hz respectively. First we measured the percolation temperature and dielectric spectra of microemulsions without polymer at different droplet sizes. Then we investigated the influence of increasing polymer content on the percolation transition and the dielectric spectrum of a microemulsion with fixed droplet size.

As result we see an increase in percolation temperature with decreasing droplet size or increasing polymer content. Furthermore we observe a relaxation in the high frequency regime. Its relaxation time increases with decreasing droplet size. In the microemulsion with polymer we observe an additional relaxation in the low frequency regime with increasing relaxation strength on increasing polymer content.

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Surface and disorder efects in aerosil dispersed liquid crystals

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Aerosil nanoparticles are dispersed in liquid crystals to introduce disorder. The particles form a hydrogen bonded network, which interferes with the normal liquid crystalline order. Among other techniques, broadband dielectric spectroscopy has been applied to these systems, and two main differences have been observed [1].

First, a new slow relaxation process has been seen, about 2 decades slower than the bulk rotation around the short axis. Its strength increases with aerosil concentration and it is interpretated as a retarted relaxation due to surface interaction with the aerosil particles [2]. In the particular case of cyanobiphenyl liquid crystals, a hydrogen bond is involved.

Second, an acceleration of the rotation around the short molecular axis is seen both in the ordered nematic phase and in the isotropic phase. In both cases, the disordering influence of the aerosil particles is the cause of this acceleration, alhough the exact mechanism is different. In the nematic phase, the liquid crystalline phase becomes divided into domains by the aerosil network. The presence of such domains disturbs the nematic long range orientational order, and the sample appears more isotropic-like. Therefore the relaxation shifts towards the values in the isotropic phase, and for the rotation around the short axis this means an acceleration [3]. In the isotropic phase, however, the acceleration is only observed for the associating cyanobiphenyl molecules: these molecules have a strong terminal dipole moment, and form dynamically antiparallel dimers. The aerosil particles disturb the normal dimer formation. The molecules then have to overcome less interaction and can rotate faster, thus resulting in a faster relaxation process in the isotropic phase [4].

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Conductivity and glass transition dynamics in imidazolium ionic liquids

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Ionic liquids are organic salts with a melting point below 100°C, which have a high potential for industrial applications in electrochemistry and catalysis, due to their intrinsic electrical conductivity and their wide tunability of chemical properties. Apart from this, many of them can easily be supercooled and form glasses. We have applied dielectric spectroscopy in the frequency range from 10^{-2} to 10^{7} Hz over a broad temperature range to several series of ionic liquids based on the imidazolium cation. From these data, conductivity values were extracted and their temperature dependence has been analyzed on the basis of the VFT equation.

Here we present results from a series of alkyl-methylimidazolium tetrafluoroborate ionic liquids, which are characterized by a variable length of the cationic alkyl chain beween 2 and 11 carbon atoms. For short and medium chain lengths, an increasing glass transition temperature and a decreasing fragility, upon increasing chain length was revealed, while the long chain length molecules of the series tend to crystallize before vitrifying. Apart from this, the Vogel temperature is was found to be nearly for this series.

In a second study, the effects of different anions on the thermophysical properties of ionic liquids have been studied. Here the change of the interaction between anion and cation is very important: we can, on the basis of fragility values, distinguish two classes of ionic liquids. Lower fragility values indicate ionic liquids in which the interaction between cation and anion is mainly Coulombic, whereas higher fragility values are observed for ionic liquids with an extra hydrogen bond interaction or smaller anion size.

A dielectric study near the critical point of the binary liquid mixture nitrobenzene-tetradecane: temperature and concentration dependence of the dielectric constant

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We report on detailed results for the dielectric contant ε near the critical point (T_c) of the binary mixture nitrobenzene–tetradecane. Measurements have been carried out as a function of temperature T for the critical concentration x_c and several other near-critical concentrations. Values of ε were obtained from the measurements of the capacitance of two capacitors at a different height in the cell containing the mixture as described elsewhere [1]. This setup allows simultaneous measurements in the coexisting phases in the two-phase region (below T_c). Capacitance readings were obtained with a HP 4284A LCR meter in the frequency range between 100 Hz and 100 kHz.

Because of the non-zero electric conductivity a (low-frequency) Maxwell-Wagner (MW) dispersion effect was observed near the consolute point; this fluctuation induced phenomenon is well studied and can be described in terms of a droplet model [2,3]. Static ε values are obtained for frequencies well above the (low frequency) MW relaxation frequency.

Analysis of the static data in the homogeneous phase above T_c reveals an intrinsic critical contribution consistent with a power law in $t = |T\text{-}T_c|/T_c$ with a critical exponent $\theta = 1 - \alpha_I$, with $\alpha_I = 0.109$ the Ising value for the heat capacity divergence. From the difference of ε in the two coexisting phases a critical exponent β consistent with the Ising value $\beta_I = 0.326$ is derived. The average of ε of the two phases, shows curvature arising from a critical contribution with an exponent 2β. This is not consistent with standard scaling theory of binary mixtures in the presence of an external electric field [4] but can be accounted for by properly extending the recently developed “complete scaling” formulation of asymmetric criticality [5,6]. Additional measurements on the possible influence of impurities are in progress and will be reported as well.

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Using Impedance Spectroscopy to Monitor the Regeneration of Newt Tails

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Newts can regenerate their limbs; people can't. In recent years considerable interest has developed regarding what factors control this regeneration with the goal of improving wound healing, or perhaps eventually developing some form of limb regeneration, in mammals. One of the first steps in this process is to monitor newt tail regeneration as various potential control factors, such as retinoic acid or n(ewt)AG protein, are added. A noninvasive method which would allow continual monitoring during the entire regeneration process would be very useful. We have examined the use of impedance spectroscopy for such monitoring and found that it has considerable potential. Using a Solartron 1260 Impedance Analyzer between 1 Hz and 10 MHz, we measured the variation of impedance spectra with needle electrode separation and determined that the tail can be modeled electrically as a series combination of two parallel CPE/R elements and another resistor that accounts for dispersions above 10 MHz. We measured the impedance spectra and the dimensions of the regenerating tail for nine newts at weekly intervals for up to 105 days. The conductivities associated with one CPE/R term and the high-frequency term showed a definite increase during the stage when differentiation was beginning in the tail and then levelled off. The other CPE/R term exhibited considerable variability. We conclude that the onset of differentiation might be identified with minimal invasiveness using impedance spectroscopy.

Dielectric relaxation spectroscopy of aqueous amino acid solutions

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Proteins are made of amino acids arranged in a linear chain and joined together by peptide bonds being amino acids the building blocks of proteins. They play a central role in metabolism, i.e. the set of chemical reactions that occur in living organisms in order to maintain life. Amino acids contain at least and amino group (-NH_2), a carboxylic group (-COOH) and differing only in the structure of the R-group or the side chain. Its ionization state depends on the pH. At neutral pH the stable structure is the zwitterion ($^{+}H_3N$-CHR-COO^{-}).

Zwitterionic solutions play an important role in aqueous mixtures being a main topic in biology. Thus, the study of the amino acid hydration at different pH could be a new route to understand the major problem of protein hydration.

The aim of this study is to investigate the dielectric response on aqueous solution of several amino acids in both a wide range of concentrations and pH values (from 1 to 11). For most of the systems analyzed, two relaxation processes were observed in the frequency range of $5x10^{8}$ to $5x10^{10}$ Hz. The fastest one can be attributed to the reorientation of water molecules in the mixture whereas the slowest one is related to the amino acid in the solutions. In this work we will discuss the variation of the shape parameters of the observed relaxations with the amino acid type, concentration and pH values.

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Entropy and Entropy Production in Dielectric and Magnetic Relaxation

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It is shown that many electromagnetic metrology areas can be formulated using entropy production. Many high-frequency electromagnetic measurements are based on the relationships between dissipation and fluctuations. In nanotechnology an understanding of fluctuations of thermal and electromagnetic energy and the effects of nonequilibrium are particularly important. The approach used here is based on a derivation of an entropy evolution equation using an exact reversible Liouville-based statistical-mechanical theory. In this paper we develop an exact equation for entropy rate in terms of time correlations of the microscopic entropy production. This equation is an exact fluctuation-dissipation relation. We then define the entropy and its production in electromagnetic driving, both in the time and frequency domains, and apply this equation to dielectric and magnetic material measurements, cavity resonance, noise, and power. We apply this equation to study entropy fluctuation-dissipation equations for dielectric and magnetic susceptibilities, impedance and resonant systems, and Johnson-Nyquist noise. We relate entropy production to cavity resonance and relaxation loss peaks and derive a relation for the positivity of the permittivity loss factor.

Dynamics of protein-solvent systems in hard confinement studied by Broadband Dielectric Spectroscopy and Neutron Scattering

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Biochemical studies performed in the last years on protein activity in the intracellular environment made the biophysical community aware that molecular *crowding* and molecular *geometrical confinement* could be extremely relevant factors in the comprehension of the relationship among dynamics, structure and function of proteins in their *real* biological environment. In this work we investigated an essential aspect of this complex scenario: the role of confinement in restricted geometries and the influence of solid surfaces on the dynamics of globular proteins and of surrounding solvent. We have chosen an experimental approach suitable to obtain, through the sol-gel technique, solid matrixes of silica where both protein and solvent were confined within nanometric cavities.

A description of dynamical effects at different space and time scales has been achieved by using two different experimental techniques: broadband dielectric spectroscopy (in the 10^{-2}-10^{7} Hz range) and neutron scattering. In order to highlight the specific effect of confinement in the silica matrix, a comparison with another confined system has been performed: Myoglobin (Mb, the oxygen storer in the tissues) encapsulated inside a silica gel at different hydrations $h \equiv [gr\ water]/[gr\ Mb]$ has been compared with Mb hydrated powders (where proteins are confined by other proteins), at the same h values.

Data reported in this work propose a scenario of the effects of hard confinement on the dynamics of both protein and hydration water. Protein-water systems in *hard* confinement exhibit a clear perturbation in the relaxation properties of water (as showed by dielectric spectroscopy and quasi-elastic neutron scattering), and a relevant reduction of average local dynamics (as suggested by the reduction of mean square displacements measured by elastic neutron scattering). Anyway, it's very interesting that even in these *extremely confined* conditions, protein dynamics at high temperature (i.e. above the solvent dependent *dynamical transition*) is sizeably dependent on the hydration level, as it has been shown in this work for the first time. Moreover, the effect of confinement is at his maximum when the hydration corresponds to a complete first shell of water molecules on protein surface, thus evidencing the importance of the so called *biological water*.

The reported data can be explained in terms of protein-solvent coupling and of water dynamics in confinement. The results suggest that the confinement effect is related to a perturbation of solvent collective dynamics (α-relaxation) due to the restricted geometry, rather than to direct protein-matrix interactions. This is clearly evidenced by dielectric spectroscopy measurements which give a direct picture of relaxation dynamics nature: super-Arrhenius relaxations observed in Mb powders are not present in Mb encapsulated in silica gel.

Structural, Dynamic and Thermodynamic Changes in Properties of Polymer Glasses Subjected to Plastic Deformation

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Plastic deformation seriously changes structure and many properties of solids. In this work we studied structural, dynamic and thermodynamic property changes in several polymeric glasses, PC, PMMA, PS, Epoxy and several others. We deformed the polymers glasses and measure their dielectric, dynamic mechanical and thermodynamic (expended mechanical work W, deformation heat Q and the stored energy of cold work ΔU) properties. It was found that large fraction of W is transformed upon deformation into internal energy changes ΔU stored by glass. The excited state of glasses is saturated by localized shear transformations (deformation defects) carrying local strains ε_{def}^{loc} and the energy excess ΔU^{loc}. Scale and properties of the transformations were visualized and analyzed by molecular dynamic computer simulations. Experimental measurements of complex dielectric response of deformed glasses by BDS technique in frequency range $f=10^{-5} - 10^{6}$ Hz was performed. New structure of the deformed state of glass is gives new dielectric spectrum (ε' and ε" which overlaps with dielectric response of non-deformed sample. Results had shown that the deformed state of glasses shows new dipolar structure which did not existed in a non-deformed state of the materials. Appearance of shear transformations changes dynamic mechanical response of materials also. Comparison of dielectric and dynamic mechanic properties of deformed glasses is performed. Strain component responsible for storage of energy excess in deformed glasses were separated and their kinetic properties were analyzed and discussed. It's shown that new structure of deformed glasses is responsible for well known "rejuvenation phenomenon". Mechanical and thermal treatments produce completely different structures of glass. Mechanical deformation saturates glass by new deformation defects of high energy, but thermal treatment erases the defects and move glass closer to equilibrium structure. Mechanical and thermal treatments never can produce same structure. Kinetics of energy growth of the glasses during deformation is traced. Kinetics of thermally stimulated recovery of shear transformations accumulated by materials upon straining was measured and analyzed. Recovery of dielectric and dynamic mechanical spectra with storage time and thermal treatment was measured and analyzed. Structural picture of deformation defects is presented. Interpretation of mechanical and dielectric data is given in terms of structure of the deformed state of glass.

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Features of Harmonic Spectrum of A_2BX_4 Crystals Related to Domain Wall Dynamics

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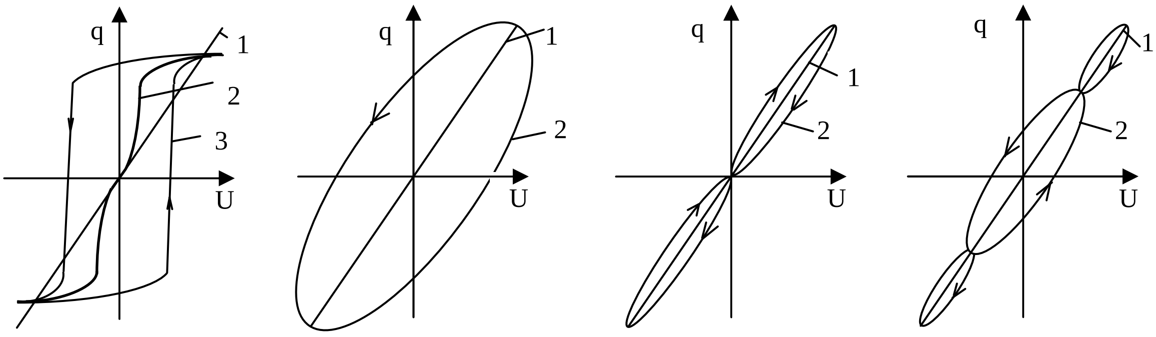
Harmonic analysis is one of the perspective methods that promise to trace basic regularity of domain dynamics [1]. The current harmonic analysis method is used in the abstract to research nonlinear dielectric properties of A_2BX_4 family crystals in view of these properties dynamic changes. The method is placed on amplitudes (I_k) and phases (φ_k) measurements of spectral component of current that flow through the sample if harmonic voltage source U(t) having U_m amplitude and ω_0 frequency is connected ($U(t)=U_m\cos\omega_0 t$). Satisfying Dirichlet conditions periodic function I(t) of current that flow through the sample can be presented by Fourier series:

$$I(t)=\sum_{k=1}^{\infty}(I_k'\sin k\omega_0 t+I_k''\cos k\omega_0 t)\,, \qquad (1)$$

where $I_k'=I_k\sin\varphi_k$ and $I_k''=I_k\cos\varphi_k$.

Voltages proportional to current harmonics (k=5) was impressed to the integrant adder unit. The integrator output was connected to two-coordinate plotter amplifier Y input, the voltage $U(t)=U_m\cos\omega_0 t$ was impressed to amplifier X input. So coulomb-voltage dependences q(U) have been recorded (fig. 1).



a) *b*) *c*) *d*)

Fig. 1. A_2BX_4 family crystals coulomb-voltage dependences q(U) in case of different combinations of current harmonics flowing through the sample

Fig.1, *a* (curve 3) shows the dependence q(U) when all harmonics are presented. Curve 1 (fig.1, *a*, *b*, *c*, *d*) shows the dependence q(U) when only one harmonic $I_1\sin\omega_0 t$ is presented. Curve 2 (fig.1, *a*, *b*, *c*, *d*) shows the dependence q(U) when harmonic combinations $I_1'\sin\omega_0 t+I_3'\sin 3\omega_0 t+I_5'\sin 5\omega_0 t$; $I_1'\sin\omega_0 t+I_1''\cos\omega_0 t$; $I_1'\sin\omega_0 t+I_2'\sin 2\omega_0 t+I_4'\sin 4\omega_0 t$; $I_1'\sin\omega_0 t+I_3''\cos 3\omega_0 t++\ I_5''\cos 5\omega_0 t$ are presented correspondingly.

The obtained data are explained in terms of different polarization mechanism and dissipations which are concerned with interactions of domain boundaries and defects and are evidence of use availability of current harmonic analysis as indirect fine method of domain boundaries changing process in defects field research.

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High-frequency Broadband Dielectric Spectroscopy on Sugar Alcohols below Tg

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Dielectric dispersion of supercooled liquid shows a dielectric loss minimum in the frequency range between low frequency relaxation peaks and boson peak. It is pointed out that the value of loss minimum is larger than that expected from the peaks. Fast-beta process and NCL (Nearly Constant Loss) are suggested to explain such excess loss [1]. However, since the loss becomes so small as temperature decreases, the behavior of the minimum below glass transition temperature (Tg) has not been investigated sufficiently.

We have investigated the high-frequency flank of the J-G beta process of some sugar alcohols in the frequency range 10^1~10^6 Hz at temperatures below Tg [2]. However, such frequency range is not high enough to avoid the contribution of the J-G beta process to the range of dielectric loss minimum.

In this study, we examine the complex permittivity of some sugar alcohols, sorbitol, xilitol and glycerol, in the frequency range upto 10^{10}Hz at temperatures 130K~ 300K to reveal the behavior of low frequency slope of the minimum. The behavior of the slope for below Tg will be discussed.

