



Strasbourg (France)

E-MRS Spring Meeting 2002
June 18 - 21, 2002

SYMPOSIUM N

Nano and Micro-Composite

Symposium Organizers:

Michel Gerspacher, Forth Worth Research Center, USA

Rex P. Hjelm, Los Alamos National Laboratory, USA

Alain Le Mehaute, ISMANS, France

Robert Schuster, DIK, Hannover, Germany

François Tsobnang, ISAMANS, France

Papers will be published in Composites Science and Technology

SYMPOSIUM N

E-MRS 2002 SPRING MEETING

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Tuesday, June 18, 2002
Mardi 18 juin 2002

Morning
Matin

09:00 Introduction of the Symposium by all Co-Chairs

09:20 NANO AND MICROCOMPOSITES OF POLYMERS AND ELASTOMERS, MATERIALS AND THEIR REINFORCEMENT

Prof. Emeritus J.B. Donnet, ENSCMu/ICSI-Mulhouse, France

The enhancement of polymers and elastomers physical and mechanical properties which is called "reinforcement" and obtained using nano and/or micro particles as fillers, shall be illustrated by several actual examples from the carbon and silica solid particles family and the elastomers and polymers field.

The very high efficiency and flexibility of the fillers at disposal shall be emphasized and some new possible fillers briefly discussed, the current paths of research and developments will be presented. Finally the remaining important question to answer as to the complete satisfactory understanding of the reinforcement mechanisms at the molecular and/or atomic interactions level shall be underlined and the contrast between the striking advances obtained recently with the new characterization methods (physical and physico-chemical) and the still non solved fundamental al remaining questions will be shown.

Session I: Theory and Modelization

Session Chair: Michel Gerspacher

10:00 **N-I.1** SIMULATING MESOSCOPIC STRUCTURES AND DYNAMICS OF POLYMER INTERFACES USING DENSITY FUNCTIONAL TECHNIQUES

Toshihiro Kawakatsu, Department of Physics, Tohoku University, Sendai 983-0803, Japan

In order to simulate the structure and dynamics of polymer composites, it is important to appropriately model the architecture of the polymer chains, the chain conformation, the interaction between the chains and the surface of the dispersed particles, and so on. One of the useful techniques for this purpose is the density functional (DF) technique combined with the self-consistent field (SCF) description of polymer chains. This DF-SCF technique has been successfully used in predicting equilibrium interfacial structures in polymer composites. We extend this DF-SCF technique so that it can be applied to the dynamics of polymer interfaces in non-equilibrium states where the chains are strongly deformed by the flow field or by the external stress. Using this approach, we simulate various problems characteristic to the polymer composites, such as the dynamics of phase separating polymer blends, the interaction between two entangling polymer-blushes as a model of interacting filler surfaces, etc. We show that our approach overcomes the difficulties of the standard DF-SCF technique that is basically justified only for equilibrium or nearly-equilibrium systems.

10:40 **BREAK**

Session Chair: Robert Schuster

11:00 **N-I.2** ABOUT PREDICTIVE THERMODYNAMIC CALCULATIONS IN THE HYDROTHERMAL METHODS FOR Hap/ZrO₂ COMPOSITE FILMS SYNTHESIS

Lidia Cristea(a), Roxana Piticescu(b), (a)University Politehnica Bucharest, Anton Pann 48, Bucharest, Romania, (b)Institute for Non-ferrous&Rare Metals, 102 Biruintei Blv., Bucharest-Pantelimon, Romania

The non-conventional processes to obtain Hap/ZrO₂ composite films are colloidal sol-gel or hydrothermal, because these processes allow the stoichiometric control and also the formation products purity and morphology control.

The hydrothermal process has been chosen in this paper because it has some advantages like an ecological procedure, powder composition is easy to control and with this procedure can be obtained also whiskers of Hap with superior properties compared with pure hydroxyapatite.

This paper presents Eh-Ph diagrams with the stability domains of the different species in the water solutions. The Eh-pH diagrams are known as Pourboix Diagrams.

To estimate the behavior, in solution, in hydrothermal conditions of the aqueous species involved in the formation of hydroxyapatite has been drawn the Pourboix Diagrams for the systems Ca(NO₃)₂·4H₂O-NH₄H₂PO₄-NH₄OH, respectively Ca(NO₃)₂·4H₂O-NH₄H₂PO₄-Zr₂(NO₃)₄-NH₄OH.

It has been used the HSC Outokumpu program. All the predictive thermodynamic calculation were performed in IMNR SA, Bucharest, Romania.

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- 11:20 **N-I.3** **THE TOUGHNESS MECHANISM OF NANO-BIOCOMPOSITES BASED ON MULTI-SCALE INVESTIGATION**
Baohua Ji(a), Yong Kong(a), Huajian Gao(a,b), (a)Max Planck Institute for Metals Research, 70174, Stuttgart, Germany, (b)Division of Mechanics and Computation, Stanford University, Palo Alto CA 94305, USA
Hybrid organic-inorganic nano-biocomposite materials are known to exhibit superior mechanical strength and toughness in comparison with their protein and mineral constituents. In this paper, the mechanism of high toughness of nano-biomaterial is studied based on multi-scale modeling combining atomistic simulations with continuum treatments. In comparison with traditional composites, bio-composites exhibit very large modulus ratio between organic and inorganic constituents, which is believed to play a critical role in arresting microcrack growth and eliminating stress concentration at crack tips or other non-uniform deformation sites. The interface between organic and inorganic phases is also a key factor: partial debonding between these phases would result in significant modifications in the stiffness and strength. A better insight into the properties of the interface could be achieved through atomic level analysis and calculations. A continuum FEM code having cohesive modeling capability, the so-called Virtual-Internal-Bond (VIB) method, is used to model the deformation and fracture of organic and inorganic phases and their interface. We demonstrate that the VIB method can be used to simulate multiple crack nucleation and growth in a complex material system without ad hoc fracture criteria. We try to estimate the parameters in the VIB model by using ab initio calculation based on the density functional theory to study the binding energy between organic and inorganic phases.
- 11:40 Poster's Oral Presentation
- 12:00 **LUNCH**