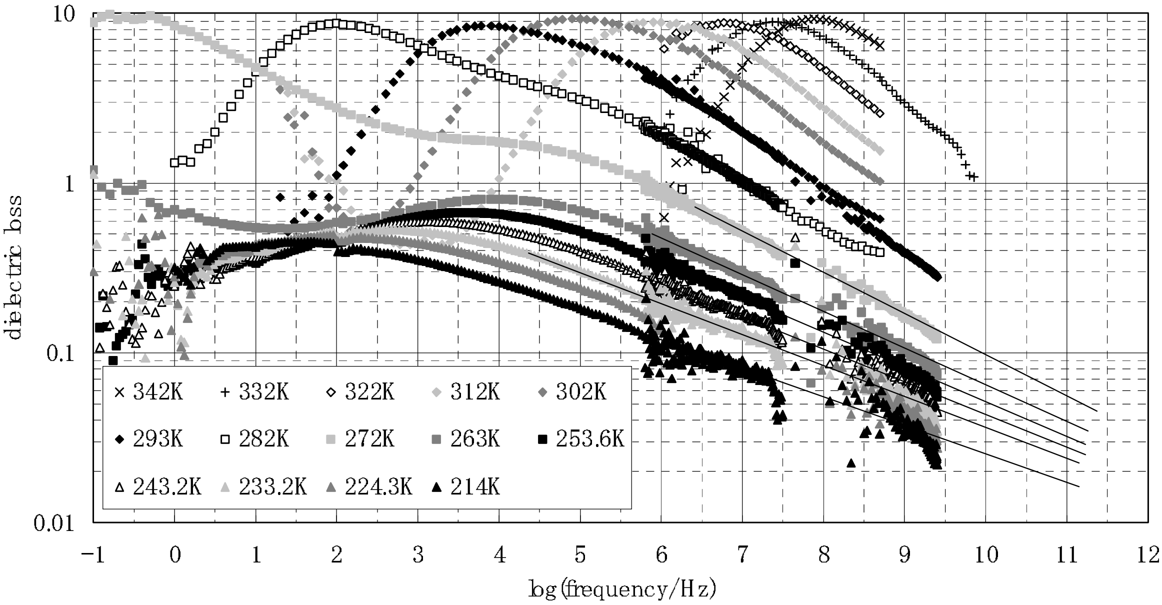

Figure 1. Example of dielectric loss of sorbitol.

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Revisiting the molecular weight effects on dielectric relaxations of linear cis-polyisoprene 1,4

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The dielectric relaxation of cis-Polyisoprene 1,4 [PI] is sensitive not only to the local and segmental dynamics but also to the larger scale chain (end-to-end) fluctuations. We have performed a careful dielectric investigation on linear PI with various molecular weights in the range of 1000 to 76000 g/mol. The broadband dielectric spectra of all the samples were measured around 250 K to get both the alpha and normal mode relaxation peaks inside the accessible frequency window in the same isothermal measurement. In this way we are able to observe simultaneously the effect of molecular mass on the segmental dynamics and on the end-to-end relaxation time of PI. Furthermore, simultaneous dielectric and rheological experiments has been performed. The main result of our analysis is that we have decoupled the direct effect of molecular mass on the normal mode from that due to the effect on the monomeric friction coefficient. Namely, the normal mode relaxation time has been scaled with the alpha relaxation time. Based on this analysis we find a crossover around a molecular weight of $M_c=4850\pm150$ *g/mol*. This value has been obtained by direct fitting of the data with the following equation: *constant* for $M < M_c$ and $\propto M^x$ for $M > M_c$. Furthermore, this fitting provides a power law with exponent *3.32±0.02* for the dependence on the molecular mass of the end-to-end fluctuations in the entanglement regime. These values are significantly different from those reported by Adachi *et al* [1] and Kremer *et al* [2] (crossover molecular weight ~ *10000 g/mol* and power law in the entangled regime with exponent ~ *3.7*). We have verified that our raw data were consistent with those reported by these authors. Nevertheless, our data are significantly more accurate, in part due to improvement in the performance of the modern dielectric equipment. In particular, it should be noted that all the data have been collected on the same dielectric cell following the same protocol in order to minimize the possible difference between nominal and actual sample temperature. Moreover, the scaled normal mode time results rather insensitive to any small difference among the temperature of the experiments corresponding to the different samples. These dielectric results will be discussed in regards of the rheological properties and the current theoretical approaches.

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Dynamics Of An Ionic Liquid Supercooled With Pressure

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Ionic liquids are a relatively new class of chemicals which consist only of anions and cations, and that remain liquid down to unusually low temperatures, even below room temperature. Some ionic liquids can be supercooled, showing similar properties as conventional glass formers, like the presence of secondary relaxations, despite presenting Coulomb interactions in addition to Van der Waals and H-bonds [1,2]. We investigate here the supercooling process with pressure in the ionic liquid 1-butyl-1-methylpyrrolidinium bis[oxalate]borate (BMP-BOB) by dielectric spectroscopy in the temperature range 123 – 300 K and varying pressures from 0.1 MPa up to 0.5 GPa. We find the BMP-BOB presents a secondary relaxation and undergoes a glass transition when applying pressure. The relaxation time of the primary relaxation τ_α strongly increases with applied pressure whereas that of the secondary relaxation is almost insensitive to pressure [3]. Thus, elevated pressure separates the secondary relaxation and suggest the appearance of an excess wing on the high frequency flank of the primary relaxation. Interestingly, the spectral shape of the main relaxation broadens with increasing pressure or decreasing temperature, but is found to be the same when the relaxation time is fixed, independently of the particular pressure and temperature conditions [4,5]. The pressure dependence of the glass transition temperature and the isobaric fragility show also similarities with non-ionic glass-formers [3,4].

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Scaling Behaviour in Dielectric Relaxation of Poly(dimethyldiallylammonium chloride) in Dilute and Semidilute Solutions

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Dielectric measurements were carried out on Poly(dimethyldiallylammonium chloride) aqueous solutions without added salts with different mass fractions in the frequency range from 40 Hz to 110 MHz. Two relaxations namely low frequency (10-100 kHz) and high frequency (1-10MHz) were found and their dielectric parameters presented some interested scaling behaviour. First of all, crossover concentration between dilute and semidilute region was observed in scaling behaviour of relaxation time and relaxation amplitude. Additional, scaling behaviour of polymer concentration dependences of relaxation time and relaxation amplitude of low frequency relaxation were shown in the figure and of high frequency relaxation were summarized as: $\tau_h \sim c^{-2/3}$, $\triangle\varepsilon_h \sim c^{1/3}$ below crossover concentration, $\tau_h \sim c^{-1}$, $\triangle\varepsilon_h \sim c^{0}$ above crossover concentration.

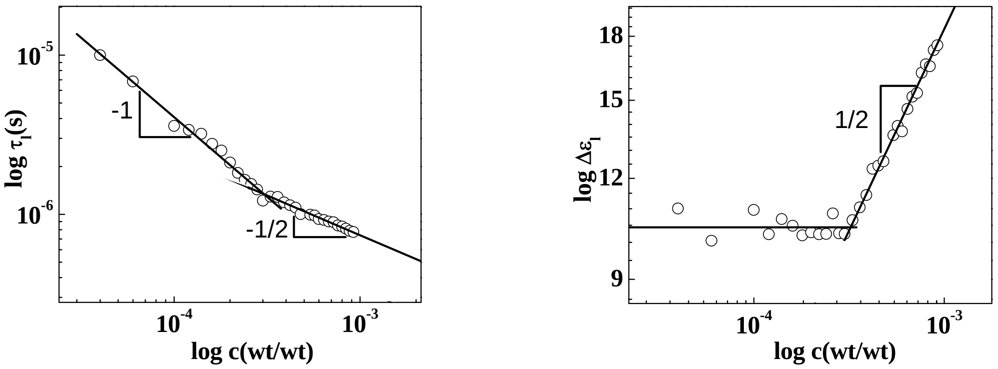

Figure: Scaling behaviour of polymer concentration dependences of relaxation time and relaxation amplitude of low frequency relaxation

Finally, the scaling behaviour was analysed in the light of the scaling approach which recently, in aspect of broadband dielectric relaxation, summarized by Bordi [Bordi F, Cametti C and Colby R H, Journal of physics: condensed matter, 2004, 16, R1423]: although the theory can explain the observed dielectric parameter of high frequency relaxation, the dielectric parameter of low frequency relaxation can not. Nevertheless, the theory can remain explain the observed dielectric parameter of low frequency relaxation if we suppose that it originated from polarization of the condensed counterions along a entire chain of polyions which slightly curved and the dependence of polymer concentration of its length was $L_c \sim c^{-1/2}$ in the dilute region and transitioned to end-to-ed length distance in the semidilute region instead of an entire polyelectrolyte chain which didn't curved neither in the dilute region nor in the semidilute region, this can be supported by the scaling behaviour of both relaxation time and dielectric amplitude and the conformity of the scaling behaviour of them, this suppose could better demonstrated the changing process of polyelectrolyte chain when the polymer concentration gradually changed.

Generalization of the Ryabov-Feldman formula : the case of cylindrical symmetry

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It is known that Ryabov-Feldman formula connecting the characteristic relaxation time with power-law exponent is applicable for self-similar systems with spherical symmetry [1]. In paper [2] this formula has been generalized for the case of anomalous diffusion processes but the basic supposition about the spherical geometry of a cluster was conserved

$$\alpha = \frac{\theta d_G}{2} \cdot \frac{\ln(\tau/\tau_s)}{\ln(\tau/\tau_0)}, \tag{1}$$

where α is the Cole-Cole exponent, d_G is the fractal dimension, τ is the relaxation time, τ_s is the characteristic time of the diffusion process, τ_0 is the cutoff time of the scaling in time, the exponent $\theta = 1$ corresponds to normal diffusion process, for $\theta > 1$ we obtain superdiffusion and for $\theta < 1$ subdiffusion processes, correspondingly.

Here we want to show how to generalize expression (1) for the clusters having cylindrical symmetry. It is obvious that many films have this type of symmetry and ordinary Ryabov-Feldman formula is not working properly. The generalization is related to consideration of a self-similar sum of the type

$$S(z) = \sum_{n_1}\sum_{n_2} b_1^{n_1} b_2^{n_2} f\left(z\xi_1^{n_1}\xi_2^{n_2}\right), \tag{2}$$

where $S(z)$ is the Laplace image of the memory function, $z = j\omega\tau_0$ is the modified Laplace parameter, b_i and ξ_i are dimensionless parameters which determine the structure and dynamics of the fractal media considered, respectively. It becomes possible to prove that this sum satisfies to the following exact functional equation

$$b_1 b_2 \cdot S(z\xi_1\xi_2) = b_1 S(z\xi_1) + b_2 S(z\xi_2) - S(z) + C, \tag{3}$$

where C is a constant having rather cumbersome form and it is not given here. The further investigations show that this sum can be presented in the form of couple power-law exponents

$$S(z) = z^{-\nu_1}\pi_1(\ln(z)) + z^{-\nu_2}\pi_2(\ln(z)) + C/(b_1 - 1)(b_2 - 1), \tag{4}$$

where $\nu_1 = \ln(b_1)/\ln(\xi_1), \nu_2 = \ln(b_2)/\ln(\xi_2)$, $\pi_1(\ln(z))$ and $\pi_2(\ln(z))$ are complex doubly log-periodic functions with real periods $\ln(\xi_1)$ and $\ln(\xi_2)$.

Finally, it was found that expression (1) kept its form but the characteristic parameters should be replaced as $\tau \to \tau_{eff} = \left(\tau_1^{d_1}\tau_2^{d_2}\right)^{\frac{1}{d_G}}$, $\tau_s \to \tau_s^{eff} = \left(\tau_{s1}^{d_1}\tau_{s2}^{d_2}\right)^{\frac{1}{d_G}}$, where d_1 and d_2, ϕ_1 and ϕ_2, ϕ_{s1} and ϕ_{s2} are corresponding fractal dimensions, relaxation times and characteristic times of the diffusion process along the radius and along the axis of the cylinder, respectively. Application of this generalization is now discussed and compared numerically.

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Influence of solvent on the network structure formed by free radical polymerization of triethyleneglycol dimethacrylate: a dielectric study

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Molecular mobility of a series of tri-ethylene glycol dimethacrylate (TrEGDMA) samples polymerized with different amounts of ethyl acetate as diluent was investigated by dielectric relaxation spectroscopy. Samples with 0, 10, 20, 30 and 40% by weight of solvent were prepared. Two series of isothermal dielectric spectra between -120°C to 200°C were collected in the frequency range 10^{-1} to 10^{6} Hz.

In the first measuring scan, in which the sample is heated up to 200°C, the samples show three relaxation processes: the γ process related to the twisting motions within the ethylene glycol moiety, the β process assigned to hindered rotations of carboxylic groups residing in non-bonded ends of the monomers linked to the network only by one side of the molecule, the β-pol process at higher temperatures, ascribed to rotations of carboxylic groups bonded to the main chains; the main relaxation process of the polymer network was not observed in this highly cross-linked system [1-2].

During the first measuring scan post-polymerization takes place consuming the remaining double bonds. Two relaxation processes are shown in the second measuring scan: the γ process and the β-pol process; the β process is not present. This behaviour is related with the complete polymerization of the network, the γ process is not affected and the β process goes to extinction upon polymerization because the mobility associated with the rotation of the carboxylic should be more affected by polymerization than local twisting motion in the ethylene groups [1].

The strength of β relaxation measured in the first scan increases with the amount of solvent present in the initial polymerization process, although only small changes, if any, of the form parameters of β and γ relaxation, as characterized by Havriliak-Negami function, were found. Nevertheless, in any case β relaxation completely disappears in the second scan. Thus, the strength of β process appears as an interesting parameter to characterize the influence of the reaction conditions on the structure of the polymer network formed by isothermal free radical polymerization.

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Differential Thermostimulated discharge current method for studying of electrets

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The thermally stimulated discharged current method is widely used for the study of charge storage mechanisms in electrets [1]. A new discharge technique, called "differential" which consist in discharging the charged sample through an otherwise identical but uncharged one has been proposed by J.-P. Reboul and A Toureille [2].

In the present paper a new version of a differential thermally stimulated discharged current method is advanced. The designed measuring cell consists of two sets "electrode-sample-electrode" set up apart. In this way the heating of the samples is more uniform. The temperature differences between various points of the measuring cell at heating rate of 1.95 K/min do not exceed 0.6K.

The measuring cell enables one to perform various experiments.

- The measuring cell allows to charge one of the samples and to subject the other sample to the same thermal treatment.
- The measuring cell allows performing an experiment which is analogous to the described in [2] (as in the case of samples which are connected in series).
- In contrast to the differential technique described in [2], the measuring cell allows to realize typical differential techniques (as in the case of samples which are connected in parallel). In this case the measuring system records the difference of the thermally stimulated currents of two samples which were preliminary charged (or thermal treated) under different conditions.

Samples of 20μm thick polypropylene were used to demonstrate operation of the developed differential TDC method.

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Influence of low pressure on electrets behaviour at various air gaps

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In the present paper samples of 20μm thick PP films were studied. The films were initially cleaned in an ultrasonic bath with alcohol. From the clean film 30mm diameter samples were cut. All the samples were put on the same diameter metal pads. The charging of the samples was carried out by means of a conventional corona triode.

The voltage of the corona electrode was U_c=-5kV and the voltages of the grid were 350V, 500V, 650V, 800V and 950V. After charging the initial surface potential of the electrets was measured using the method of the vibrating electrode with compensation.

The samples together with their metal pads were placed in a vacuum chamber, between two short circuited plate electrodes and stored under various low pressures (0.1–10^3) mbar for 30 minutes. Between the samples and the upper electrode various air gaps were created.

The air gaps were 0.84mm, 1.16mm, 1.69mm and 3.0mm.

The dependences of the surface potential decay on the pressure under which the electrets were stored were obtained.

The results show that:

- For all the values of the initial surface potential V_0 there is a pressure range in which the surface potential sharply decays;
- The sharp decay range is shifted towards the lower pressure values as the air gap increases;
- The voltage in the air gaps at 0.1mbar is reduced to the value bellow the breakdown voltage minimum for each gap according to the Paschen's law.

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Reliability of advanced Cu/Low-k interconnects analyzed by impedance spectroscopy

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The drastic reduction of intra-level dielectric spacing in advanced interconnects involves problems for reliability. Advanced Cu/low-k interconnects are usually composed of amorphous materials whom characterization is made difficult by their weakness against strong charges injection. Non-destructive characterization is necessary to better understand the behavior of the whole structure and obtain a global diagnosis of reliability. Our materials are integrated in comb-comb structures within a complex dielectric stack where dielectric spacing is in this study an important parameter (Figure 1). Comparison between conductivities measured at very low frequencies and those measured in ohmic regime by electric tests (DC current-voltage) present differences (Figure 2). These differences will be discussed by phenomena such as interfacial relaxation and electrodes polarization as identified by dielectric spectroscopy (Novocontrol Alpha-AN) at the low frequencies (figure 3).

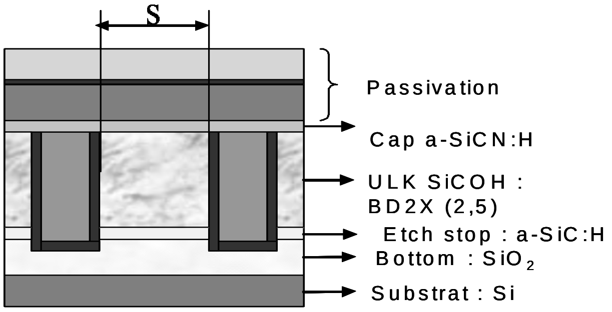

Figure 1: Details of materials of the dielectric stack. The test structures contain only one Cu level.

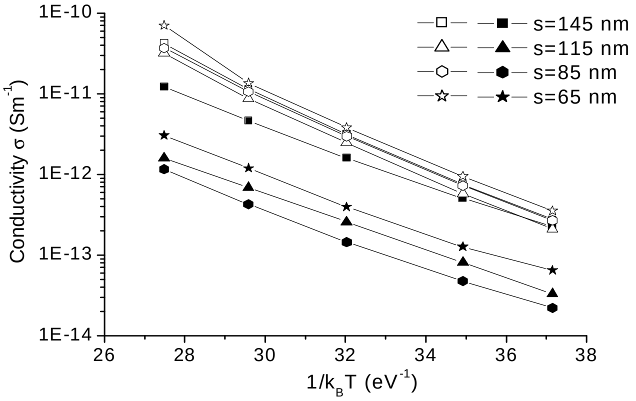

Figure 2: Conductivities against temperature for four dielectric spacings (noted s) measured in ohmic regime by electric tests (open symbols) and at very low frequencies by impedance spectroscopy (closed symbols).

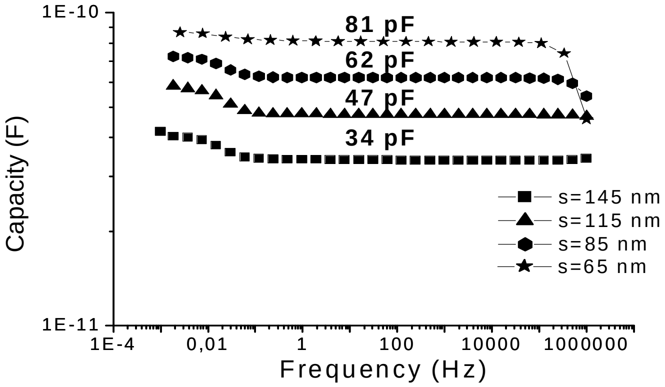

Figure 3: Capacitance against frequency for four dielectric spacings (measure carried out at 120°C)

Characterization of lutetium oxide-based thin-film capacitors by impedance spectroscopy

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Impedance spectroscopy is a very popular technique involved in examination of different dielectric materials. This technique has been applied by us for diagnostic of lutetium oxide-based metal-insulator-metal (MIM) thin-film structures. The measurements have been carried out in frequency domain between 10^{-5}Hz–10^{7}Hz and for temperatures from 300K to 500K with Alpha type Novocontrol Frequency Response Analyser (FRA).

This paper deals with the study of dielectric response of the specimens with a different insulator thickness, from 0.1µm to 0.5µm.

We have shown that the impotent contribution to the total dielectric response comes from (a) the examined dielectric Lu_2O_3 film, (b) near-electrode regions (at the bottom and at the upper M/I boundary) and also from (c) resistance of electrodes and leads. The equivalent electrical circuit model has been proposed to description of dielectric response in wide frequency range. This model contains the following elements: R_e (series resistance of electrodes and leads); R_v, C_v, CPE_v, (resistance, capacitance and constant phase element, which characterize volume the film) and R_b, CPE_b, (resistance and constant phase element, which characterize near-electrode regions). We have determined values of the R_e, R_v, C_v, CPE_v, R_b, CPE_b for different temperatures.

The parameters: Q_v, Q_b ,n_v and n_b in the admittance equations for the CPEs:

$$Y_{CPE-V}(\omega) = Q_V \cdot (j \cdot \omega)^{n_V} \qquad Y_{CPE-B}(\omega) = Q_B \cdot (j \cdot \omega)^{n_B}$$

have been determined and discussed. We have shown that the resistances of the interior and near-electrode regions were thermally activated according to Arrhenius relations.

Dielectric Relaxation of Polymer/Carbon Dioxide Systems

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1. Introduction Pressurized carbon dioxide, CO_2 has been widely used for polymer processing because the dissolution of CO_2 provides the lower glass transition temperature and good processability. However, the effect of CO_2 dissolution on polymer chain dynamics has not been well established. In the present study, we investigate dielectric segmental mode of polymer chain under pressurized CO_2. For the case of ordinary solvents, the segmental motion is broadened with dissolution of solvents through the concentration fluctuations. We show that for the case of CO_2, the broadening of segmental motions is quite small.

2. Experiment Poly(*d*,*l*-lactic acid), PLA was used as dielectrically active polymers. Isothermal dielectric measurements were performed with a home-made autoclave at various CO_2 pressure, p_{CO2}. Details of dielectric cell and autoclave were reported elsewhere.[1]

3. Results and Discussion Figure 1 shows dielectric loss curve at various p_{CO2}. The dispersion corresponds to the segmental mode of PLA, related to local chain dynamics. With increasing of p_{CO2}, the segmental mode shifts to higher frequencies.

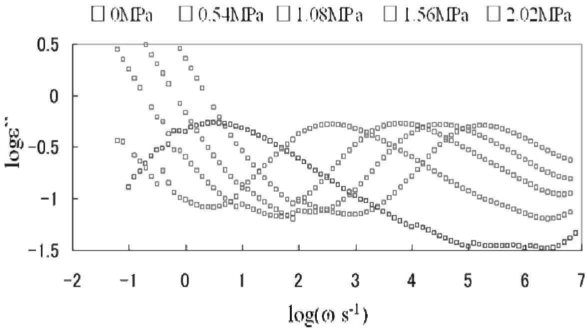

Figure 1. Dielectric loss curve measured at various CO_2 pressure.

Motivated by the frequency – temperature superposition principle, each loss curve at different p_{CO2} was superposed on the data at $p_{CO2} = 0$. The result is shown in Figure 2. The superposition worked quite well. This means that local motion of PLA is equally accelerated with dissolution of CO_2. This result is in contrast to those for ordinary organic solvents, for which dissolution of solvent causes broadening of segmental motion due to concentration fluctuation. For the case of CO_2, a similar concentration fluctuation would exist, but the size of plasticizer is small so that the dynamic coupling between CO_2 and polymer would be very weak.

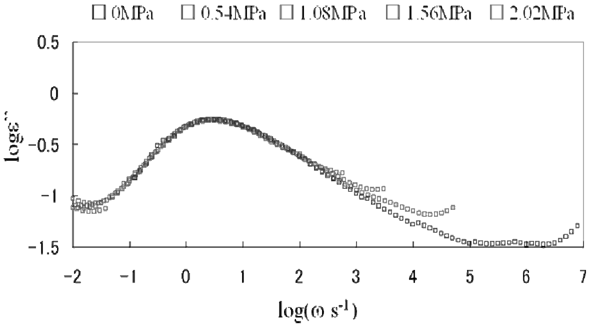

Figure 2. Superposition of dielectric loss curve.

4. Conclusions Broadening of the segmental motion of plasticized systems is often explained with the concept of concentration fluctuation of solvents. However, the present study shows much more importance of dynamical coupling between the solvent and polymer, which strongly depends on molecular size of the solvent.

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Crystallization behavior of acetaminophen in the bulk and under confinement

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Dielectric spectroscopy is shown to be a powerful method to study the crystallization kinetics of acetaminophen being a pharmaceutical model system (also known as paracetamol). Isothermal crystallization experiments in a wide temperature range from slightly below to significantly above T_g at 24°C are presented. It is shown that the changes in the dielectric spectra during crystallization are well described by a simple two-phase model considering the coexistence of amorphous and crystalline fractions. Results from calorimetric experiments detecting the cold crystallization process are given for comparison and fit quite well to the data from dielectric spectroscopy [1]. In a second part it will be demonstrated based on results for acetaminophen confined in controlled porous glasses (CPGs) with untreated pore walls and well defined pore diameters d in the range 4-20nm that nanoconfinement is a handle to increase the lifetime of amorphous pharmaceuticals, as required for controllable and efficient drug delivery. This is interesting for pharmaceutical applications since amorphous drugs have favorable properties like good bioavailibility and solubility, but usually a bad long-term stability. The observed amorphization of acetaminophen in nanopores with diameters $d < 5$nm can be explained based on thermodynamic effects in nano-sized systems. Possible changes in crystallization kinetics and nucleation behavior due to immobilized surface layers and size restrictions for heterogeneous nuclei are also discussed. Calorimetric and x-ray scattering data for acetaminophen in CPGs with larger pores (20nm < d < 100nm) clearly evidence that the metastable form III of acetaminophen can be obtained in high yields allowing us to determine thermodynamic parameters of this usually inaccessible crystalline form. We conclude that studies on polymorphic pharmaceuticals under confinement may enhance the general understanding of their crystallization behavior and that nanoconfinement is an interesting approach to produce metastable crystalline forms and amorphous pharmaceuticals that persist for application relevant shelf-times [2-4].

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Dielectric relaxation in double potassium yttrium orthophosphate $K_3Y(PO_4)_2$ and sodium yttrium orthophosphate $Na_3Y(PO_4)_2$

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The double alkali metal yttrium orthophosphates with general formula $M^IY(PO_4)_2$ (M^I = Na, K) occur in the system $YPO_4 – M^I_3PO_4$ and are formed at the molar ratio $YPO_4:M^I_3PO_4$ = 1:1. $K_3Y(PO_4)_2$ melts incongruently at 1460˚C [1]. $Na_3Y(PO_4)_2$ melts congruently at 1515 ˚C and is stable down to room temperature [2]. Both compounds can be synthesized through a reaction in the solid phase by sintering a stoichiometric mixture of the initial orthophosphates at 1200 ˚C for 4 h ($K_3Y(PO_4)_2$) [1] and at 900 ˚C for 15 h ($Na_3Y(PO_4)_2$) [2]. The potassium yttrium phosphate $K_3Y(PO_4)_2$ crystallizes in a monoclinic system (space group $P2_1/m$). Its structure can be described as a disortion of glaserite [3]. The sodium yttrium phosphate $Na_3Y(PO_4)_2$ has the orthorhombic structure (space group $Pbc2_1$) [4].

The orthophosphates: $K_3Y(PO_4)_2$ and $Na_3Y(PO_4)_2$ were studied in order to examine its dielectric relaxation processes. Measurement of the frequency and temperature dependency of dielectric properties give information about dynamical reorientation of molecules with permanent or long lasting induced electric dipole moment μ. Measurements of the dielectric permittivity and dielectric losses were performed in function of temperature (-40 ˚C – 140 °C) and frequency (100 Hz – 1 MHz). Samples were measured as pellets 10mm in diameter and about 1-2 mm in thickness. Before experiment, samples were annealed at a temperature of 170˚C in vacuum in order to decrease the number of electric charges. High number of charges give rise to an apparent electric permittivity because of high electric conductivity.

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How do sugars influence some structural, vibrational and dynamical properties of proteins ? An Insight from Molecular Dynamics simulations

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Sugars have received a huge interest over the past few decades for their preservation capabilities of biosystems such as cells, vaccines, or therapeutic proteins employed in the pharmaceutical industries. Indeed, disaccharides such as trehalose, maltose or sucrose can be added to biologically active solutions to overcome the limited stability range of proteins (pH, temperature, salt concentration, etc.). These additives prevent the partial or even total degradation of biomolecules due to the lethal thermal or dehydration stresses encountered during industrial conservation methods (lyophilization), where trehalose has been found the most effective. However, the molecular mechanisms at the origin of the superior capabilities of trehalose and, more generally, of the biopreservation phenomenon itself still remain unclear, despite various experimental and theoretical works. Several hypotheses (glass transition temperature, water molecules replacement, hydrogen bonding destructuring effect, preferential excluded volume,…) have been proposed, but none of them can be considered as fully accepted.

In order to better understand the physical properties of sugars and their influence on the protein stability we have performed Molecular Dynamics investigations of hen egg-white lysozyme in presence of three homologous disaccharides: trehalose, sucrose and maltose [1]. This study shows that the hydrogen bonds network of water is highly dependent on the presence of sugars and contributes to the stabilization of lysozyme. The privileged interaction of trehalose with water is confirmed below a threshold weight sugar concentration of about 50 %. Above this concentration, trehalose becomes less efficient to distort the tetra-bonded HB network of water than maltose. This result is interpreted as a competition between sugars and lysozyme to bind to water molecules. At high sugar concentration, trehalose molecules are found less capable to perturb water molecules which bind preferentially to lysozyme consistently with the preferential hydration hypothesis. The analysis of the relative concentration of water oxygen atoms around lysozyme suggests that lysozyme is preferentially hydrated. Trehalose is seen more excluded than maltose and sucrose. The dynamical slowing down of the solvent is suggested to mainly arise from the homogeneity of the water/sugar matrices controlled by the percolation of the sugar hydrogen bonds networks.

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Nonlinear dielectric effect and critical phenomena of ternary critical mixture

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NDE technique has exceptional significance in investigations of critical phenomena. The method is very sensitive to thermodynamic and critical fluctuations. Non-linear dielectric effect consists in measurements of a change of electric permittivity caused by application of strong electric field. The sample is subjected the influence of two parallel fields; the measuring one - of high frequency and low amplitude, and the polarising one - of high amplitude, usually applied as rectangular short pulses.

The NDE increment is defined as $\Delta\varepsilon_{NDE} = \varepsilon_E - \varepsilon_{E\to 0}$, where ε_E, $\varepsilon_{E\to 0}$ is the permittivity measured at strong and at low electric field, respectively. In the vicinity of critical mixing point very strong increase of the NDE increment is observed what is frequently used for investigations of critical phenomena in the vicinity of second order phase transitions. Most of NDE experiments in critical systems concern binary critical mixtures, whereas the anomaly of NDE in ternary liquids is little-known. In the contribution we present measurements of the NDE increment in acetonitrille – cyclohexane - *p*-xylene ternary mixture. The NDE increment was measured in function of composition in one phase region. The temperature was kept constant. In the vicinity of critical mixing point of the ternary mixture a strong increase of the NDE increment is observed what remembers the anomaly detected in binary mixtures close to the critical mixing temperature.

The effects of pressure on the cooperative and non-cooperative dielectric processes in KTN ferroelectric crystals

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The effects of pressure on the phase transition in ferroelectric crystals in general and KTN in particular have been extensively studied. Disturbing the delicate balance between the competing long- and short-range forces inhibits the formation and subsequent evolution of polar nanoregions shifting the transition to lower temperatures [1]. The result of introducing additional defects whose behavior is mediated by these nanoregions [2] is also directly influenced. While in the vicinity of the phase transition universal dynamics dominate, above the Burns Temperature the unique case specific effects of pressure begin to become manifest. We examine the behavior of two different defect related dielectric processes and their response to the application of pressure. The first a non-cooperative activated Arrhenius process related to electron hopping and the second a cooperative relaxation of Cu defects. In both cases, analysis of the pressure dependence of the Cole-Cole (α) shape parameter is shown to be directly related to the nanoregion correlation length and to the spatial fractal nature of the underlying matrix. The results may shed additional light on the nature of the ferroelectric-relaxor crossover.

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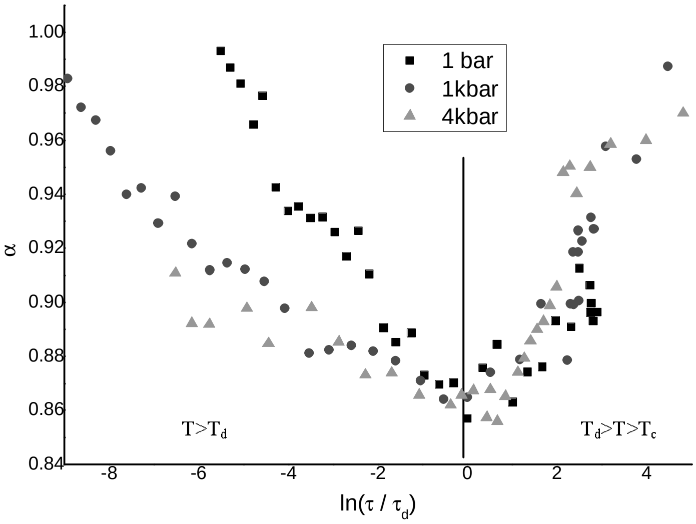

Figure 1 Alpha – ln(tau) dependence depicting the independent region above Td and the universal behavior below.

The effect of temperature on electric conductivity of veins applied in Coronary Aortic Bypass Grafts (CABG) operations

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First time electric conductivity – temperature relationship (σ-T) have been applied in studies on bone, which have been carried out by Behari, Liboff and Shamos. Since then, the method has been used in studies on elastin, keratin, collagen, nucleic acids and more complex biological materials. The method makes it possible to observe phase processes, such as thermal denaturation, water release and thermal decomposition, occurring in heated biological materials.

The most important features in the σ-T relation of vein walls derive from the major molecular constituents of the tissue, that is collagen and elastin. Therefore during the analysis of the obtained results electric properties of collagen and elastin become in the focus of attention. Solid-state proteins are characterized by relatively high temperature of denaturation and their physical properties are deeply affected by the water content. Electric conductivity increases with increasing water content and the activation energy of charge conduction process is reduced [1,2]. The aim of this work was to study the effect of temperature on electric conductivity of the vein wall enabling one to determine temperatures of the phase transitions and activation energy of the charge conduction process.

Measurements of σ-T were carried out during monotonic temperature changes in the temperature range of 295-520K. Samples of veins applied in CABG operations were burden with any pathological changes and were taken from a group of 30 patients 50-60 years old. Prior the measurement of electric conductivity, each sample was maintained at 380K for a period of one hour. At this time the release of free water took place [3]. Then, the sample was cooled to room temperature and heated again from 295K to 530K. The peak temperature of the σ-T curve along with the temperature of kink of the σ-T curve, show the temperature of phase transition of proteins constituting vein wall. Enthalpy of the charge conduction process was determined using the Arrhenius plot. The calculations were performed at the intervals of the linear dependence of $\ln\sigma = f(T^{-1})$ ($r \geq 0{,}999$).

Enthalpies, determined in the temperature range of 330-430K, were significantly higher for patients suffered from blood hypertension and myocardial hypertrophy than for other patients.