SYMPOSIUM N

Tuesday, June 18, 2002
Mardi 18 juin 2002

Afternoon
Après-midi

Session I: Theory and Modelization
Session Chair: Jim Martin

- 13:40 **N-I.4** **THEORETICAL ASPECTS OF THE BOUND RUBBER PHASE**
Thomas A. Vilgis, Max-Plank-Institute for Polymer Research, Theory Department, 55021 Mainz, Germany
In this talk the theoretical aspects of the bound rubber phase in filled rubbers are discussed. The main emphasis is put on static and dynamic properties of chains localized at heterogeneous surfaces.
In carbon black (cb) and silica filled elastomers, the polymer adsorption on the filler surfaces is substantial as there exists a strong binding of the chains, leading to a layer of localized polymers, the "bound rubber". The surfaces of the filler particles are known to be rough and even fractal on many decades of their size, down to the molecular size range, as well as highly energetically heterogeneous: the distribution of interaction strengths can be characterized by high energy sites surrounding a relatively low energy background. Therefore in principle both kinds of disorder should be incorporated in a theory which is supposed to explain the bound rubber phenomenon. It was shown that any disorder enhances the binding of polymers and rubbers on the surface. The chains become localized and form the bound rubber phase. The special properties of the localized phase determine many features such as a contribution to the static modulus.
Another important feature of the chain localization is a significant change in the dynamics of the polymer segments. Indeed the local dynamics of the bound rubber phase will contribute to the high frequency behavior of the filled elastomer. Several experimental studies suggest even that the polymer segments close to filler surfaces show even "frozen" dynamics, which is also monitor by a strong decrease of the glass transition temperature. This can be already seen in simple dynamical scaling pictures which will determine the typical time scales. In the localized (bound rubber) phase the dynamics of the polymers is changed by two main points: (a) the dynamics of the different polymer segments is no longer the same for all Rouse modes. In the weak localization regime (less active fillers) the local segment dynamics are still determined by the typical time scales. The long wave length modes are frozen from certain modes, which are determined by a the strength of disorder, i.e., the filler activity. In the strong localization regime (very large filler activity), the dynamics of the localized (bound rubber) phase is changed completely. For a certain strength of the filler activity the chain dynamics appears glassy. Only local motions are possible. Of course, this means, that locally the glass transition temperature is increased by the filler activity (or disorder in the theoretical language).
- 14:20 **N-I.5** **SIMULATION OF NANOSTRUCTURED POLYMER MATERIALS: LINKING ATOMISTIC, MESOSCALE AND FINITE ELEMENT MODELS**
Gerhard Goldbeck-Wood and Simon McGrother, Accelrys, Cambridge, UK, Albert H. Widmann-Schupak, MatSim GmbH, Zürich, Switzerland
We have combined, in a hierarchical approach, commercially available software packages (from Accelrys and MatSim) to obtain mechanical and transport properties of nano-structured materials from atomistic information. For a system of arbitrary composition, we calculate Flory-Huggins interaction parameters for each pair of species using classical atomistic molecular dynamics in Accelrys' Materials Studio environment. These parameters become input to mesoscale algorithms (DPD and MesoDyn) which return the evolution of morphology and structure. A wide range of bulk properties can be obtained from such calculations, directly or by using the results as input to finite element methods such as Palmyra from MatSim. The overall method is illustrated by determining the nanostructure of polymer mixtures, and investigating the effect of compatibilizer on the structure as well as the mechanical and transport properties. The results will be discussed with reference to experimental observation.
- 15:00 **N-I.6** **STRUCTURAL CHARACTERIZATION OF SEGMENTED POLYURETHANE BY SMALL ANGLE NEUTRON SCATTERING**
Loren I Espada, Joseph T. Mang, E. Bruce Orlor, Debra A. Wroblewski, David A. Langlois and Rex P. Hjelm, Los Alamos National Laboratory, Los Alamos NM 87545, USA
The beneficial mechanical properties of segmented polyurethanes derive from microphase separation of immiscible hard and soft segment-rich domains at room temperature. We are interested in the structure of the domains, how these are affected by hydrolytic aging, and how the structure is modified by low molecular weight plasticizers. Segmented poly(ester urethane) with various weight fraction hard segment content, both deuterated and non-deuterated were synthesized and the morphology assessed using small-angle neutron scattering. We also assessed the distribution of the plasticizer in polyurethane. We have analyzed the results in terms of a simple model in which the contrast, $\Delta\rho = \rho_H - \rho_S$ between the hard and soft segment-rich domains is varied by the amount of deuterated hard segments or presence of deuterated or hydrogenated nitroplasticizer, using the fact that $I(Q) \sim \Delta\rho^2$. Modeling results give us key information on the domain structure of polyurethane, the segregation of the hard and soft segments in each domain and determined that plasticizer partitions into the soft segment-rich domains.