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Broadband Dielectric Spectroscopy of poly (dimethoxybenzyl methacrylate)s

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With the aim to investigate the influence of slight differences in the chemical structure of a family of polymers on the response of these to electric perturbation fields, the relaxation behavior of three dimethoxy phenyl isomers of poly(benzyl methacrylate) have been studied. Specifically, poly(2,3-dimethoxybenzyl methacrylate) (P2,3DMeOxM), poly (2,5-dimethoxybenzyl methacrylate) (P2,5DMeOxM) and poly(3,4-dimethoxybenzyl methacrylate) (P3,4DMeOxM), are studied by broadband dielectric spectroscopy (DRS) in the frequency range of 10^{-1}–10^{8} Hz and temperature interval of 153-408 K.
The three isomers show complex dielectric relaxational spectra. The three isomers show ostensible glass-rubber relaxations centered in the vicinity of 320K (P2,3DMeOxM), 310K (P2,5DMeOxM) and 330K (P3,4DMeOxM) at 1 Hz. The spectra exhibit prominent α peaks, followed in increasing order of frequency by a wing with no clear definition of further dipolar peaks. This is probably due to the overlapping between the α -relaxation with possible secondary processes existing in the polymers under study. On the other hand, conductivity contributions to the loss hide the left hand side of the spectra. Since, the relaxational response of polymers to perturbation fields is more clearly defined in the retardation time distribution spectra than in the frequency domain, the characterization of each process was carried out by a numerical procedure that allows us to obtain the retardation time distribution as an intermediate step to obtain the decay functions. The relaxations were analyzed by means of the empirical Havriliak-Negami equation. All isomers present several subglass absorptions which appear overlapped, thus being complicated its characterization.
According to the results, the dielectric strength of dielectric α-relaxation for the 3,4-dimethoxy isomer is, respectively, nearly six and four times lower than the strength of the 2,3 and 2,5 isomers. For this reason, although the three polymers have similar chemical structures, significant differences between the dielectric behaviors of these polymers have been observed. The polarity of the three polymers, expressed in terms of the molecular dipole moment evaluated by molecular mechanics calculations, is very sensitive to the location of the dimethoxy groups in the phenyl group. It gives a good account of the differences observed in dielectric strength of dielectric glass-rubber relaxation.

Influence of the Structural Characteristics on the Broadband Dielectric Spectroscopy of napthyl substituted acrylate Polymers

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A comparative study of the dielectric relaxation behavior of two polymers containing aliphatic-aromatic side groups in their structures was carried out in order to get a better understanding on how slight differences in the chemical structure influence the responses of polymers to perturbation fields. Specifically, the poly(2-[naphthylacetyloxy]ethyl acrylate) (PNAA) and poly(2-[naphthylacetyloxy]ethyl methacrylate) (PNAMA) are studied by broadband dielectric spectroscopy (DRS) in the frequency range of 10^{-2} to 10^{8} Hz and temperature interval of 298 to 403K. Both polymers show complex dielectric relaxation spectra. These spectra show almost three relaxations processes in the temperature-frequency range studied. The isotherms representing the dielectric loss as a function of frequency, show important conductive contribution especially at high temperature and low frequencies. However, the real component of the complex permittivity increases as frequency decreases in the low frequency region and the departure of ε' from the plateau shifts to higher frequency as the temperature increases. The two polymers show ostensible glass-rubber relaxations centered in the vicinity of 309K (PNAA) and 330K (PNAMA) at 1 Hz, close to the calorimetric glass transition temperatures of these materials. The relative closeness of the T_gs of PNAMA and PNAA suggests that the methyl group in the former polymer only slightly affects its conformational versatility presumably as a consequence of the large and flexible side groups of the polymers. As a result, the T_g and fragility index of PNAMA are only slightly higher than those of PNAA. Owing to the conformational versatility of the side groups, it is important to compare the dynamics of the chains with that of the side groups. A study of dielectric behavior of 2-(acetoloxy)ethyl-2-(2-naphthyl) acetate (ANA), model compound of the repeating unit of the polymers was investigated.

The characterization of each process was carried out by a numerical procedure that allows us to obtain the retardation time distribution as an intermediate step to obtain the decay functions. According to the results, the evolution of τ_0 with temperature obeys to the VFTH equation whereas the stretch exponent does not follow a definite trend. Thus β_{KWW} seems to be independent of temperature for PNAA whereas the value of this parameter slightly increases with temperature for PNAMA. The fact that β(PNAMA) > β(PNAA) may be due to the fact that the higher rigidity of the former polymer, caused by the methyl group, hinders the accessibility of the polymer to some parts of the conformational frequented by PNAA. Then PNAMA is less complex than PNAA from a dynamic point of view and hence the higher value of the stretch exponent for the former polymer.

According to the results, it is possible to conclude that the replacement oh the hydrogen atom of the C^{α} backbone of the repeat unit by a methyl group slightly shifts the α relaxation to higher frequency and increases the activation energy of secondary processes. The β relaxation corresponding to the model compound ANA and the polymers PNAA and PNAMA strongly overlaps with the α relaxation, resembling the “excess wing” appearing in the high frequency peak of the latter process in the dielectric spectra of some supercooled liquids.

Relaxation Processes In Polymers Filled With Nanoparticles

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We report on the influence of filling of poly(n-alkyl methacrylates) with nanoparticles on relaxation processes and glass transitions as investigated by Dielectric Spectroscopy and Differential Scanning Calorimetry. The diameter of nanoparticles was 12 nm. The agglomeration even of 2-3 volume percent of Aerosil particles in polymer forms a 3D-network dividing the polymer into random domains with liner size of several hundred nm, depending on the concentration of filling particles. The filling of polymers with nanoparticles has at least two effects: random field effects imposed by the network and a very developed area of the particles surface that imposes interfacial effect on polymers. In order to estimate the role of interfacial effects at nanoparticle-polymer interface we used two types of Aerosil particles: with hydrophilic and hydrophobic surfaces.

We have found that the relaxation times of alpha-relaxation process (sensitive to glass transition) in polymers filled with both hydrophilic and hydrophobic particles were faster than those of bulk polymers measured at the same temperatures. This might be interpreted as reduction of glass transition temperature in the filled polymers. Semiquantitatively this reduction is in accordance with the Vogel-Fulcher data analysis of the temperature dependencies of the alpha-process relaxation times. We assign the observed influence of the nanoparticles on polymer bellow glass transition temperatures mainly to interfacial effects. The influence of random field effects seems to be less important in glass forming systems because of their intrinsic random structure. However, we observed that relaxation processes were not completely frozen bellow “formal” (calculated from Vogel-Fulcher formula) glass transition temperature and the relaxation rates were higher for filled than for pure polymers. This suggests that the influence of randomness due to the filling of polymers with network forming nanoparticles is in certain way equivalent to an increase of free volume that has resulted in the observed effect.

The beta-relaxation process was slower for bulk than for filled polymers, but the activation energies of this process were about the same for all three types of samples (pure polymer and polymer filled with hydrophilic and hydrophobic nanoparticles). The influence of filling of polymers on the relaxation times of beta-relaxation process was clearer for polymers with shorter side group. This could be due to the fact that the interactions of macromolecules with surface of filling particles is mainly due to interaction of backbone of the macromolecule with the surface rather than of side groups – particle interactions. We compare the results on the influence of filling of polymers on glass transition obtained in DS experiments with data obtained by DSC.

Some Biophysical Properties Of Castor Oil Esterified With Some Acid Anhydrides

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A series of castor oil adducts were synthesized by esterification of castor oil with acid anhydrides: phthalic, maleic and succinic anhydrides. The chemical structure of castor oil and the prepared adducts were characterized by means of IR and ^{1}H NMR spectroscopy. The number average and weight average molecular weight were measured by gel permeation chromatography. The electrical properties were studied through the permittivity, dielectric loss and conductivity measurements. Dielectric data were fitted in the frequency domain using Frohlich and Havriliak-Negami functions. These functions ascribe Maxwell – wagner effect and the mobility of the main chain and the attached group of the reacting esters. The electrical conductivity which describes the ionic mobility of the systems was found to be in the range of 10^{-9}-10^{-12} Scm^{-1}. This indicates that castor oil and its esters could be used for antistatic applications.

The viscosity η and the activation energy E_η obtained from the dependency of viscosity on temperature using Arrhenius equation were found to increase by increasing the molecular weight of the system.

The effect of different concentrations of castor oil and its esters on the growth activities of sugarbeet pathogens R. Solani, S.rolfsii were studied through the determination of percent germination, average length of hyphal extensions, dry mass yield and the production of Sclerotia. The obtained data indicate that the esterification of castor oil with anhydrides improves the antifungal activity.

Key words: Castor oil adducts, electrical conductivity, dielectric properties, viscosity, antimicrobial activity.

Scaling Behaviour in Dielectric Relaxation of Poly(dimethyldiallylammonium chloride) in Dilute and Semidilute Solutions

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Dielectric measurements were carried out on Poly(dimethyldiallylammonium chloride) aqueous solutions with different mass fractions in the frequency range from 40 Hz to 110 MHz. Two relaxations namely low frequency (10-100 kHz) and high frequency (1-10MHz) were found and their dielectric parameters presented some interested scaling behaviour. First of all, crossover concentration between dilute and semidilute region was observed in scaling behaviour of relaxation time and relaxation amplitude corresponded to the one calculated from the theoretical scaling expressions derived by Odijk [1]. Additional, scaling behaviour of polymer concentration dependences of relaxation time and relaxation amplitude of low frequency relaxation were shown in the figure and of high frequency relaxation were summarized as: $\tau_h \propto c^{-2/3}$, $\Delta\varepsilon_h \propto c^{1/3}$ below crossover concentration, $\tau_h \propto c^{-1}$, $\Delta\varepsilon_h \propto c^{0}$ above crossover concentration.

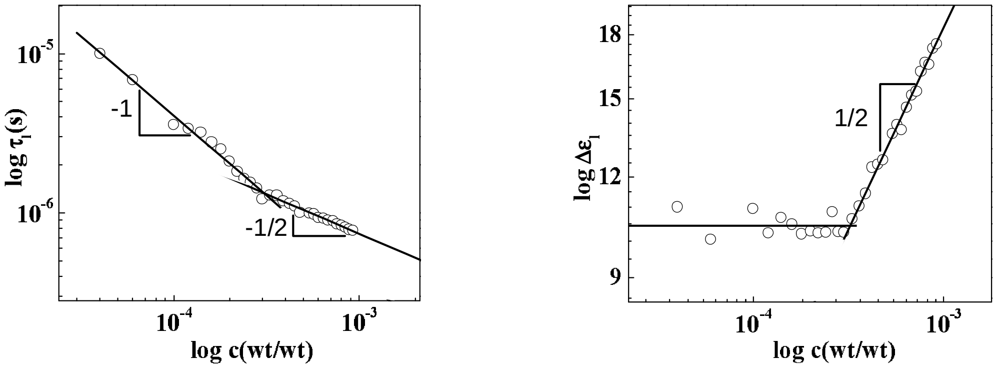

Figure: Scaling behaviour of polymer concentration dependences of relaxation time and relaxation amplitude of low frequency relaxation

Finally, the scaling behaviour was analysed in the light of the scaling approach which recently, in aspect of broadband dielectric relaxation, summarized by Bordi [2]: although the theory can explain the observed dielectric parameter of high frequency relaxation, the dielectric parameter of low frequency relaxation can not. Nevertheless, the theory can remain explain the observed dielectric parameter of low frequency relaxation if we suppose that it originated from polarization of the condensed counterions along a entire chain of polyions which slightly curved and the dependence of polymer concentration of its length was $L_c \propto c^{-1/2}$ in the dilute region and transitioned to end-to-ed length distance in the semidilute region instead of an entire polyelectrolyte chain which didn't curved neither in the dilute region nor in the semidilute region, this can be supported by the scaling behaviour of both relaxation time and dielectric amplitude and the conformity of the scaling behaviour of them, this suppose could better demonstrated the changing process of polyelectrolyte chain when the polymer concentration gradually changed.

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Elaboration par le procedé sol-gel et etude physicochimique et dielectrique de PbTiO3 dopé au Cérium

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Les poudres céramiques de titanate de plomb (PT), dopé au cérium et lanthane (PCeLT) ont été préparées par voie sol-gel moyennant la méthode de la déstabilisation de solution colloïdale (DSC). Cette technique présente, notamment par rapport aux autres techniques de synthèse couramment utilisées (voie solide, coprécipitation, pulvérisation cathodique), l'avantage d'être relativement simple à mettre en œuvre.

Du plomb est ajouté, en excès (10%), lors de la préparation de ces poudres afin de compenser les pertes éventuelles du plomb durant les traitements thermiques. L'effet de la température sur les échantillons obtenus a été étudié par spectroscopie infrarouge à transformée de Fourier (IRTF), par analyse thermogravimétrique (ATG), par analyse thermique différentielle (ATD), par RAMAN et par diffraction des rayons X (RX). L'effet du dopage en cérium et lanthane sur la structure cristalline a été examiné. Les poudres PLCeT calcinées à 600°C, cristallisent dans la phase perovskite de structure cubique.

L'étude du frittage a été menée en suivant l'évolution microstructurale dans le but d'en optimiser les paramètres pour une efficacité meilleure. Nous avons opté pour une durée de frittage de quatre heures à 1100°C. Ces résultats sont confirmés par les mesures diélectriques réalisées sur toutes les compositions étudiées. La composition PCeLT présente les meilleures propriétés diélectriques.

Dynamics Of Orientationally Disordered Mixed Crystals Sharing Cl-Adamantane And CN-Adamantane

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Crystals composed of molecules more or less spherical in shape may exhibit significant orientational disorder. These compounds, named plastic crystals or "orientationally disordered (OD) crystals", either may display at least one additional transition accompanying a relatively large entropy change, in such a way that crystals melt in successive steps, the rotational degrees melting at the ordered-disordered low-temperature phase transition or, in many cases by sufficiently fast cooling, the high-temperature dynamically disordered state can be supercooled, avoiding complete orientational ordering can be quenched given rise to orientational glasses (OG). Concomitantly, the dynamics shows the continuous slowing down over many orders of magnitude that is typical also for the canonical glass forming liquids.[1]

Some adamantane ($C_{10}H_{16}$) derivatives are well-known examples of compounds showing the OD phases and its non-ergodic OG states. The aim of this study is to investigate the dynamics of mixtures sharing a prototype compound displaying an OG state, CN-adamantane[2] (CN-a for short) and a close molecular size compound of the same series, Chloro-adamantane (Cl-a), by means of broadband dielectric spectroscopy. Both molecules are structurally characterized by a flexible side-group or atom (CN- and Cl-, respectively) and by a rigid entity ($-C_{10}H_{15}$).

Several mixtures of the two-component system $(\text{Cl-a})_{1-X}(\text{CN-a})_X$, for $0.62 \leq X \leq 1$, have been dynamically characterized for temperatures down to the glass transition temperature. Despite that substitution of Cl-a molecules into the CN-a lattice does not noticeably change the average of the available volume of the cubic lattice (as shown by density measurements) and that Cl-a molecules have a faster dynamics, molecular mixed crystals slow down with decreasing the mole fraction, i.e. the content of Cl-a molecules. This effect is interpreted by the existence of cooperative effects which are enhanced by the substitution process.[3]

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Dielectric Spectroscopy and Conductivity of Two Hyperbranched Polyamidoamines

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Abstract

The broadband dielectric spectroscopy was used to investigate the relaxation behavior of two hyperbranched polyamidoamines (with different nitrogen content). Hyperbranched polyamidoamine samples exhibit, in the relatively low temperatures, two sub-glass processes named in increasing order of frequency β and γ. These two relaxations were analyzed in terms of Havriliak-Negami equation. At high temperatures the glassy dynamics (α- process) seems to be screened out by both electrode polarization and the conductivity contribution. The diffusion coefficient due the charge migration is found to be in good correlation with the translational diffusion measured using Pulsed Field Gradient (PFG) NMR.

Preparation, Characterization and Dynamic Relaxation of Some Hyperbranched Polyurethanes

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Two samples are prepared through the reaction of either 2,4-toluene diisocyanate (TDI) with glycerol for the aromatic polymer, or isophorone diisocyanate (IPDI) with glycerol to give aliphatic structure. The prepared polymers were characterized using ^{1}H NMR, FTIR, GPC, DSC and TGA. The methods of Dielectric Relaxation Spectroscopy (DRS), DSC and Thermally Stimulated Depolarization Currents (TSDC) were employed on pellets, prepared by applying pressure of about 10 tones at ~ 110 ^{o}C, to investigate the dynamic relaxation behavior. The obtained results were discussed in terms of local and segmental relaxations and of fractal architecture of the polymeric structure. The investigation of the conductivity relaxation imply conformational and/or structural changes of the hyperbranced polyurethanes at temperatures far below (lower than 100 degrees) the calorimetric glass transition of the polymers.

Structural Insights from the Cole-Cole Function

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Recent theoretical work has demonstrated that Cole-Cole dielectric behaviour can be explained as a dipole matrix interaction over a fractal time set [1]. In this case the Cole-Cole parameter, α, is in fact the fractal dimension of the number of interactions over the time set.

$$\alpha = \frac{\ln N}{\ln \zeta} \tag{1}$$

Where N is the number of interactions and ζ is a dimensionless time interval. The model was further refined by considering the relaxation process as self diffusive, leading to

$$\alpha = \frac{D_g}{2}\frac{\ln(\omega_0 \tau)}{\ln(\tau/\tau_0)} \tag{2}$$

Where D_g is the spatial fractal dimension, ω_0 is the characteristic frequency of the diffusive process and τ_0 is a microscopic time scale related to the time interval.

In our paper we demonstrate how these concepts can be extended to incorporate anomalous diffusive processes. Furthermore we introduce a new parameter, φ, characteristic to the system being measured.

$$\alpha = \frac{D_g}{2}\left(1 + \frac{\ln(\varphi)}{\ln(\tau) + \ln(\tau_0)}\right) \tag{3}$$

This parameter, in conjunction with τ_0, quantifies whether the process will be governed by macroscopic constraints such as the size of the region in which diffusion can happen, R_0, or by microscopic factors such as the characteristic times for a step. Anomalous Diffusive processes are shown to modify $D_g \rightarrow \gamma D_g$ where γ is the anomalous exponent defined by the mean square displacement and the characteristic time for the displacement, $R \sim \tau^{\gamma}$.