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- 15:20 **N-I.7** **ROUGHNESS OF RUBBER COMPOUNDS SURFACES**
Claude Tricot
Experimental rough surfaces, such as road track or rubber interface, show uniform irregularities over a large range of scales. There exists a crossover value λ_0 such that the surface may be considered as fractal at a scale $\ll \lambda_0$, and smooth or even flat for $\gg \lambda_0$. Brownian surfaces are the best-known models for fractal surfaces, but they are not convenient here since the crossover is not observed. The same remark can be made on any self-affine or statistically self-affine model, which should therefore be disregarded in this case. We show that simple models can be constructed which fit better to the experimental data, with a well-defined crossover value. The fit is controlled by using multifractal techniques. For analyzing the irregularity, we prefer not to use the classical auto-correlation function which itself is very irregular. We develop specific roughness functions which average the local oscillations. The corresponding log-log plots are smooth and allow a precise estimation of λ_0 . Comparison is made between several surfaces obtained with different grades of carbon black and various mixing times, together with the unfilled polymer surfaces. Experiences show that the crossover value (around 10 microns) and the slope of the log-log plot (fractal dimension) does not vary much with the type of surface. The interesting parameter is the value of the roughness function at λ_0 . By using various mixing times we derive from this analysis a "roughness ratio" which is independent of the time and of the polymer. It characterizes the geometry of the filler and may help to give a precise description of the notion of dispersion.
- 16:00 **BREAK**
- Session II: Advanced Nano and Micro Composites
Session Chair: François Tsobnang
- 16:20 **N-II.1** **GENERATING STRANGE INTERACTIONS IN PARTICLE SUSPENSIONS: CLASSICAL MOLECULES AND PARTICLE FOAMS**
James E. Martin, Robert A. Anderson and Rodney L. Williamson, Sandia National Labs, Albuquerque NM 87185-1421, USA
We have discovered a method of generating strange interactions in particle suspensions. These interactions can be attractive or repulsive, and lead to a variety of unexpected effects, including stable particle clusters with molecular geometries, the emergence of a particle foam state, and amusing collective dynamics. Through this interaction novel isotropic particle structures can be made that cannot be produced by any other known means, leading to a new class of composite materials with unusual properties.
- 17:00 **N-II.2** **CARBON NANOTUBE – FLUOROPOLYMER NANOCOMPOSITES FOR APPLICATIONS IN EAP ACTUATORS AND PYROELECTRIC DETECTION**
D.L. Carroll, Clemson, USA
Recent studies in the rheology of fluoropolymer - nanotube composites have shown that excellent nanotube dispersion naturally results from simple blending techniques. These composites have been characterized using a wide variety of methods including XRD, TEM, electrical transport, optical scattering and pyro-electric coefficient determinations so that the overall architecture of the nanocomposite can be correlated with the properties. Specifically, property evaluations for insertion of these materials into applications including electro-active polymer actuators, pyroelectric detection, and supercapacitors have been made. In this talk, it will be demonstrated that drastic increases in the system capacitance, enhanced conductivity, as well as microstructural changes within the polymer matrix result from the nano-dispersant and can be exploited to provide superior performance in electro-active polymer applications as compared to the native polymer. This work represents an exciting new approach to modification of electro-active polymer properties.

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- 17:40 **N-II.3** **MAGNETIC ELASTOMERS: NEW CHALLENGE IN THEORY AND APPLICATION**
Miklós Zrínyi, Department of Physical Chemistry, Budapest University of Technology and Economics, 1521 Budapest, Hungary
Composite materials consisting of rather rigid polymeric matrices filled with magnetic particles are long time known and called magnetic elastomers or magnetoelasts. These materials are successfully used as permanent magnets, magnetic cores, connecting and fixing elements in many areas. These traditional magnetic elastomers have low flexibility and practically do not change their size, shape and elastic properties in the presence of external magnetic field.
The new generation of magnetic elastomers represent a new type of composites, consisting of small (mainly nano-sized) magnetic particles dispersed in a high elastic polymeric matrix. The particles couple the shape of the elastomer to the external magnetic fields. Since the particles can not leave the polymer matrix, so that all of the forces acting on the particles are transmitted directly to the polymer chains resulting in either locomotion or deformation. Shape distortion occurs instantaneously and disappears abruptly when external fields are applied or removed, respectively. Combination of magnetic and elastic properties leads to a number of striking phenomena that are exhibited in response to impressed magnetic fields. The appearance of the unique ability of such materials to change their size and mechanical properties in a reversible manner has inherent interest if for no other reason than the uniqueness having giant elastic response to magnetic polarization. Giant deformational effect, tunable elastic modulus, non-homogeneous deformation and quick response to magnetic field open new opportunities for using such materials for various applications. Since the magnetic fields are convenient stimuli from the point of signal control, therefore it is of great importance to develop and study such flexible magnetic systems. The presentation may be useful for design of active soft and large motion actuators, tuned vibration absorbers, stiffness tuneable mounts and suspensions.
- 18:20 **N-II.4** **CARBON NANOTUBES FIBERS**
C. Zakri(a), B. Vigolo(a), M. Maugey(a), P. Launois(b), A. Derre(a), P. Poulin(a), (a)Centre de Recherche Paul Pascal, Pessac, France, (b)Laboratoire de Physique du Solide, Orsay, France
Carbon nanotubes were discovered 10 years ago and have very interesting electrical or mechanical properties. In particular, they are 10 times lighter than steel and 6 times more resistant. Their potential industrial applications are important, especially related to their electromechanical properties which could emerge on new actuators. The problem is that the nanotubes powder issued from synthesis is relatively impure, few dense, disordered and then difficult to utilise.
We have proposed a new method of making up, which associates nanotubes in ribbons or fibbers. We elaborated a process using the strong anisotropy of nanotubes to form a macroscopic fibber of aligned nanotubes. The first step is a good dispersion of the hydrophobic material in water, using a surfactant. The second step is to force the dispersed nanotubes to re- aggregate into a shear and These fibbers have a diameter of a few tens of microns and can easily be manipulated. The observations we already realised show interesting properties. We have characterised these fibbers at the same time by X-ray diffraction, mechanical and electrical measurements.
- 19:00-19:20 Poster's Oral Presentation

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Wednesday, June 19, 2002
Mercredi 19 juin 2002

Afternoon
Après-midi

Session III: Advanced Nano and Micro Composites (Ctnd)

Session Chair: Patrick Bertrand

- 13:40 Poster's Oral Presentation
- 14:00 **N-III.1** **STRUCTURE AND MAGNETIC PROPERTIES OF FERROFLUIDS SUSPENDED IN GELS**
Alvaro V. Teixeira, Isabelle Morfin, Françoise Ehrburger-Dolle, Cyrille Rochas, Pierre Panine, Pedro Licinio, **Erik Geissler**, Laboratoire de Spectrométrie Physique UMR CNRS 5588, Université J. Fourier de Grenoble, B.P.87, 38402 St Martin d'Hères cedex, France, European Synchrotron Radiation Facility, ESRF, BP 220, 38043 Grenoble Cedex, France, Departamento de Física - ICEx, Universidade Federal de Minas Gerais, C.P. 70230.123-970 Belo Horizonte, MG, Brazil
When dispersed inside a gel matrix a ferrofluid loses its translational degree of freedom, but the particles remain free to rotate and locally deform the surrounding polymer matrix. Small angle neutron and X-ray scattering methods were used to investigate the structure of dilute suspensions of two different ferrofluids dispersed in soft polyacrylamide hydrogels. The particles both in the free fluid and in the gel are shown to be fractal aggregates composed of smaller elementary units of radius ca. 5 nm. The volume fractal dimension D of the aggregates is strongly sample dependent, taking the value 1.7 in one case and 2.9 in the second. In presence of a magnetic field the aggregates orient along the direction of the field, but owing to the translational constraint, are unable to form linear arrays as in the free fluid. At high magnetic field strengths (ca. 1 T), the magnetization of the elementary particles aligns along the field and the aggregates tend to stretch in that direction.
- 14:40 **N-III.2** **NEW ADVANCES IN POLYMER NANOCOMPOSITES**
Emmanuel P. Giannelis, Department of Materials Science and Engineering, Cornell University, Ithaca NY 14853, USA
Work in polymer nanocomposites has exploded over the last few years. The prospect of a new materials technology, which can function as low-cost alternative to high-performance composites for applications ranging from automotive to food packaging to microelectronics has become irresistible to researchers around the world. In this talk I will review our current efforts in nanocomposites for applications ranging from batteries to tissue engineering. Additionally, I will focus on correlating their properties to nanostructure and interfacial dynamics.
- 15:20 **N-III.3** **FORMING SPATIALLY ORDERED NANOCOMPOSITES FROM MIXTURES OF NANOPARTICLES AND BLOCK COPOLYMERS**
Russell B. Thompson, Jae Youn Lee, David Jasnow and **Anna C. Balazs**
The interactions between mesophase-forming copolymers and nanoscopic particles can lead to highly organized hybrid materials. The morphology of such composites depends not only on the characteristics of the copolymers, but also on the features of the nanoparticles. To explore this vast parameter space and predict the mesophases of the hybrids, we developed a mean field theory for mixtures of soft, flexible chains and hard spheres. We apply this theory to a blend of AB diblock copolymers and a mixture of spherical nanoparticles. The particle mixtures contain both A and B spheres or spheres that display a dispersity in size. The introduction of particle mixtures leads to novel effects in the distribution of the solids and the overall morphology of the system. We rationalize our findings through a scaling theory in the strong segregation limit. Our results indicate that particle mixtures can be exploited to modify the mesophases of the diblock copolymers and thereby create nanocomposites with new structures.
- 16:00 **BREAK**

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Session IV: Material Reinforcement/Toughening

Session Chair: Marilyn Hawley

- 16:20 **N-IV.1** **DESIGNING NANOSTRUCTURED PARTICULAR FILLERS FOR ELASTOMERS. ROLE OF NANOSTRUCTURE AND POLYMER FILLER INTERACTIONS IN RUBBER REINFORCEMENT**
Jacques Persello, Université de Franche-Comté, LCMI, 25030 Besançon, France
The incorporation of filler into elastomers imparts many interesting and useful properties to the particle filled composite material. It is well known that the properties mainly depends on the dispersion condition of filler particles and their principal relevant properties : particle size, surface area, aggregate structure, surface activity and on rubber filler interactions.
We present some qualitative ideas on the reinforcement mechanism of rubber filled with nanostructured aggregates of silica. Self assembling concepts are used in order to explain the role of the silica-rubber and silica-silica interactions on the positioning of silica aggregates in three dimensional structures. Osmotic compression allows us to confinement of particles domains which sizes are determined by the hydrodynamic forces in the system. The osmotic pressure, or its volume derivative, the bulk modulus, is used as a physical parameter directly related to these interactions. Depending on the nature of the silica-rubber and silica-silica interactions, phase separation may be induced in filled elastomer systems. The phases of interest are the disordered "silica domain" and the long range correlated "silica network".
The nature of the Silica surface have a strong influence on the macroscopic properties of Silica-filled rubber compounds. Not only does it affect the compounding process, but it also dictates properties like rolling resistance, and Payne effect. Its surface properties can be controlled by reacting with silanes compounds.
From a practical point of view, this presentation is concerned with investigations using model rubber systems to experimentally elucidate the role of the morphology of silica aggregates and of the surface modification with polysulfidic organosilanes on the rubber - silica bonding, silica particles "dispersability" in the rubber network and of the long range structure of the silica network. The model systems consisting of hydrocarbon and silicone elastomers filled with different nanostructured silica aggregates, is investigated with regard to their dynamic viscoelastic properties and structural properties. The effect of various coupling agents is examined in order to demonstrate the specific role of the filler-elastomer interactions.
Small Angle Neutrons Scattering (SANS) techniques is used to study the short range arrangement of silica aggregates and the structure factor of the filled elastomer system. It have been shown that the structure factor is an important means in the characterization of the interaction forces between the silica aggregates.
Rubber reinforced with nanostructured aggregates of silica, develop a long range structure which have the scale invariance of a fractal object. The structure obtained have a density-density correlation function and can be probed by electronic microscopy observations.
- 17:00 **N-IV.2** **RHEOLOGICAL PROPERTIES OF NANOFILLED POLYMERS: FILLER-MATRIX INTERFACES AND NON-GAUSSIAN CHAIN STATISTICS**
S.S. Sternstein and Ai-Jun Zhu, Materials Science and Engineering Department Rensselaer Polytechnic Institute, Troy NY 12180, USA
The dynamic mechanical moduli of filled elastomers are highly nonlinear with strain amplitude. An erroneous conclusion drawn by many from Payne's and similar studies is that filler network formation is solely responsible for this nonlinearity, and that the polymeric nature of the fluid is irrelevant. In this paper, we demonstrate that polymeric melts with filler levels well below the percolation threshold exhibit levels of viscoelastic nonlinearity comparable to those due to filler network formation observed in other systems. It is shown that the polymeric matrix is responsible for both the strain nonlinearity and abnormally high levels of reinforcement by the filler. Experimental studies on nanofilled, but uncrosslinked, polymer melts are reported both at and above T_g, with filler concentrations up to 12 % vol. and with various filler surface treatments and matrix molecular weights. The rheological evidence all point to a unified conclusion, namely that the high reinforcement by nanofillers results from a trapped entanglement network that promotes highly non-Gaussian (Langevin) chain behavior. The relaxation of dynamic moduli with strain amplitude is due to the release of these trapped entanglements, a stress assisted kinetic process. Data around T_g support the conclusion that the interaction is largely a surface phenomenon, and that the far field effects seen in the filled melts are due to the trapped entanglement interactions, which can only be probed at large strains.