The functional form of equation (2) provides an adequate description of $\alpha(\tau)$ curves for C-C behaviour for many different systems such as water-polymer mixtures [2], microcomposite materials [2], electron hopping in doped Potassium Niobate Tantalate ferroelectric crystals or water trapped in mesoscopic pores in porous glasses [3]. The implication of equation (3) for these systems is explored.

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Dielectric Spectroscopy in Nanostructure Ferroelectrics.

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The preparation of ferroelectric Langmuir-Blodgett (LB) films of copolymer vinylidenefluoride with trifluoroethylene P(VDF/TrFE) permitted investigation of ferroelectric switching on the molecular scale [1]. These films reveal the intrinsic coercive field Ec=0,5 10^9 V m^{-1}, which means that domains do not play essential role in ferroelectric switching [2].

Dynamic dielectric measurements were carried out for Langmuir-Blodgett films (5-30 monolayes) (ML) of copolymer P(VDF/TrFE) over the frequency range 10^{-1}-$2{\cdot}10^7$ Hz for temperature interval 25-130°C. Unlike [3] copolymer P(VDF/TrFE) with different compositions (75/25, 70/30, 60/40, 55/45) were investigated. The observed dielectric relaxation follows the Debye-type frequency dependence of ε*. Because the dipoles H-F in copolymer are rigidly attached perpendicular to the polymer chain, the dipolar motions are the result of rotational motions of chain molecules. Cole-Cole diagrams $\varepsilon''=\varphi(\varepsilon')$ correspond to the Cole-Cole theory, which is the modification of Debye theory. Graphic calculations show that relaxations in LB films are monodisperse in broad interval of temperatures 25-130°C . The experimental values of the relaxation time τ for LB films are in the interval 10^{-8}-10^{-7}s. The relaxation time τ enhances with the increasing temperature near the phase transition *Tc*. The temperature dependence of τ has a critical slowing-down character in full agreement with theory [3].

Note should be taken that this phenomenon was not revealed for thick casting films of P(VDF/TrFE). Perhaps this failure was connected with imperfect crystalline structure of casting films, caused by amorphous phase. The critical slowing-down phenomenon was not observed also in ferroelectric phase of another ferroelectrics that can be explained by domain existence. For the first time this theoretically predicted phenomenon was found in polymer ferroelectric nanostructures. The Debye relaxation was observed in the ferroelectric phase of P(VDF/TrFE), where domain walls could lead to a more complicated behavior. Therefore, the obtained results additionally confirm the conclusion that in ultrathin LB films domains do not play essential role.

LB films cannot be treated as ideal dielectrics. For conducting materials, the frequency dependence of the complex permittivity contains a contribution associated with the conductivity, which likewise is a complex quantity. The typical situation for conducting polymer materials is that the real part of the conductivity increases strongly with increasing frequency of the field. In disordered polymer systems, where the hopping mechanism predominates, the conductivity should increase, since as the frequency of the field increases, a contribution arises from charge carriers moving in smaller regions (conducting clusters). The temperature dependences of conductivity σ of LB films have Arrhenius behavior. The peculiarities of temperature dependences of $\ln(\sigma T)$ and $s=\ln\sigma/\ln\omega$ for P[VDF/TrFE] 60/40 film were investigated in the phase transition from ferroelectric to paraelectric phase.

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Broadband Dielectric Response And Mechanical Relaxations In Silver Borate Glasses

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Broadband dielectric spectroscopy has been used to investigate the dynamical response of a series of silver borate glasses as a function of frequency between 10^{-3} Hz and the microwave region. The electrical response of samples of different composition has been studied from 450 K down to cryogenic temperatures in terms of complex permittivity, frequency dependent conductivity and complex modulus. The results have been discussed in comparison with the results of mechanical spectroscopy at ultrasonic frequencies aiming to highlight: (i) the existence of analogies between the two kinds of dynamical response; (ii) the dependence on the composition and the possible role of the microscopic structure.

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Positron Annihilation Lifetime Response And Broadband Dielectric Spectroscopy: Propylene Carbonate

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A phenomenological analysis and common description of the ortho-positronium (o-Ps) lifetimes from positron annihilation lifetime spectroscopy (PALS) and the dielectric α-relaxation times from broadband dielectric spectroscopy (BDS) on glass-forming *propylene carbonate (PC)* are presented. As known from other glass formers, the temperature dependence of the o-Ps lifetime, τ_3, shows a sigmoidal increase with increasing temperature, which can be ascribed to an increase of free volume. The onset of the high-temperature plateau at $T_{b2} \sim 200\,\mathrm{K}$ seems to correspond to the merging temperature of the mean relaxation times of the primary α- and secondary β-process as determined from the dielectric results. In addition, it is approximately related to a crossover of the α-relaxation time $\tau_\alpha(T)$ from non-Arrhenius to Arrhenius behavior. This crossover can be described by a free volume version of a two-order parameter model that involves a crossover function between liquid-like and solid-like domains leading to a modified Vogel-Fulcher-Tammann-Hesse function. Within this phenomenological framework, also the sigmoidal form of $\tau_3(T)$ can be described by using the same parameters as obtained from the analysis of the dielectric relaxation of *PC*. In addition to the PALS results, the significance of the crossover temperature, T_m^c, is supported by findings from small-angle x-ray scattering and calorimetric data on *PC*. Overall, the performed simultaneous description indicates a close connection between the PALS response and the dielectric relaxation for *PC*. It seems to support the physical picture of liquid-like and solid-like domains determining the properties of the disordered phase, indicating close links between the decrease in free volume, the evolution of solid-like domains, and the slowing down of the dielectric α-process.

Positron Annihilation Lifetime Response And Broadband Dielectric Spectroscopy: Poly (Propylene Glycol)

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We present the results of phenomenological analysis of the dielectric relaxation spectra from broadband dielectric spectroscopy (BDS) treated using the Williams-Watts (WW) ansatz and of the ortho-positronium (o-Ps) lifetime from positron annihilation lifetime spectroscopy (PALS) on *poly(propylene glycol) (PPG)* as well as their common description within the framework of the two-order parameter (TOP) model. As is well known, the o-Ps lifetime, τ_3, as a function of temperature shows a sigmoidal course which can be ascribed to an increase of free volume. Mutual comparisons of PALS and BDS data indicate that a deviation toward the plateau level in a quasi-sigmoidal form is related to a merging of the relaxation times of the primary (α) and secondary (β) processes and that the own quasi-plateau level at the characteristic PALS temperature T_{b2}^{L} lies in the vicinity of a crossover of the main relaxation process from the non-Arrhenius to the Arrhenius behavior. The whole τ_3 vs. T plot can be described within a free volume version of the TOP model by an expression containing the fraction of liquid-like domains from a phenomenological analysis of the dielectric relaxation times of *PPG* using the modified Vogel–Fulcher–Tamman-Hesse (MVFTH) equation.The characteristic PALS temperature, T_{b1}^{L}, close to the characteristic TOP temperature, T_{m}^{c}, is connected with the changes in time and intensity parameters of the secondary effective β-relaxation and these features may be related to the dominance of solid-like regions. This simultaneous description indicates a close connection between the PALS response and the dielectric relaxation behavior for *PPG*. This seems to support the liquid-like and solid-like domains physical picture of the disordered phase over the whole temperature range of disordered systems. Additionally, it also demonstrates the intrisic links between the decrease in the free volume, the evolution of solid-like domains, the slowing down of the primary α-process and the changes in parameters of the secondary effective β- process for *PPG*.

Miscible Polymer Blends With Dynamical Asymmetry As A Potential New Class Of Materials For Solid State Electrolytes

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Solid state ionic conductors are systems combining the ionic conductivity of a liquid with the mechanical properties of a solid. For this purpose, clay/polymer nanocomposites have been widely investigated in recent years. In these materials the high ionic conductivity possessed by the polymer in the liquid state is associated with the mechanical stability of the clay. In these systems the good miscibility of the polymer with the clay is critically dependent on the rather subtle balance between enthalpic and entropic forces, which implies a technological limitation in the production of these materials.

In this contribution, we present results on the ionic conductivity obtained by means of Broadband Dielectric Spectroscopy (BDS) of miscible polymer blends with large dynamic asymmetry, i.e. very different glass transition temperature, and provide positive indications on the potential applicability of these systems as solid state ionics. In particular, our results suggest that an ionic conductivity comparable to that of a pure liquid can be achieved while retaining the properties of a solid. This is a consequence of the selective occurrence of the glass transition of the two components of the blend that implies that one of the two polymers is liquid in a temperature range where the other is solid. In addition, we infer that the confinement at a molecular scale induced by the more rigid polymer be responsible for the change in the temperature dependence of the ionic conductivity of the more flexible polymer. This undergoes a crossover from a marked non-Arrhenius to a milder Arrhenius temperature dependence. We explain this crossover as a consequence of the impossibility of the cooperative length for the structural relaxation to grow freely with decreasing temperature due to the presence of the physical barrier created by the rigid polymer of the blend.

Dielectric Relaxation And Cooperative Dynamics In Non-Polymeric Glass-Formers

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The existence of a typical length scale underlying the occurrence of the glass transition in non-crystallizing melts has been subject of intense research. In this contribution, we provide a route to determine the characteristic length scale of the glass transition in low molecular weight glass-forming systems combining the Adam-Gibbs (AG) theory with the "self-concentration" concept. To do so we consider the dynamics of several glass formers in different environments as probed by Broadband Dielectric Spectroscopy (BDS). In this way, the material specific parameter α connecting the characteristic length scale of the glass transition to the configurational entropy is obtained. This size results to be in the range 8–20 Å at the glass transition temperature depending on the glass former. Finally, we determine the energy barrier per particle of the AG theory and compare it with the high temperature activation energy of the structural relaxation. In doing so, we provide arguments for the effective equivalence between the length scale obtained through self-concentration arguments and the size of cooperatively rearranging regions (CRR) of the AG theory.

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The Assessment of the Influence of Temperature of Selected Parameters of the Approximation Method of Depolarization Current Analysis of Paper-Oil Insulation

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The paper presents the results of experimental investigations of paper-oil insulation samples from the point of view of the assessment of the influence of temperature on the parameters of the approximation method of the time characteristics analysis of depolarization current. Three types of equations: Debye's function with a single relaxation time, Curie-von Schweidler's function with triple Debye's function (taking into account short, average and long relaxation times of paper-oil insulation), and Jonscher's function with Debye's function with a single relaxation time, were selected as approximation functions, as recommended by literature [1, 2]. The investigated insulation samples were diversified in respect of the degree of dampness and aging [3]. Summing-up focuses on verification of the determined parameters of approximation equations in relation to the influence of insulation temperature and presents recommendations for their application in diagnostics carried out by the PDC (Polarization and Depolarization Current) method.

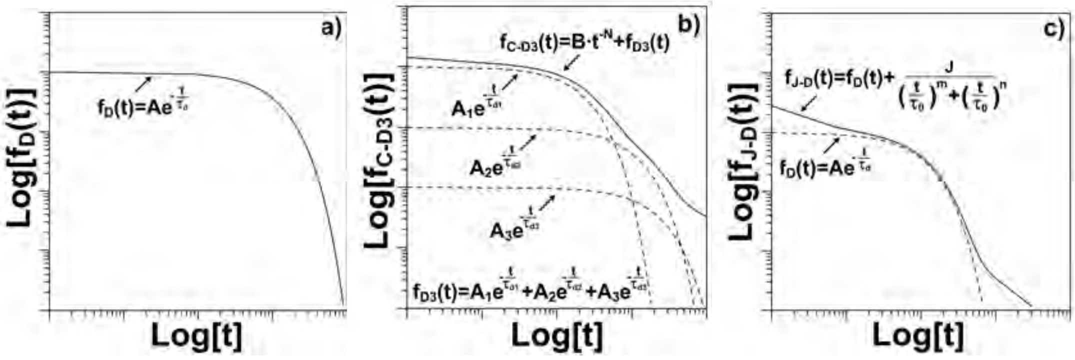

Fig. 1. Equations of approximation functions
a) Debye's function with a single relaxation time
b) Curie-von Schweidler's function with triple Debye's function
c) Jonscher's function with Debye's function with a single relaxation time

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The Influence of Geometry of Transformer Insulation System on Return Voltage Parameters Using an Equivalent Circuit Diagram X-Y

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The paper presents investigations of the influence of geometry of a power transformer main insulation system on selected parameters of return voltage (diagnostics of the paper-oil insulation condition by the RVM) [1, 2]. For this purpose, an equivalent series-parallel circuit diagram type X-Y (Fig. 1), simulating the above-mentioned paper-oil insulation system, was used [3]. The analysis results were based on time characteristics of voltage response of diagram X-Y, obtained through a computer simulation of the system excitement with constant voltage. The investigations were carried out in compliance with recommendations of the RVM diagnostics of paper-oil insulation system of power appliances. The element values of the equivalent circuit diagram X-Y were selected in such a way as to be able to simulate the system of the insulating board – oil insulation of a high-power transformer as accurately as possible. The paper presents an analysis of the influence of cumulated insulating board barriers and insulation system separators on the return voltage parameter values obtained from the characteristics.

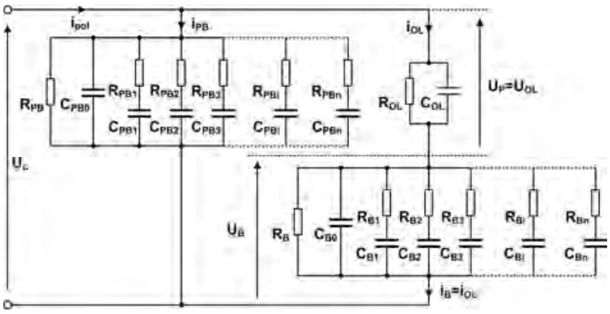

Fig. 1. Electric equivalent circuit diagram of the transformer main insulation according to model X-Y U_c- charging voltage, i_{pol}- polarization current, i_{PB}, i_{OL}, i_B- currents flowing through separators, oil channels and barriers, respectively, U_P, U_{OL}, U_B- voltage drops on separators, oil channels and barriers, respectively, $R_{PB,}$ R_{OL}, R_B- current leakage resistance, C_{PB0}, C_{B0}- geometric electrical capacities, C_{OL}- electrical capacity of oil channels, R_{Pbi}, C_{Pbi}, R_{Bi}, C_{Bi}- elements simulating values of time relaxation constants of insulating board

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Coupling Of *SAFES (Systematic Approach to Food Engineering Systems)* Methodology And Dielectric Spectroscopy In Order To Explain The Structural Changes In "*Granny Smith*" Apple During Drying Process

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Food quality and safety are the main concerns of consumers and the principal target of the food industry processes. The concept of food process engineering for product quality has been arising in the last years with the aim of designing and controlling processes to produce food products with very specific properties of quality and safety, previously defined on the basis of market opportunities analysis [1].

The role of the structure in quality and safety properties of dehydrated foods is essential and determines other parameters such as nutritional aspects. The SAFES (Systematic Approach to Food Engineering Systems) methodology recognizes the complexity of food system and allows coordinating the information about food structure, composition, thermodynamics, etc. in adequate tools to develop real foods and processes [1].

Dielectric spectroscopy can be used to describe physicochemical aspects, components interactions and structural changes in foods [2]. Due to this fact, accurate measurements of these properties can provide scientists and engineers with valuable information for monitoring manufacturing processes to improve food quality control [2]. In this context, the dielectric properties measurements, especially the dielectric spectra in a wide range of frequencies, appear as a useful method to process quality control and for optimizing some processes in the industry. These measurements are non-destructive and very fast, and some of these techniques can be even non-contacting. These latest characteristics make the dielectric properties measurements even more attractive to control food processes on line.

Coupling *SAFES* methodology approach and dielectric spectroscopy studies of dehydrated apple can bring useful information about its structure during the dehydration operation. In conclusion, the *SAFES* methodology tries to describe this operation trying to predict the changes in the food structure and allows us determining the mechanisms involved in this operation.

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Dielectric Spectroscopy Studies To Control Meat Salting Processes

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Salting is one of the most traditional preservation methods employed at food industry. One of its main problems is the difficulty to control the simultaneous water and NaCl fluxes into the product throughout processes.

Dielectric properties of salted porcine meat are strongly related to its structure and composition: moisture, water activity, salt and fat content [1]. As consequence, dielectric properties measurement appears as a promising method in non-destructive and on-line control of salting processes in meat industry.

Dielectric spectroscopy studies have been performed on raw and salted *longissimus dorsi* pork samples. Meat cylinders of 2 cm of diameter and 1cm of thickness were salted by immersing into 25% NaCl brine for 5, 10, 15, 30, 45, 70, 100 min, 2, 8 and 24 hours. Dielectric spectra were measured in the frequency range 200 MHz-20 GHz by a coaxial probe (HP 85070E) connected to a Network Analyzer (HP E8362B) immediately after salting and also after 8 and 16 hours. Salt content, moisture, water activity and volume were also measured. The *SAFES* methodology was used to analyze the obtained results. A good correlation between salt content and ε'' was found at frequencies below 10 GHz and with moisture content at higher frequencies. It could be concluded that dielectric measurements are a good method for on-line control of salting processes.

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Dielectrical And Mechanical Analysis Of Pet/Ldpe Blends Containing Secondary Materials

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Plastics used in the packaging industry, especially in the form of carry bags and bottels, manifest a formidable threat to the environment because of their non-biodegradable nature. Addition of both natural and synthetic fibers to these materials improves their performance, replacing the conventional materials like wood, metal, and ceramics in the majority of industrial applications. All main polymers used for this study in their neat form were also processed in the similar manner as that of a blend. The binary and compatibilized blends containing secondary PET (PETr) and LDPE (PEr) and reactive compatibilizing agent as commercial maleated ethylene-propylene rubber (EP-MA) have been processed by melt mixing in a counter-rotating twin rotors HAAKE RHEOCORD 9000 mixer (mixing chamber with capacity of 48.3 cm^3).

The results of dielectrical spectroscopy show a different behaviour of blends function of percent used in the system. The PET/LDPE blends has been also evaluated by following the rheological behaviour during processing and dynamic testing as well as tensile characteristics. Overall, the experimental results highlight the possibility of producing materials with modulated and new properties from secondary PET and LDPE by overcoming the lack of interfacial adhesion of polyolefin-PET blends typical of an immiscible system.

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Analysis Of Candied Apple "*Granny Smith*" Isotherms By Using Dielectric Spectroscopy. Study Of Sucrose Transitions And Water-Solid Matrix Relationships.

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Candying of fruit is a common operation in the industry of sweets, pastries and others. In this operation, the kinetic control is very important in order to preserve the quality and safety of the product. Non-destructive techniques to control the fruit candying, as microwaves and radio frequency signal technologies, could be an opportunity to improve the quality and safety properties of the products. One option to understand the behaviour involved in the fruit dehydration could be analyzing the dielectric spectra in the range of 0.5 to 20 GHz of samples dehydrated at different treatment times [1].

Although, in most cases, food tissue is considered as homogeneous and composed by a single phase; to model real foods it is important to consider their polyphasic and multi-component structure. The objective of this work is to analyze the water and sugar distribution in a polyphasic food matrix and also to correlate these components with the sample dielectric spectra in order to control apple candying process.

The *Granny Smith* apples were dehydrated in 65° Brix sucrose solution at selected times, to obtain samples with different sugar/dry matter ratios. Osmodehydrated samples were introduced in a hot air drier to obtain the moisture desorption isotherms. Before and after treatments, the dielectric spectra were obtained by a coaxial probe connected to a Network Analyzed. Dielectric spectra coupled with a thermodynamic model is a strongly tool to describe the crystallization behavior in a heterogeneous system and to quantify the water shearing in dehydrated food.

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Relaxation Dynamics Of Glass-Forming Propylene Glycol Oligomers

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Aside of the α relaxation, glassy matter reveals a variety of further dynamic processes, which are believed to play an important role for the glass transition but up to now are only poorly understood. Among the most prominent ones is the Johari-Goldstein (JG) β relaxation [1]. In dielectric loss spectra, it shows up as a second peak at frequencies beyond the α relaxation. However, its microscopic origin is still controversially discussed. For its explanation various rivalling concepts exist. Another important feature of glassy dynamics is the so-called fast β process, which usually is observed in the GHz-THz frequency regime and was predicted by the mode-coupling theory (MCT) of the glass transition [2]. Interestingly there are recent speculations that MCT may also explain the JG-relaxation [3].

In the present contribution we report broadband dielectric spectra on glass-forming propylene glycol and its di- and trimer. In addition to a detailed study of the α relaxation, we focus on the dynamics at higher frequencies. While the monomer of propylene glycol has a well-developed excess wing, a characteristic spectral feature of glassy dynamics beyond the α relaxation [4], the di- and trimer show a JG β relaxation [5]. In fact, as revealed by long-time aging experiments performed in our group [4], the excess wing in propylene glycol also can be ascribed to a canonical β relaxation. The data are analysed in the framework of various models as the coupling model [6] and the minimal model [7]. In addition we discuss the relation between the MCT Cole-Cole peak [3], and the experimentally detected β relaxation in these glass formers. Furthermore, very recent results up to THz frequencies will be presented here and are discussed in terms of the fast β process of MCT.

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Concentration Dependence Of Ionic Relaxation In Lithium Doped Polymer Electrolytes

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Polymer electrolytes are commonly doped with salt in order to achieve high ion conductivity, which in general is due to both anions and cations [1]. These systems exhibit a dielectric relaxation in a frequency region above the one, where the ion conductivity dominates the dielectric response, and below the region of the relaxations of the polymer host. The frequency of this relaxation, multiplied by the relaxation strength, has been found to be proportional to the ion conductivity, and the relaxation has therefore been assigned to short-range ion pair motion in the polymer. It exhibits characteristics similar to conductivity relaxations in inorganic solid ion conductors [2].
In this paper we investigate the dependence of the relaxation strength on the salt concentration (c), for polyethylene oxide (PEO), polypropylene oxide (PPO) and random copolymer P(EOPO) electrolytes containing the salt LiTFSI. The molecular weights in atomic units of the polymers were 400 for PEO and PPO and 600 in the case of P(EOPO). For the PEO and P(EOPO) electrolytes the relaxation strength per added salt dipole depends on the concentration approximately as $c^{-2/3}$. This can be explained by noticing that the relaxation strength is proportional to the square of the cation-anion distance, and that the average ion distance is proportional to the –1/3 power of the ion concentration, if at least one of the ions is mobile. However, the PPO electrolyte exhibits a strikingly different behaviour. For high ion concentrations the ion pair relaxation and the structural relaxation of the polymer host interact strongly, as noted before [3], leading to an almost concentration independent relaxation strength (equivalent to an apparent dependence of 1/c per salt dipole). It seems that the ionic motion is more strongly coupled to the structural rearrangements of the polymer chains in the case of PPO than for the other electrolytes in this study.

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Confinement, the Ratio $E_V*/H*$, and the Defect Diffusion Model

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In the defect diffusion model (DDM), dipole reorientation takes place when a dipole under the influence of an electric field is visited by a mobile single defect (MSD). Defects are packets of free volume and the volume associated with a MSD (localized region of low density) is larger than that associated with clustered defects (localized, immobile, rigid region of high density). Consequently, a central feature of the DDM model is heterogeneity. The DDM has been used to explain a wide variety of experimental results [1]. Early work included the origin of the widely observed stretched exponential (SE), a Vogel-Fulcher-Tammann (VTF)-like equation, the concept that the glass transition occurs when rigidity percolates, and physical aging. More recently, the formalism has been extended to the effect of high pressure and the physical basis of fragility was explained. In addition, the DDM was used to explain the linear relationship between the pressure derivative and logarithmic temperature derivative of physical properties. Next, the theory was used to explain the variation of free volume with temperature inferred from positron annihilation lifetime spectroscopy (PALS) data. More recently, the DDM was used to explain the widely different pre-exponentials and exponents in the Vogel-type laws that materials exhibit. In addition, a qualitative explanation was given of the liquid-liquid transition (T_B), the crystalline melting temperature (T_M), different values of the characteristic temperature (T_C), that some materials exhibit for different physical measurements, the origin of secondary relaxations such as the excess wing and the β relaxation, and the boson peak. Most recently, it has been shown how the theory accounts for the roles of volume and temperature in the dielectric properties of a material via the ratio of the isochoric activation energy to isobaric activation enthalpy known as E_V/E_P or $E_V*/H*$. In the present work further aspects of the theory of $E_V*/H*$ are presented. It is shown how that ratio can either increase or decrease with temperature depending on the nature of the material. In addition, the DDM is used to comment on the effects of confinement on dielectric relaxation. It is pointed out that the theory can account for increases, decreases or constancy of the α relaxation time depending upon the nature of the material and confining medium. Specifically, if the concentration of MSDs increases upon confinement, the relaxation frequency increases and vice versa. Further, changes in the concentration of the packets of free volume depend upon the interaction of the material and the confining medium. While the interface is of critical importance, attention must also be paid to the bulk properties of each material. In the case of nano-scale confinement, complications arise due to the correlation length.

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Dielectric Studies of Tetraaryl and Triaryl Polycarbonates

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Bisphenol A polycarbonate (BPA-PC) has a wide range of applications including optical recording media, prescription eyeglasses, architectural window glazing, automotive moon roofs, and aircraft canopies. Over the past few years, new transparent, amorphous tetraaryl and triaryl polycarbonates have been synthesized with higher glass transition temperatures (from190°C to 350°C vs. 150°C) with concomitant retention of ductility owing to the high entanglement densities [1]. In the present work, broadband dielectric spectroscopy studies of the new high-temperature polycarbonates have been carried out over the range 5.5-550 K and the results are compared with data for BPA-PC. First, the α relaxation is analyzed and the results are interpreted in terms of the defect diffusion model (DDM). For BPA-PC the DDM parameters are used to predict the ratio of the apparent isochoric activation energy to the isobaric activation enthalpy, E_V^*/H^* or E_V/E_P. The results are found to be in good agreement with experiment. In addition, the DDM is used to predict values of the correlation lengths of dynamic heterogeneities in the region above T_g. Next, the β relaxation region is analyzed. While this β process is sometimes treated as a single, broad relaxation, the data clearly imply that this relaxation region comprises several closely spaced relaxations. This agrees with previously reported dielectric relaxation studies for BPA-PC [2]. (Reference 2 also presents a thorough review of earlier dielectric studies for BPA-PC.) Ab initio quantum calculations have been undertaken in an attempt to understand the molecular origin of the relaxations. A picture of the β relaxation region is presented in terms of the DDM.

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Broadband Dielectric Spectroscopy Characterization Of The Relaxations Of Polyamides Plastified [Or Not] By Solvents.

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One of the specificity of polyamides is their high sensitivity to polar solvents (water, ethanol) due to the affinity of their amide groups with other polar functions. By disrupting hydrogen bonds established between polyamide chains, polar solvents induce an increase of molecular mobility that manifests by a strong decrease of the glass transition temperature. In order to study the molecular mobility of polyamides in the presence of solvents, a specific device was developed, aiming to generate a solvent atmosphere with controlled activity (partial pressure relative to saturating partial pressure) of a solvent or a mixture of solvents. This solvent atmosphere is then introduced into a closed dielectric cell of a broadband dielectric spectrometer containing a sample mounted between two porous electrodes made of sintered metal. In this work, aliphatic polyamides (PA6, PA66, PA12) where characterized in the dry state as well as in the presence of different solvent (water, ethanol, toluene) activities. The study of dry samples evidenced the presence of a relaxation in a temperature range higher than the alpha relaxation process. In the presence of solvents, this relaxation as well as the other "classical" relaxations of polyamides (glass transition and subglassy relaxations) are modified. The origin of this high temperature relaxation is discussed in terms of the semi-crystalline nature of polyamide.

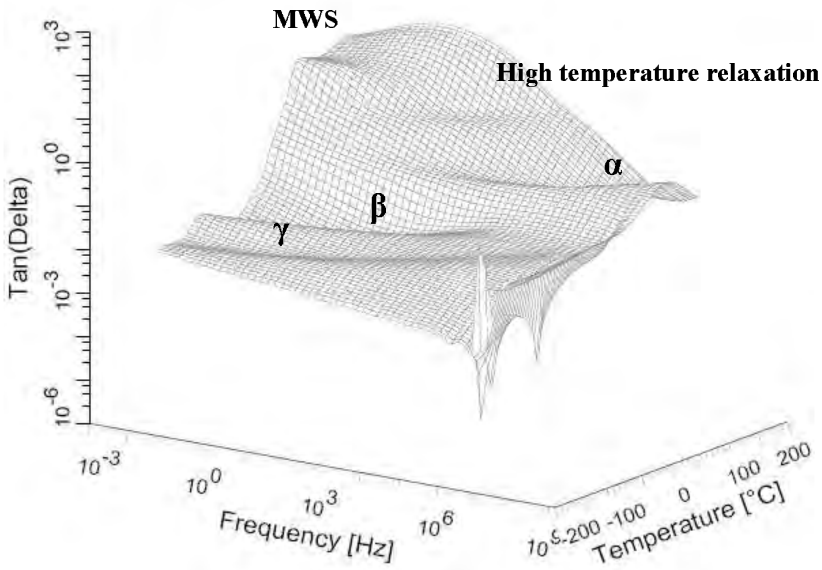

Fig. 1: dielectric 3D map of the loss factor of dry polyamide 6

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Determination of electronic structure by impedance spectroscopy

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It has recently been appreciated that various electrochemical techniques can be used to obtain a qualitative determination of the electronic density of states (DOS) of a number of intercalation compounds [1-3]. Ions and charge-balancing electrons are intercalated into the material under study by electrochemical techniques. The electrons enter previously unoccupied states above the Fermi level of the unintercalated host material. Provided that the inserted ions have a negligible influence on the electronic structure of the material, the number of inserted electrons as a function of voltage will give a qualitative picture of the conduction band DOS. When using electrochemical impedance spectroscopy (EIS), information on the DOS can be obtained from the so called chemical capacitance [4], which can often be observed in the low frequency range.

In this paper we report on the applicability of EIS to determine the electronic DOS of transition metal oxides used as electrochromic materials. We present novel results for the electrochemical DOS of tungsten and iridium oxide thin films over energy ranges of 1-2 eV. Generally good qualitative agreement with bandstructure calculations for the crystalline oxides is found. Differences in details are probably due to the disordered, porous and sometimes amorphous nature of our films. However, our results suggest that the EIS method can be used to reliably obtain the DOS only if the conduction band states are localized. The electrochemical density of states is often smaller than the computed one due to kinetic effects, i.e. very slow relaxations of the charge carriers. Nevertheless, the highly sensitive EIS method opens new vistas for studying the electronic structure of disordered intercalation materials.

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Viscoelastic and Dielectric Relaxation of a Cayley-Tree Type Polyisoprene: Test of Molecular Picture of Dynamic Tube Dilation

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For an entangled Cayley-Tree type cis-polyisoprene (CT-PI) composed two classes of arms, tri-functionally branched inner arms each carrying two outer arms (Mi = $24._7 \times 10^3$ and Mo = $12._3 \times 10^3$ for each inner and outer arm, respectively), the molecular picture of dynamic tube dilation (DTD) was examined through viscoelastic and dielectric data. The global motion of the arms was dielectrically active because they had the so-called type-A dipole parallel along their backbone. The dielectric relaxation function $\Phi(t)$ thus measured for CT-PI enabled us to experimentally evaluate the survival fraction of the dilated tube $\varphi'(t)$, a key quantity in the DTD picture. In the conventional picture of full-DTD, relaxed portions of the arms are regarded as a simple solvent thereby allowing the number of mutually equilibrated entanglement segments per dilated segment, $\beta(t)$, to fully increase to that in a corresponding solution, $\beta_{\text{f-DTD}}(t) = \{\varphi'(t)\}^{-d}$ with $d = 1.3$ for PI. The corresponding full-DTD relationship between and the normalized viscoelastic relaxation function $\mu(t)$, $\mu_{\text{f-DTD}}(t) = \{\varphi'(t)\}^{1+d}$, did not hold for the $\varphi'(t)$ and $\mu(t)$ data. In contrast, in the molecular picture of partial-DTD, $\beta(t)$ is determined through competition of the constraint release (CR) motion of the focused chain and the motion of surrounding chains, the former determining the maximum possible $\beta_{\text{CR}}(t)$ value in a given time scale, t. In this picture, the length and time scales are consistently coarse-grained on the basis of the CR mechanism. The partial-DTD relationship, $\mu_{\text{p-DTD}}(t) = \varphi'(t)/\beta^*(t)$ with $\beta^*(t) = \min[\beta_{\text{f-DTD}}(t), \beta_{\text{CR}}(t)]$, was found to hold for the $\varphi'(t)$ and $\mu(t)$ data satisfactorily. These results were in harmony with those found for regular star-branched chains, suggesting the importance of the consistent coarse-graining in molecular description of the dynamics of branched chains in general.

Annealing effects of a polymer system by Broadband Dielectric Spectroscopy

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The stratospheric balloons are the only vehicles which can stay aloft in the stratosphere (altitude range between 12 and 45 km). The stratospheric pressurized balloons have been specially developed for an onboard mass of 15 to 50 kg at an altitude near 30 km, during a flying up to 3 months. Their specifications require good mechanical strength of the polymer system in a broad temperature range, from –90°C (through the troposphere at about 10 km altitude) to +170°C (manufacturing conditions).

Their envelopes are made of a polymer multilayer with a semi-crystalline PET outer layer assembled with a polyester adhesive tape.

The purpose of this work is to characterize the materials and the adhesion in relation with the mechanical strength of the assemblies. In the future, treatments will be envisaged to enhance the adhesion for longer using.

The physical structure of the PET film and the adhesive tape are determined by Differential Scanning Calorimetry (DSC) and the dielectric relaxations by Broadband Dielectric Spectroscopy (BDS).

Two primary relaxation modes for the PET film are observed for the dielectric manifestation of the glass transition. A three-phases model with two amorphous phases (one rigid and another one mobile) is highlighted.

A third glass transition, observed by DSC and BDS, and also a third melting of the adhesive appear with the long-storage of many years. The physical structure of the adhesive evolves with storage and could explain the expiry date of the adhesive tape for a good adhesion. The dielectric analysis corroborate the calorimetric results.

Moreover, interactions between adhesive and PET film have been supported by the molecular mobility, observed by dielectric relaxations. The mobility of the adhesive appears influenced by this of the PET support.

In conclusion, the physical structure and the adhesion are analysed by calorimetry and confirmed by dielectric analysis. The storage duration of the adhesive tape is an important parameter for the mechanical strength of the polymer system.

Molecular mobility in a polyepoxy adhesive under hydrothermal ageing conditions by Broadband Dielectric Spectroscopy measurements

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During spacecraft integration - in clean room - materials are used under humid and thermal controlled conditions. During the operational mission in flight, typical environmental conditions are a combination of vacuum and thermal cycling. The characterization and the simulation of ageing phenomena in bonded assemblies are a challenge to improve their conception and their durability. Checking these assemblies after the launch is impossible. One alternative is to use accelerated testing based on space industry knowledge and ESA normative data. But, the link between accelerated testing and true ageing is unknown. The aim of this study is to shed some light on this correlation.

This study concerns an epoxy-amine adhesive used in aluminium assemblies. The joint is cured for 7 days at 21 ± 2°C, 50 ± 5%HR. The curing conditions for this study are the same as those applied during the manufacturing process. We will focus on ground ageing (also called humid ageing).

During accelerated hydrothermal ageing tests, the joints are exposed to a warm humid environment during 7 days. The temperature range is from 20°C to 80°C (step=20°C) and the relative humidity in the range from 20%HR to 100%HR (step=20%HR). Real ageing process consists in sampling bonded assemblies after different ageing times spent in clean room.