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- 17:40 **N-IV.3** **A STUDY OF THE EVOLUTION OF LAMELLAR MESOSTRUCTURED SILICA UPON HEATING**
C. Henrist, Laboratory of Inorganic Structural Chemistry, University of Liège, building B6, 4000 Liège, Belgium, M.A. Rodriguez, Ceramics and Glass Institute, C.S.I.C., Arganda del Rey, 28500 Madrid, Spain, R. Cloots, Laboratory of Inorganic Structural Chemistry, University of Liège, building B6, 4000 Liège, Belgium
It is reported a study of the structural evolution of a lamellar mesostructured silica subjected to a progressive heat treatment in order to highlight the phenomenon's that take place and the characteristics of the resulting calcined powder. By combining information from several physical methods, i.e. TG-DTA, XRD, TEM, nitrogen adsorption and FTIR, it has been possible to evidence the formation of very thin sheets of nearly crystalline silica at a temperature around 450°C, exhibiting a very high value of aspect ratio, consequently to the template loss by combustion. At a temperature higher than 530°C, the dehydroxylation phenomenon promotes a decrease in the surface area, followed by the sintering process at higher temperature which nearly annihilate the surface area of the particles.
- 18:00 **N-IV.4** **NANO-POROSITY IN SILICA REINFORCED METHYLTRIMETHOXYSILANE COATINGS STUDIED BY POSITRON BEAM ANALYSIS**
R. Escobar Galindo, A. van Veen, H. Schut, Interfaculty Reactor Institute, Delft University of Technology, Mekelweg 15, 2629 JB Delft, The Netherlands, A.R. Balkenende, Philips Research Laboratories, Prof. Holstlaan 4, 5656 AA Eindhoven, The Netherlands, G. de With, Eindhoven University of Technology, 5600 MB Eindhoven and J.Th.M. De Hosson, Materials Science Centre, Nijenborgh 4, 9747 AG Groningen, The Netherlands
The aim of the present work is to study porosity in particle reinforced sol-gel coatings. Silica particles are introduced in MethylTriMethoxySilane to increase the hardness, the elastic modulus and the fracture toughness. Earlier measurements showed that the improvement of mechanical properties was lower than expected. These results suggested a porous structure in the matrix, but alternatively the particles might also be porous. Positron Beam Analysis (PBA) using the Doppler Broadening (DB) technique and positron lifetime measurements were performed for detailed structural analysis. Four samples with different volume concentrations (10, 20, 33 and 63%) of silica particles of typically 100nm in diameter and treated at different curing temperatures (623 and 723K) were measured. With increasing filler content we observed a decrease in the positron annihilation parameter. By neglecting positron diffusion we can separate porosity in the matrix from that in the particles. This assumption is valid as long as the expected positron diffusion length is short compared to the size of the filler particles, as is in our case. A more detailed description takes into account the local environment of the filler particles affecting their adhesion to the matrix. In addition, the interfacial adhesion properties of the coating as a function of the filler content studied by DB during in-situ 4-point bending tensile or compressive condition will be discussed.
- 18:20 Poster's Oral Presentation

SYMPOSIUM N

Thursday, June 20, 2002
Jeudi 20 juin 2002

Morning
Matin

Session V: Material Reinforcement/Toughening (Ctnd)