Dielectrical experiments were carried out using broadband dielectric spectroscopy. It gives information about molecular mobility in wide temperature and frequency range (from -150 to 150°C, 10^{-2} to 10^{6} Hz).

The first step is to identify relaxation phenomena related to molecular motions in the studied adhesive after curing. The epoxy-amine system exhibits five relaxation modes. The numerous studies devoted to relaxation phenomena in polyepoxy systems permits to identify these modes. In this study, we will focus on γ associated with CH_2 mobility in aliphatic chain sequences, β_1 associated with hydroxyether mobility and α the dielectric manifestation of glass transition.

After simulated and real ageing, γ, β_1 and α behaviours change compared with after curing properties. Relaxation times and activation energy associated with molecular mobility is studied. It allows us to understand the evolution of the studied adhesive with hydrothermal ageing from localised to delocalised scale.

Scanning of the molecular mobility in a peptides/collagen system by thermal analysis.

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The diversification of the applications of collagen, peculiarly in the health domain, was supported by the improvement of the scientific knowledge. In the cardiovascular research, one of the major functional problem is the poor long term durability of bioprostheses essentially due to calcification and fibroblast proliferation. Consequently, a new material with collagen and peptides was synthesized. The particularity of this new biomaterial is the addition of functionalized peptides which could be able to allow the cross-linking between collagen and elastin with molecules of same nature, potentially suited to take part in the physiological process of degradation and regeneration as original tissue.

The aim of this work is to specify the influence of treatments on the chain dynamics of new collagen. For this purpose, four kinds of samples were analyzed: pure collagen, collagen irradiated with UV (λ=254 nm), collagen mixed with peptides and collagen mixed with peptides and irradiated with UV (λ=254 nm).

The influence of different parameters such as irradiation or addition of peptide and the molecular mobility of these samples were studied in FT-IR (Fourier Transform InfraRed), DSC (Differential Scanning Calorimetry) and TSC (Thermally Stimulated Currents).

FTIR spectra were similar for the four sets of samples without any significant differences between the vibration bands of C-H, amid I and II of differently treated collagen.

The DSC analyses revealed a decrease of the collagen denaturation temperature for all the treated collagen, implying a slight destabilizing effect of treatment on the thermal stability of the triple helix domain of collagen.

The analyses by TSC highlighted the influence of the irradiation on the chain dynamics of collagen with and without peptides. Indeed, the relaxation temperatures represent a fingerprint of each constituent on the complex dynamic structure in connective tissues, and the analysis of compensation phenomena is useful to define the specific answer of these constituents. The TSC analyses showed an evolution of the localized motions with the UV irradiation. A restriction of cooperative motions was observed, probably due to the rupture of physical bonds (such as hydrogen bonds). Moreover, a scission between proper collagen motions and proper peptides motions was observed for the collagen/peptides mixture. Finally, for the collagen/peptides mixture submitted to UV irradiation, a coupling was observed between the collagen and peptides localized motions, with a chain dynamics quite similar to the pure collagen.

These preliminary analyses suggest a crosslinking effect of irradiation between collagen and peptides. These results are quite promising for the conception of a new type of collagen.

In order to optimize the characterization of the collagen/peptides system analyses will be made with less damaging UV (λ=366 nm).

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Thermal-and Photo-switching of the dielectric permittivity of spin-crossover complex observed by broadband dielectric spectroscopy

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Thermal-switching [1, 2] of the dielectric constant has been demonstrated experimentally for the spin-crossover compounds. The conversion between the high spin (HS) (S=2) and low spin (LS) (S=0) states can be triggered by temperature and irradiation by light [3, 4, 5]. The thermal variation of the dielectric constant displays hysteresis loop corresponding to a spin transition temperature. The change in dielectric constant results from structural modifications accompanying the spin-state change and is correlated through DFT calculations with the change in electronic polarizability [2].

Photo-induced changes in the dielectric properties of the spin-crossover complex $[Fe(Ligand)(CN)_2]$ H_2O were measured at 100 K using broadband dielectric spectrometer under Ar^+ Laser beam irradiation. The dielectric constant upon irradiation displays a partial spin state transition to the HS state [5]. A slow polarization relaxation from light-induced metastable state was observed after laser source was switched of and the stable LS state is reached after more than 12000 s at 115 K. These results are in good agreement with magnetic susceptibility measurements.

The electric detection of photo-induced spin-state changes opens new opportunities for the use of spin-crossover complex as switchable capacitors in electronic devices for information storage.

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Interplay between the charge transport phenomena and the charge-transfer phase transition in FeMn Prussian Blue Analogues using Broadband Dielectric Spectroscopy

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Charge transport and dielectric measurements were carried out on compacted powder and single-crystal samples of bistable $Rb_xMn[Fe(CN)_6]_y.zH_2O$ in the two valence-tautomeric forms ($Mn^{II}Fe^{III}$ and $Mn^{III}Fe^{II}$) [1-5] as a function of temperature (120-350 K) and frequency (10^{-2} to 10^6 Hz) using broadband dielectric spectroscopy. The complex conductivity data $\sigma^*(\omega)$ reveal universal conductivity behavior and obey the Barton-Nakajima-Namikawa (BNN) relationship [5]. The charge transport is accompanied by a dielectric relaxation that displays the same thermal activation energy as the conductivity. Surprisingly, the activation energy of the conductivity was found very similar in the two valence-tautomeric forms (ca. 0.54 ± 0.03 eV) and the conductivity change between the two phases is governed mainly by the variation of the pre-exponential factor [6]. The phase transition is accompanied by a large thermal hysteresis of the conductivity and the dielectric permittivity [2- 4] In the hysteresis region, however, a crossover occurs in the charge transport mechanism at T < ~220 K from an Arrhenius-type to a varying activation energy behavior conferring an unusual “double-loop” shape to the hysteresis.

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Broadband dielectric spectroscopy of organic/inorganic ferroelectrics nanomaterials

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In the last decades, a great interest has been devoted to ferroelectric polymers, but their low activity prevents them from wide applications. Specific electroactive activity of inorganic ceramics and attractive engineering behaviour of polymers can be combined. For this purpose, ferroelectric inorganic nanofillers have been dispersed in a thermoplastic polymer, to improve their electroactive properties and to realize hybrid nanocomposites [1].

In this work, polyamide 11 (PA 11) has been chosen as matrix and barium titanate (BT) nanoparticles ranging from 50 to 700 nm as fillers. Polymer/$BaTiO_3$ 0-3 nanocomposite with a volume fraction of BT ranging from 0.024 to 0.4 was elaborated by solvent casting method and hot pressing to form films of 100 µm thick. As the coercitive field of BT is much lower than the coercitive field of polyamide 11, unpoled polymer/ poled BT composites were elaborated. Suitable piezoelectric and pyroelectric activity was obtained close to the poled polyamide 11 with composite of 20% in volume of BT.

The quality of the dispersion of nanoparticles into the polymeric matrix at a nanometric scale has been checked by Scanning Electronic Microscopy. A good dispersion of nanoceramic into the organic matrix is required to ensure a synergy between physical properties of organic and inorganic components.

Specific properties of the matrix (dielectric properties, cristallinity rate) and of the nanoceramic as a function of size (physical structure, dielectric properties) have been measured for the purpose of optimization.

Physical characterization of unpoled composites has been performed by means of thermal analysis (thermogravimetric studies, differential scanning calorimetry). The dielectric behaviour has been analysed by broadband dielectric spectroscopy (DDS) and thermo stimulated current technique (TSC).

The influence on the dielectric properties of the fillers nanosize, the volume fraction of BT on the one side and molecular mobility of polyamide 11 one the other side was studied.

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Broadband Dielectric and Conductivity Spectra (1 kHz - 2 THz) of Strain Sensitive Polyisoprene-Carbon Nanocomposites

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Polyisoprene-carbon nanoparticle composites (PCNC) possessing a giant electric resistance dependence on mechanical strain near the percolation threshold [1] were studied by broadband dielectric spectroscopy. Dielectric permittivity (ε'), dielectric loss (ε'') and conductivity (σ) spectra of the composites were measured at room temperature in a very broad frequency range (100 Hz – 2 THz) using low frequency, high frequency, microwave and terahertz techniques.

Dielectric/conductivity dispersion was observed in the whole frequency range of our study. Increase of a carbon nanoparticles (CNP) concentration results in: 1) increase of the composites' dielectric permittivity, loss and conductivity in the whole frequency range; 2) enhancement of the frequency dependence of permittivity and loss; 3) weakening of the frequency dependence of conductivity. The power-law dispersion of conductivity and permittivity characterizes response in the microwave and THz range for all studied PCNC. For the compositions with low CNP content, below the percolation threshold, it also prevails at low and high frequencies. For the compositions with high CNP content, above the percolation threshold, the conductivity tends to saturate at low frequencies, loss maxima are observed and the conductivity plateau screens the power-law dispersion at low frequencies. We attribute the low-frequency conductivity plateau to the dc CNP network conductivity (in percolated clusters) and the high-frequency power-law dispersion – to the local ac CNP conductivity in finite clusters (i.e., to the dynamics of the charge carriers in the fractal conducting network). No anomaly of conductivity with CNP concentration increase was observed near the percolation threshold in the microwave and THz ranges, while there is by four orders of magnitude increase of the dc conductivity. This proves that the strain sensing effect in PCNC should be related to the dc CNP network conductivity (to the creation of percolated clusters). Two contributions to the power-law dispersion were revealed. We suppose that, apart from the ac CNP conductivity in finite clusters, an inter-cluster polarization of the insulating polymer matrix makes the contribution. The ac CNP conductivity mechanism dominates at high frequencies, while the inter-cluster polarization prevails in the THz range.

Thus our broadband dielectric spectroscopy study reveals three mechanisms contributing to the dielectric and conductivity responses of PCNC. They can be attributed to: 1) dc CNP network conductivity in percolated clusters responsible for the low-frequency conductivity plateau; 2) ac CNP conductivity in finite clusters; 3) inter-cluster polarization of the insulating polymer matrix. The last two mechanisms are responsible for the power-law dispersion observed above 1 MHz.

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Ac conductivity analysis and dielectric dispersion in unidirectional PZT fibres/epoxy resin composites

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Abstract

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. Firstly, the dipolar relaxation mechanisms were revealed in the frequency range and temperature interval of the measurements. Secondly, the ac conductivity data are analysed 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.

Keywords: Composite materials; Polymers; Dielectric response; Ionic conduction

Electron emission kinetics from lithium niobate crystal

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Thermostimulated electron emission (TSEE) from the surface of ferroelectric materials attracts attention both from the basic and applied points of view. Among various aspects of the emission problem a prominent place is occupied by the issues concerning kinetics. Research of emission relaxation regularities, knowledge of the characteristic emission current decay times enables us to discuss the future application of ferroelectrics as cold emitters and understand the principle mechanisms of the emission phenomena in crystals more thoroughly.

The results of investigation of emission current relaxation from the surface of the lithium niobate crystal are presented in the present paper. The emission current was measured under standard procedure in vacuum of 10^{-5} mm hg in the temperature range of 20÷100 °C, which is rather far form the phase transition point, which equals +1210 °C for lithium niobate.

In the above cited investigations of TSEE in TGS crystals in the vicinity of the Curie point (~49 °C) it was found out that TSEE from the surface of a ferroelectric may be observed only under the change of spontaneous polarization of the crystal. When temperature stabilizes a distinctive decline of emission current is observed. The obtained emission current relaxation curves for lithium niobate samples at various stabilization temperatures are presented herein (Fig. 1). The connection between emission properties of a ferroelectric and the change of its spontaneous polarization was experimentally proved. When sample temperatures stabilizes the emission decline is observed, which is closely approximated by the exponential law. The calculation, carried out by taking the logarithm of experimental curves showed that the characteristic decay time in the temperature range under investigation declines with the temperature increase from 16 minutes at 55 °C to 3 minutes at 85 °C.

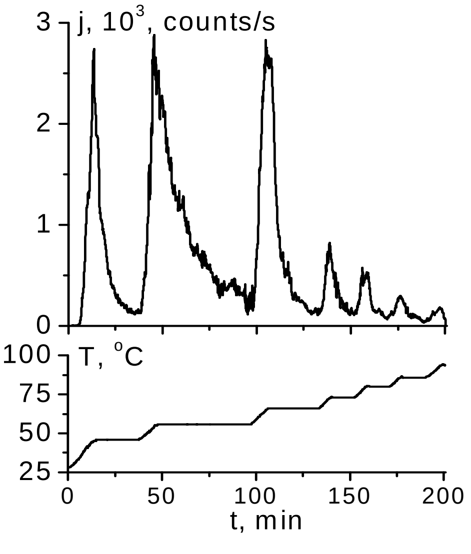

Fig.1 TSEE current relaxation in lithium niobate crystal.

The results of the presented research are in good correlation with the model of autoelectronic emission from the surface states in ferroelectrics.

Experimental study on dielectric relaxation in Alfa fiber reinforced polyester composites

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Over the past decade, there has been a growing interest in the use of lignocellulosic fibers as reinforcing element for polymer matrix. The specific properties of fibers, such as low cost, light weight, renewable character, high specific strength and modulus, availability in a variety of form throughout the world, reactive surface and the possibility to generate energy, without residue, after burning at the end of their life cycle, motivate their association with organic polymers to elaborate composite materials. These advantages, however, are reduced by the marked hydrophilic character of these macromolecules which, on the one hand, limits their compatibility with widely used hydrophobic polymer matrix and, on the other hand, can reduce the mechanical properties of the composite if moisture is absorbed as they age. Interfacial adhesion and resistance to moisture absorption of natural fiber composites can be improved by suitable modification of fiber surfaces.

In this work, investigation on dielectric properties of polyester composite based on cellulosic fibers has been carried on. Dielectric spectra were measured in the frequency range 0.1Hz-100 KHz and at temperature intervals from ambient to 170°C. Two relaxation processes were identified, namely the α mode relaxation associated with the glass transition of polyester matrix and interfacial or Maxwell-Wagner-Sillars relaxation that is attributable to the accumulation of charges at the Alfa fibers / polyester interfaces. The interfacial relaxation is used to test the influence of the surface treatment on the blocking nature of the interface. Dielectric relaxation analysis revealed that the chemical treatment of the fibers can strongly influence the dielectric properties and interfacial polarization processes in composites.

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Dielectric relaxation and cations hopping at aluminosilicate surfaces: water adsorption

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When applied to adsorption phenomena, Gibbs-Duhem equation shows that surface energy associated to ions trapping, i.e. exchangeable cations located at the surface, decreases with the increasing number of adsorbed molecules. In this work, we propose a microscopic representation of this phenomenon. It is based on a model describing the cation/surface interaction energy and its evolution upon water adsorption. This model provides a simple mathematical expression derived from Density Functional Theory in which the system, i.e. cation/surface, energy is a functional of the electronic density. Therefore, the adsorption of small molecules as water and the resulting modification of surface electronic density and, hence, of the electrical potential modifies the barrier for cation hopping[1,2]. The model presented here is favourably compared to experimental data of cation hopping barrier measured by dielectric relaxation, i.e. impedance spectroscopy and thermally stimulated current, on various aluminosilicate solids: zeolites (Na-Faujasite and Na-Mordenite) and clay minerals (Na-Montmorillonite Fig.1) upon water adsorption.

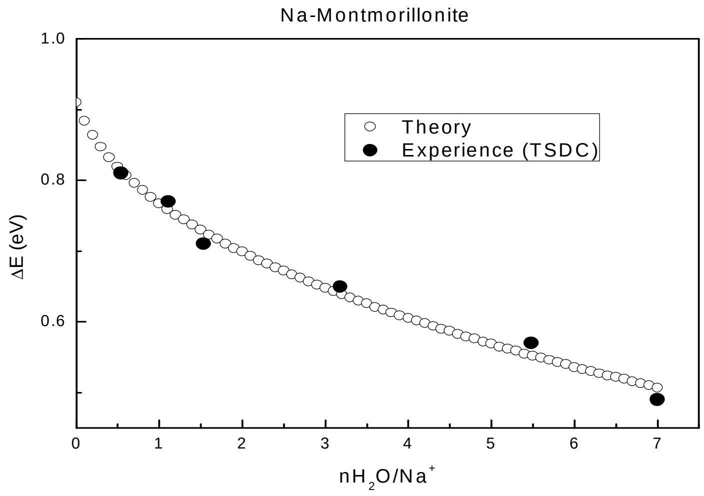

Fig. 1

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Uniaxial pressure effect on dielectric properties of $AgTaO_3$ single cristals.

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The $AgTaO_3$ single crystals were grown from high-temperature solution ($8Ag_2O$-$5V_2O_5$) by slow cooling. The crystallization process was carried out in temperature range from 1150°C to 930°C. Transparent slightly yellow crystals without inclusions of rectangular shape and dimension up to 5x3x3 mm^2 were obtained. The investigations of temperature dependence (30-550°C) of the electric permittivity of these crystals, stress-free and under stress (0-1000 bar) has been carried out. It was found that dielectric properties of $AgTaO_3$ are sensitive to applied stress. This includes the shift of phase transition, increase of the electric permittivity and makes its anomalies more effective. These effects can be caused by change in domain structure, the change of inter-ionic distances, change in density of defects and change in electric conductivity under the action of uniaxial pressure. The use of the $AgTaO_3$ for device application has also been indicated.