Session Chair: Waldeck Zerda

- 08:30 **N-V.1** **SMALL-ANGLE SCATTERING INVESTIGATION OF UNSTRAINED AND STRAINED NANOCOMPOSITE MATERIALS**
Françoise Ehrburger-Dolle, Erik Geissler, Isabelle Morfin, Cyrille Rochas, Laboratoire de Spectrométrie Physique, UMR 5588, Domaine Universitaire, 38402 Saint Martin d'Hères Cedex, France, Françoise Bley, Frédéric Livet, Frédéric Picca, Laboratoire de Thermodynamique et Physico-Chimie Métallurgiques, UMR 5614, INPG, Domaine Universitaire, 38402 Saint Martin d'Hères Cedex, France
Elastomers are soft materials that can be reinforced by dispersion of nanosized solid particles. Common examples are silica or carbon black aggregates. However, the mechanism is still not yet fully understood. Most investigations are devoted to the measurement of macroscopic mechanical properties. Our work consists in investigating the structure of the aggregate network spreading throughout the matrix in the initial sample and its modification during and after straining (elongation). For this purpose, we have performed a first series of small-angle X-ray scattering (SAXS) measurements by using the synchrotron radiation (ESRF, French CRG beamline D2AM). The parameters involved are the type of elastomer (EPR and SBR), the method of crosslinking (sulfur or dicumyl peroxide) and its effect on the aggregate arrangement for different fillers (carbon black, hydroxylated or hydrophobic pyrogenic silicas). The dynamics of aggregate movement during elongation and its relaxation is investigated by dynamic light scattering (or photon correlation spectroscopy, PCS) for silica filled elastomer. For carbon black filled elastomers, this method cannot be used. Therefore we have performed X-photon correlation spectroscopy (XPCS) on both carbon black and silica filled elastomers. The aim of the lecture is to describe these methods and to show their usefulness in getting a deeper insight into the physics of nanocomposite deformation.
- 09:10 **N-V.2** **ELABORATION OF EVA-NANOCCLAY SYSTEMS- CHARACTERIZATION, THERMAL BEHAVIOUR AND FIRE PERFORMANCE**
S. Duquesne, C. Jama, M. LeBras, R. Delobel, Laboratoire des Procédés d'Elaboration de Revêtements Fonctionnels, ENSCL, 59652 Villeneuve d'Ascq, France and P. Recoourt, Laboratoire de Sedimentologie et Géodynamique, FRE 2255, USTL, 59652 Villeneuve d'Ascq, France
Polymer-clay nanocomposites are hybrid organic polymer inorganic layered materials with unique properties when compared to conventional filled polymers. The mechanical properties and the fire retardancy performance for clay nanocomposite, with clay mass fraction of 5%, show excellent improvement.
Several approaches can be followed to prepare nanocomposites, in particular, melt mixing. In this study, EVA-clay nanocomposites are obtained following this process. The effect of several process parameters on the structure of the nanocomposite are investigated. The materials are characterized using small-angle X-ray diffraction and electron microprobe analysis.
In a second part, the fire performance of EVA-clay nanocomposite systems are evaluated. Flame retardant properties are improved which can be explained by a condensed phase mechanism. A reinforced char layer is formed, which acts as an insulator and as a mass transport barrier, slowing the escape of the volatile decomposition products generated as the polymer decomposes.
- 09:30 **N-V.3** **MORHOLOGICAL CHARACTERIZATION OF SINGLEWALLED CARBON NANOTUBES-PP COMPOSITES**
L. Valentini, J. Biagiotti, J. M. Kenny, Materials Engineering Center, Università di Perugia, 05100 Terni, Italy, **S. Santucci**, Dipartimento di Fisica - Unità INFM, Università dell'Aquila, 67010 Coppito (AQ), Italy
Following their unusual mechanical and electronic properties, extensive studies on carbon nanotubes (CNTs) as nano-fibers to improve the performance of a matrix or to achieve new properties have been recently reported. One of the advantages of a CNT as a fiber is its large surface area that increases the interaction with the matrix. In this work, composite based on polypropylene matrix reinforced with singlewalled carbon nanotubes (PP-SWNTs), were produced using different nanotubes concentration. The characterization of these new materials was performed by differential scanning calorimetry (DSC), Raman and infrared spectroscopy (FTIR) in order to obtain information on the crystallization kinetics, possible interaction between these two materials and especially, on the modification of the nanotubes and their organization. The results indicate that nanotubes behave as effective nucleant agents for the crystallization of polypropylene. This effect with respect to the reinforcement concentration is more marked in the presence of a low SWNTs concentration. Raman spectroscopy was successfully applied to demonstrate that in the composite films, the crystallization kinetics is strongly affected by the distance between nanotubes in bundles because of a different intercalation of polymer.
- 09:50 **BREAK**
- Session Chair: Erik Geissler

SYMPOSIUM N

- 10:10 **N-V.4** **A NOVEL BUILDING BLOCK FOR THE CONSTRUCTION OF INORGANIC-ORGANIC MATERIALS**
Byoung-Suhk Kim(a) and **Patrick T. Mather**(a,b), (a)Polymer Program and (b)Department of Chemical Engineering, University of Connecticut, Storrs CT 06269-3136, USA
Recently, the self-assembly behavior of block copolymers and of hydrophobically modified polymers has been extensively studied as a building block approach to the processing of nanostructured materials on the molecular level. In this work, we synthesized the well-defined amphiphilic telechelics incorporating polyhedral oligosilsesquioxane (POSS) by direct urethane linkage between the diol end groups of poly(ethylene glycol) (PEG) homopolymers and the monoisocyanate group of a novel POSS macromer. Indeed, POSS macromers can represent interesting building units for the construction of organic-inorganic hybrid structures compared to other hydrophobic groups, such as linear aliphatic, aromatic, or fluorinated groups. The hydrophobicity of the amphiphilic telechelics was varied by using several PEG homopolymers of different molecular weight, resulting in control over molecular architecture by hydrophilic/hydrophobic balance. The synthesized amphiphilic telechelics were characterized by ¹H NMR, GPC, FT-IR, DSC, and TGA, revealing a relatively narrow and unimodal molecular weight distribution ($M_w/M_n < 1.1$) and having close to 2.0 end-groups per PEG chain. In our presentation, we will discuss the preparation of these materials and some details concerning association behavior of these amphiphilic telechelics in the solution and melt states.
- 10:50 **N-V.5** **INFLUENCE OF CARBON BLACK AMORPHOUS PHASE CONTENT AND SURFACE ACTIVITY ON CB FILLED COMPOUNDS.**
N. Tricás(a), E. Vidal-Escales(a), S. Borrós(a), M.Gerspacher(b), (a)Material Science Lab., Institut Químic de Sarrià, Universitat Ramon Llull, Via Augusta 390, 08017 Barcelona, Spain, (b)Sid Richardson Carbon Black Co., Fort Worth Research Center, 4825 N.Freeway, Fort Worth, Texas 76106, USA.
Carbon black has been used as filler in polymeric materials for many years due to its reinforcing properties. However, neither its structure beyond the aggregates nor its role in the vulcanization reaction, even though its catalytic effect is recognized, have been completely determined. One of the most wide accepted model (developed by Sid Richardson Carbon Co.) highlights the two different carbon structures found on the surface, small crystalline regions called crystallites and amorphous carbon. To date the crystallite edges are considered as the most active regions. Following this model, three different carbon blacks with similar size but different content in amorphous carbon on their surface were studied. The variation in the surface structure was compared with the size effect using regular N-110, N-220 and N-772. Another CB with very different surface activity was used to evaluate the influence of this parameter. As a result some of the final compound properties as the filler dispersion obtained by electrical measurements was found to be more dependent on the particle size and the surface activity. On the other hand the surface structure showed a relevant influence in the low strain viscoelastic properties although the size effect is still important. The vulcanization reaction was also altered by the different carbon phases on the particle surface. The curing process was studied using squalene as a MVC (model compound vulcanization) and HPLC as analytical tool to follow the reaction intermediates at different times.
- 11:00 **N-V.6** **FILLER PHASE DISTRIBUTION IN ISOBUTYLENE-BASED ELASTOMER COMPOUNDS**
Walter H Waddell and Andy H Tsou, ExxonMobil Chemical Company, Baytown Polymers Center, Texas, USA
Tapping-mode AFM is proven to be a powerful technique for evaluating the morphology of elastomer blends. Without staining or etching, polymer domains and fillers in cryo-faced elastomer blends can be obtained by the tapping mode AFM with strong contrast. The change in phase shift provides the material contrast based on mechanical property variations among various rubber compound components. Image processing and measurement of AFM micrographs ensure the proper phase assignment, and can provide quantitative information on elastomer blends. Precipitated silica and carbon black fillers, and processing aid partitioning between the elastomers in binary and ternary blends can be measured. Applications of quantitative AFM morphological analysis to design better isobutylene-based elastomer compounds are presented.
- 11:50 **N-V.7** **STUDY OF CARBON NANOTUBES EMBEDDED IN EPOXY USING ATOMIC FORCE MICROSCOPY**
K.T. Lau and S.Q. Shi, Department of Mechanical Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong
A composite material, carbon nanotubes embedded in epoxy was studied using the atomic force microscopy (AFM). The purpose of this study was to investigate the bonding properties of the two substances as a function of time. Carbon nanotubes were embedded into thin films of epoxy in room temperature. An AFM system was modified to allow the control of temperature of the testing materials from near 0°C to over 50 °C. The testing results will be discussed in terms of thermal stress and thermal expansion properties of nanotubes and epoxy materials.
- 12:10 **LUNCH**

SYMPOSIUM N

Thursday, June 20, 2002
 Jeudi 20 juin 2002

Afternoon
 Après-Midi

Session VI: Analytical Techniques/Characterization
 Session Chair: Françoise Ehrbuerger-Dolle