Modified open-ended dielectric probe used for comparison between cancer and healthy breast tissues. Test of a new method

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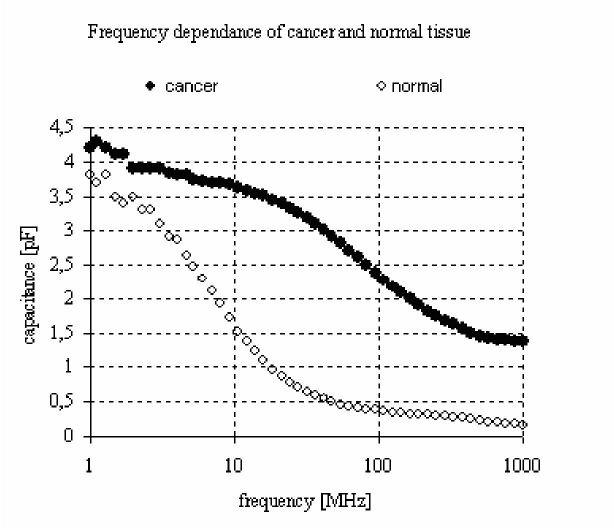
A new technique for middle operation malignant human breast tissue recognition is proposed. Using the open-ended probe with an additional separating dielectric film, we compared dielectric properties in the VHF frequency range of cancerous breast tissue samples coming from 131 patients. The modification changes considerably the dielectric response, but the differences between normal and cancer tissue are still detectable. The method was found to be not sensitive to existence of blood and electrolytes what considerably increases precision. The influence of additional layer on the dielectric characteristic of the probe were studied using a reference material. A model explaining the observed properties is presented and tested.

We found that in 94% of investigated cases the dielectric assignment is consistent with the histopathological one. High efficiency in differentiation between normal and anomalous tissue and facility to fulfilling of aseptic conditions is promising in cancer diagnostics. Basing in this concept prototypes of Intra-Operative Cancer Probes were designed and tested.



Dielectric properties of kaolinite intercalates - prospects of design of electromagnetic wave absorbers

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Kaolinite is the one of the most popular clay mineral. This platy mineral consists of plates built of parallel sheets. Single sheet consists of tetrahedral silicate layer (Si_2O_5) bound to aluminum oxide/hydroxide layer ($Al_2(OH)_4$), so that kaolinite belongs to 1:1 bilayered aluminosilicates.

Kaolinite exhibits an intriguing feature – possibility of guest molecules insertion between adjacent sheets (into an interlayer area). This process is called an intercalation. We will discuss the change of dielectric properties of the host material when polar molecules are intercalated. If only the guest molecules preserve ability to displacement or vibrations the increase of low frequency permittivity and energy absorption (close to the relaxation frequency) is observed. Measurements of the complex dielectric permittivity were performed in function of temperature (20-500°C) and frequency (10^3 – 10^6 Hz). Each material was characterized by X-ray powder diffraction, and thermogravimetric analysis. On the base of the performed experiments it is possible to propose a new class of electromagnetic wave absorbers based on natural kaolinite.

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DIELECTRIC SPECTROSCOPY OF A NEW PHOTOSENSITIVE REDOX POLYMERS

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Polymers based on coordination compounds of transition metals are promising materials for the design of sensor, chemotronic, photocatalytic, and electrocatalytic devices, as well as solid-phase electro-optical converters. The incorporation of transition metals has the potential to greatly expand the function and ultimate applications of conducting polymer systems. In conducting metallopolymers an understanding of the interactive roles that the metal centers and the organic polymer backbone play is in its early stages. Metal centers can provide efficient sites for redox conductivity. The most prospective compounds from the applied point of view are polymer structures based on the compounds of transition metals and Schiff bases (Salen) with a sufficiently high chemical stability and electroactivity [1, 2].

In this work, we have studied the polarization properties of a novel redox metallopolymers with photo- and electrical activity. The procedure for the synthesis of novel polymer based on the transition metal complexes of Ni by partial electrochemical oxidation method and a model of polymer structure are described. Dielectric behavior has been analyzed with dielectric relaxation spectroscopy as the main technique using precision LCR-meter and parallel plates. Dielectric measurements were performed at constant temperature by taking frequency scan in the range of 10Hz – 1MHz and temperature interval from 293 to 380K.

Relaxation times and activation energy of the observed polarization processes are determined. Making use of the hopping conduction model, measured frequency spectra is explained. Variations in the dielectric permittivity and losses of samples were observed to increase with the intensity of the illumination at low frequencies. Phenomenological model of this effect is discussed. Photoinduced charge transfer in reduced form of the polymer was detected. It is shown that it is possible to create a new generation of molecular rods functioning under the action of electrical field and white light. The hopping exchange of electrons between poorly mobile redox centers embedded in the polymer matrix with a low electronic conductivity can bring about the generation of dipoles, which leads to a further polarization of the polymer structure .

The received experimental results have shown that dielectric spectroscopy is the important tool for the in-situ study of electrophysical properties of a new type of redox polymers, and for the further optimization of such materials.

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Infrared spectroscopic characterization of dielectric thin films

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Abstract

The silicon oxynitride (SiOxNy) material is the subject of numerous studies over the past twenty years. This dielectric material has a good optical quality and electrical properties of both silicon composed (SiO_2 and Si_3N_4). The SiOxNy thin layer found many applications. These are good candidates for the realization of antistatic layer [1], high-reflectivity mirrors [2] and waveguides [3]. In microelectronics, they are used as insulator and passivation layer [4,6]. They are also considering to replace silicon oxide as dielectric gate in MOS (Metal-Oxide Semi-conductor) structure, whith is the aim of our study. The silicon oxynitride films were elaborated by Plasma enhanced chemical vapor deposition technique (PECVD) from a mixture of SiH_4, NH_3, NO_2 and N_2 with different gas flows. All samples have been thermaly annealing in a classic furnace at 400 ° C to 1000 ° C. Structure analysis of the deposited oxynitrure films where carried out by Fourier transform infrared spectroscopy or FTIR (Fig.1). The results of the FTIR analysis clearly show a decrease in the absorption bonds N-H and Si-H peacks intensity with the increase of the temperature. However, it is noticed that the maximum of absorption peak Si-N moves towards the high wave numbers as the temperature increases, with the appearance of the Si-O peak. This behavior can be explained by the gradual substitution of nitrogen atoms by the oxygen atoms which are more electronegatifs. This indicated the presence of two distinct phases SiO_2 and Si_3N_4.

Key words: Silicon nitride, FTIR, bonds.

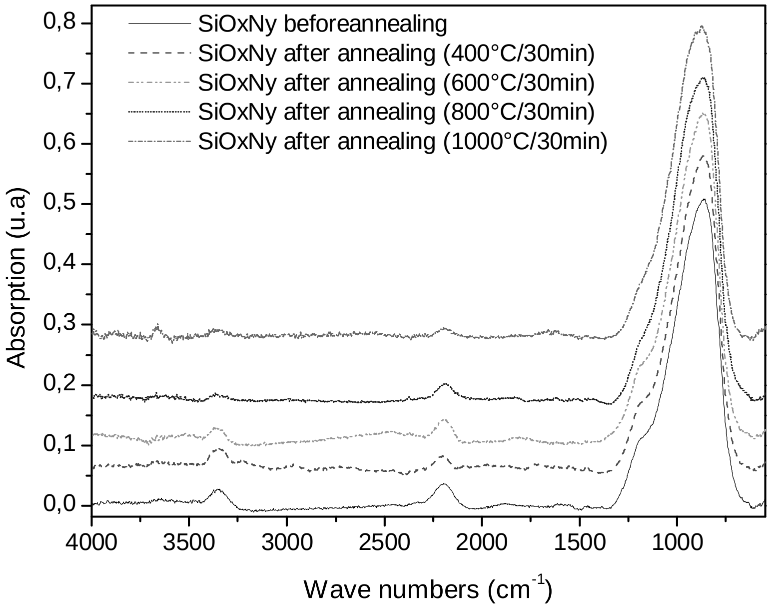

Fig. 1 : FTIR spectra of the silicon oxynitride thin

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Dielectric properties of superlattices comprising layers of disordered inorganic and organic para – and ferroelectrics

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We present the theoretical investigation of the ferroelectric phase transition, domain formation and dielectric relaxation peculiarities in a periodic multilayer structure consisting of alternate disordered ferroelectric (FE) and paraelectric (PE) layers of nanometric thickness. The layers can be either inorganic (like $KNbO_3$-$KTaO_3$ superlattice) or organic made from poly(vinylidene fluoride/trifluoroethylene) relaxor ferroelectric. Our analysis is carried out on the base of effective free energy of disordered ferroelectric or ferromagnet, calculated by us earlier [1,2] within the framework of our random field approach. In this approach, we consider both organic and inorganic disordered ferroelectrics as a result of influence of ensemble of impurities and defects of different kinds on certain ideal lattice of a host dielectric [1,2]. Above free energy, substituting the disordered dielectric or magnet by effective ordered substance, permits to apply the standard continuous formalism to calculate the static and dynamic dielectric properties of above substances. Using coupled system of Maxwell equations with those obtained by minimization of above free energy functional [3], we show the existence that the ferroelectric domains formed in the different FE layers interact with each other through the PE layers via an inhomogeneous depolarizing electric field emerging from the domains of the neighboring FE layers. We calculate the renormalization of ferroelectric phase transition temperature T_c as a function of the superlattice modulation period and its dependence on the concentration of defects and impurities of different kinds. Also, we calculate the temperature and frequency dependence of dielectric permittivity of superlattices comprising both above classes of ferro- and paraelectrics. Our theory can describe fairly well the experiments on the thickness dependence of different dielectric properties of above superlattices.

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Study of dielectric relaxation phenomena and electrical properties of conductive polyaniline based composite films.

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Among various conductive polymers, polyaniline (PANI) has attracted much attention due to its good chemical stability under the environmental conditions and its high electrical conductivity. However, PANI has some disadvantages such as fragility and insolubility in common organic solvents. One of the way to overcome these disadvantages is to blend PANI with traditional polymers in order to combine the electrical properties of the conducting polymer (PANI) and the good mechanical properties of the polymer matrix.

This study is focused on the preparation and characterization of the conducting composites based on polyurethane (PU) and polyamide-6 (PA-6) films as polymer matrix and PANI as the conducting polymer.

The composite PU/PANI and PA-6/PANI films were chemically synthesized by in-situ aniline polymerization in the presence of swelled PU and PA-6 matrices. Performed measurements of the swelling kinetics of PU and PA-6 films in aniline have shown that the maximum swelling degree for these films is 25 wt.% and 16 wt.%, respectively. In order to study the influence of the PANI content on the dielectric and electrical properties, the composite films were prepared with different aniline percentages (from 0.5 to 15 wt.%).

The performed dielectric measurements as a function of temperature and frequency have shown that the properties of composite films are close to those of the pure polymer matrix for the low PANI percentage. At higher PANI content (~2wt.%) two relaxations can be seen for PA-6 based matrix. In the same time for PU/PANI composite film only one relaxation was observed even at high PANI content (up to 22 wt.%). The found relaxation processes were explained as a phenomenon caused by the double layer structure of the composite film – one layer being PANI containing layer and the second one being pure polymer matrix. The activation energy values derived from the temperature dependencies of the dielectric relaxation time and the conductivity are very close that testify to the conducting nature of PANI containing layer.

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Dielectric spectroscopy study by time domain reflectometry (tdr)

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Abstract

Time domain reflectometry (TDR) has become a standard method for dielectric spectroscopy of polymers. One knows that the method offers rapid, non-destructive and automated measurement in a wide range of dielectric materials. Permittivity and electrical conductivity are determined from analysis of wave forms of signal travelling along transmission lines. The spectral analysis and the concept of input impedance are used to develop a wave propagation model for a TDR measurement system. It can account for dielectric dispersion of the device under test (DUT) and of course non uniform nature of the used transmission line. Finely from the knowledge of TDR impedance profile related to known dielectric properties, data measurements can be reasonably interpreted That is the aim of our paper ,specially the study of dielectric spectroscopy of some polymeric materials in frequency and temporal domains

A polar dielectric effect is characterized by a spectrum of relaxation which follows Debye's model when the relaxation time is slightly distributed

Generally the polar aspect appears through the frequency measurement of the dielectric permittivity of which the real part interprets dispersion and the imaginary part interprets the absorption.

We propose a process which allows the instantaneous description of polar dielectric material without conductivity or with a poor conductivity. Sample under test excited by a level of tension answers by another level of tension which is a temporal response, generally less well-known compared to the frequency answer

Key words: Polar dielectrics, Dielectric Spectroscopy, Time Domain Reflectometry

Dielectric Study of the Anti-Plasticization of Trehalose by Glycerol

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Recent measurements have suggested that the antiplasticizing effect of glycerol on trehalose can significantly increase the preservation times of proteins stored in this type of preservative formulation [1]. In order to better understand the physical origin of this phenomenon, we examine the nature of antiplasticization in trehalose-glycerol mixtures by dielectric spectroscopy. These measurements cover a broad frequency range between 40 Hz to 18 GHz (covering the secondary relaxation range of the fragile glass-former trehalose and the primary relaxation range of the strong glass-former glycerol) and a temperature (T) range bracketing room temperature (220 K to 350 K). We determine the temperature and composition dependence of the relaxation time τ describing a relative dielectric relaxation process appropriate to the characterization of antiplasticization. We observe that increasing the glycerol concentration at fixed T increases τ (i.e., the extend of antiplasticization) until a temperature dependent critical 'plasticization concentration' x_{wp} is reached. At a fixed concentration, we find a temperature at which antiplasticization first occurs upon cooling and we designate this as the 'antiplasticization temperature', T_{ant}. The ratio of the τ values for the mixture and pure trehalose is found to provide a useful measure of the extent of antiplasticization, and we explore other potential measures of antiplasticization relating to the dielectric strength [2]. We find that the antiplasticization of trehalose is accompanied by a significant decrease in excess permittivity ε_e. Moreover, the sharp change in ε_e from negative to positive at x_w of about 0.36 reflects the transition from a regime where glycerol antiplasticizes trehalose to one in which the strong glass formation of glycerol is modulated by the fragile fluid trehalose. Our data is consistent with expectation that the addition of glycerol makes trehalose a stronger glass former and that the addition of trehalose to glycerol makes the mixture a strong glass-former in the limits where the additive concentrations are low. Nevertheless, measurements at lower frequencies by dynamical mechanical or other methods are required to really prove that this expected behavior is true.

In bio-preservation applications, it is important to realize that this type of antiplasticization of glassy liquids only exists at low temperatures and that the same additive can serve to plasticize rather than antiplasticize at higher temperatures. The temperature at which this change occurs evidently gives basic information for the effective preservation of biological materials as well as for the adjustment of the properties of synthetic glassy polymers under processing conditions and in their applications in the field. As T_{ant} was found to be well below the glass transition temperature of the trehalose glycerol mixture and to decrease with increasing glycerol concentration, we see that increasing the concentration of antiplasticizer requires a lower temperature for the antiplasticization to be effective in the sugar-glycerol formulations.

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Shear induced conductor-insulator transition in carbon nanotube-polypropylene composites

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The blending of carbon nanotubes (CNT) into polymer matrices leads to novel materials whose properties depend strongly on the shearing rate and flow history[1]. We have constructed a rheo-dielectric spectrometer that allows simultaneous in-situ measurement of both the electrical conductivity $\sigma(\omega)$ and dielectric constant $\varepsilon(\omega)$ as a function of frequency ω, as well as basic rheological properties (viscosity, normal stresses), as part of an effort to better characterize how flow alters the properties of these complex fluids.

Measurements of conductivity indicate a conductor-insulator transition in melt-mixed dispersions of multi-wall CNT in polypropylene over a narrow range of CNT concentrations that is reasonably described by generalized effective medium theory (GEM). This novel conductor-insulator transition in σ can also be induced by shearing the fluid at a fixed CNT concentration (ϕ) near, but above, the zero shear conductivity percolation threshold. We find that the shear-induced conductor-insulator transition has its origin in the shear rate dependence of the conductivity percolations threshold (ϕ_c), which conforms well to our model that we introduced to describe this effect. According to this model, the quiescent value of ϕ_c is on the order of 0.12 vol. fraction %. (0.36 mass fraction %), while the structural relaxation time of the polymer matrix is about $\tau \approx 1$ s. The observation that ϕ_c increases with $\dot{\gamma}$ according to our model indicates that the $\dot{\gamma}$ field-induced alignment of the CNTs is along the fluid flow directions. Since ϕ_c and τ are universal parameters of the percolated network, our model can be used as a predictive tool in analysis of shear induced behavior of other materials.

The character of the dielectric loss peak extracted from the complex conductivity data indicates that the charge transport is due to multi-dimensional variable range hopping and that the dimensionality of the system decreases with shearing, consistent with the CNTs alignment discussed earlier. In the quiescent regime, the frequency dependence of the real part of conductivity follows a ‘universal’ power law scaling relation seen in many disordered materials.

Interestingly, under sufficiently high shear rates the conducting composite becomes a shear induced insulator. The conductivity of these non-equilibrium materials fully recovers upon cessation of flow. The results suggest that the presence of unstable mechanically strained structures in a stable elastic matrix (PP) can lead to materials with interesting mechanical damping characteristics.

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Relaxations theory

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The adequate use of dielectric requires an improvement of their properties as well as a good knowledge of these properties. For that progress are continuously awaited for comprehension of some elementary mechanisms; dielectric relaxation in polar materials is an example. A polar dielectric effect is characterized by a spectrum of relaxation which answers the model of Debye when the relaxation time is slightly distributed

Generally the polar aspect appears through the frequency measurement of the dielectric permittivity of which the real part interprets dispersion and the imaginary part interprets the absorption .We propose a process which allows the instantaneous description of polar dielectric material without conductivity or with a poor conductivity. Sample under test excited by a level of tension answers by another level of tension which is a temporal answer, generally less well-known compared to the frequency answer

We firstly consider standard materials well- known by their static and optical permittivity as their relaxation frequency; we proceed then to a modelling of the temporal answer which would be detected using a device based on temporal reflectometry for example; in this way we need a referential answer which can be either the short circuit or the open circuit

We know that the signal theory attests that any temporal detection is given in the form of a product of convolution in relation to the real answer and the system transfer function; the in convolution is fulfilled by the mathematical tool which is the transform of Fourier

From frequency measurements we follow the opposite way which leads to the form convoluted of the response suitable for dielectric polar considered. Tests on distilled water, butanol and Teflon were very conclusive; therefore we can consider by anticipation the response of materials which can be modelled with parameters encircled between those of Teflon and those of distilled water

Key words :Polar dielectrics, relaxation, absorption, dispersion

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