- | | | |
|-------|---------------|---|
| 13:40 | N-VI.1 | <p>DISTRIBUTION OF SILICA IN POLYMER BLENDS OBTAINED BY RAMAN MICROIMAGING TECHNIQUE
 T.W. Zerda, G. Song, TCU, Dept. of Physics, Fort Worth, TX, USA, W.H. Waddell, ExxonMobil Chemical, Baytown TX, USA</p> <p>Raman microimaging was used to estimate the effect of the silica filler on phase separation in binary and ternary polymer blends composed of BIMS, BR and natural rubber or SBR. Using a near IR laser operating at 785 nm wavelength we avoided sample degradation due to the laser induced heating and reduced the effect of fluorescence. Areas 10 micron by 10 microns were scanned with 1 micron step. At each point Raman signal was recorded and composition of the blend evaluated by fitting the whole spectrum to a theoretical spectrum. The domain sizes, concentration of polymer components within domains, and distribution of particulate silica filler were characterized for blends of different compositions. We found that: (1) addition NR or SBR improves distribution of the BR component in the blends; (2) SBR concentrates near or within the BR domains; (3) at large concentrations natural rubber forms its own network; (4) concentration of silica is increased near the edges of the BR domains.</p> |
| 14:20 | N-VI.2 | <p>EFFECT OF THE CARBON SUPPORT ON THE PERFORMANCE OF NON-NOBLE METAL-BASED CATHODE CATALYSTS FOR LOW TEMPERATURE FUEL CELLS
 Frédéric Jaouen(a,b), Sébastien Marcotte(a), <u>Jean-Pol Dodelet</u>(a), Göran Lindbergh(b), (a)INRS-Energie et Matériaux, C.P. 1020, Varennes, Québec, Canada, J3X 1S2, (b)The Institute of Royal Technology (KTH), Teknikringen 42, 10044 Stockholm, Sweden</p> <p>Non-noble metal catalysts for the reduction of oxygen in polymer electrolyte membrane (PEM) fuel cells are of current interest. As PEM fuel cells are acidic (pH ~ 1) it is impossible to use cathode catalysts made of non-noble metal particles. However, it is possible to obtain a catalyst for the reduction of oxygen by adsorbing a Fe salt (Fe acetate) onto a carbon support and heat-treating this material at 900°C in H₂: NH₃: Ar atmosphere. The following carbons have been used as a support to obtain the catalysts: Printex XE-2, Norit SX Ultra, Ketjenblack EC600JD, Acetylene Black, Vulcan XC-72 R, Black Pearl 2000, HS300 (Precommercial Graphite from Lonza), Special 1 and 2 (Precommercial Carbons from Sid Richardson), and a synthetic carbon made from the pyrolysis of perylene tetracarboxylic dianhydride (PTCDA). All these carbon supports were used either as-received or pre-pyrolyzed at 900°C in H₂: NH₃: Ar atmosphere before loading them with Fe acetate (0.2 wt % Fe nominal). The catalysts were physically and electrochemically characterized (X-ray Photoelectron Spectroscopy, gas porosimetry, rotating disk electrode and fuel cell tests). A large range of catalytic performance was obtained with these various supports. Good activities for oxygen reduction are obtained from catalysts that display sufficient surface concentrations of nitrogen (above 1 %), but other parameters have also to be taken into account to explain the observed activities.</p> |
| 14:40 | N-VI.3 | <p>MECHANISTIC ASPECTS OF THE ROLE OF COUPLING AGENTS IN SILICA-RUBBER COMPOSITES
 Jacques W.M. Noordermeer, Twente University, Fac. Chem. Techn., Enschede, The Netherlands</p> <p>Active fillers are used to enhance properties of rubber. Compared to carbon black, silica gives lower hysteretic losses in the rubber, for tyre applications leading to lower rolling resistance. Compatibility of hydrophilic silica with hydrophobic rubber polymer is poor. This compatibility is enhanced by adding bi-functional coupling agents, commonly bis-(triethoxysilylpropyl)tetrakisulfide (TESPT). However, the degree of hydrophobation of silica during rubber mixing is dependent on many mutually interacting factors. Irreproducible conditions during mixing and vulcanisation, combined with different possibilities of adding the coupling agents to the filler/rubber substrate are major causes of irreproducibility of silica-reinforced rubber compounds.</p> <p>The presentation will cover the mechanistic aspects of the reaction of various coupling agents, variants on TESPT with silica as well as with rubber. Important factors in the coupling agent itself are the sulfur rank (-S₄- and lower), the moment the coupling agent is added during mixing and corrections made for the lower sulfur ranks with elemental sulfur. Also discussed are the reaction kinetics between the coupling agent and the silica.</p> <p>Depending on the chemical composition of the particular coupling agent, the ultimate temperature obtained during the mixing process mainly governs the reaction of the coupling agent: formation of a silica &#8211; rubber bond vs. a premature reaction with the rubber leading to scorch phenomena.</p> |

SYMPOSIUM N

- 15:20 **N-VI.4** **SURFACE CHARACTERISTICS OF CARBON BLACK ON A NANOSCOPIC LENGTH SCALE**
A. Schröder, M. Klüppel, R.H. Schuster, Deutsches Institut für Kautschuktechnologie, Eupener Str. 33, 30519 Hannover, Germany and J. Heidberg, Institut für Physikalische und Elektrochemie der Universität Hannover, Callinstr. 3-3a, 30167 Hannover, Germany
The energetic surface heterogeneity of carbon black has been investigated by means of volumetric gas adsorption techniques. From very precise gas adsorption isotherms at a coverage of about 0.001 up to 1 monolayer of different molecular probes - comparable to polymer segments - the energy distribution functions of adsorption sites are calculated by an iterative analytical integration method. Four different species of energetic adsorption sites have been identified in all furnace black grades investigated. The fractions of the different adsorption sites e. g. the surface activity of the carbon black grades under consideration depends significantly on the manufacturing process and its conditions. For furnace black grades the site energy distribution is governed by the mean particle size. After heat treatment (graphitization) the surface becomes energetically homogeneous.
- 15:40 **BREAK**
- Session Chair: Walter Waddell
- 16:00 **N-VI.5** **STRUCTURE-PROPERTY RELATIONSHIP IN CARBON BLACK FILLED NATURAL RUBBER COMPOUNDS.**
E. Vidal-Escales, S. Borrós, Material Science Lab., Institut Químic de Sarrià, Universitat Ramon Llull, Via Augusta 390, 08017 Barcelona, Spain
A satisfactory understanding of the fundamental properties of carbon black (CB) is the focus of many research groups. This target leads towards the elucidation of structure-property relationship to develop tailored CBs for specific composites. Included in this research line, the present work lay out on the elucidation of the relationship between CB surface active sites and their interaction with polymer and vulcanization intermediate compounds from the composite polymeric phase. To achieve this objective, inverse gas chromatography (IGC) has been performed to elucidate the amount of surface active sites and their nature. Regular CB grades of different size as N-990, N-330, N-550 and N-110 have been studied to evaluate the influence of this parameter and to have a background of information. To extend the range of possible active sites observed, CBs with a particular behavior (Durex-0 and treated N-774) or feedstock origin (SC N-990) have been also studied using a wide range of probes. Results show that increasing CB size decrease the number of active points. On the other hand, it is suggested that process, treatments and feedstock can generate different amount and type of active sites, as the heal points generated using a feedstock with impurities, modifying the surface activity of the Carbon Blacks. Besides, CB surface activity influence has been observed in the vulcanization of the polymeric phase of the composite. One of the most spectacular effects is the interaction with the accelerator. It can be concluded that the higher surface activity the lower accelerator decomposition time. These results encourage us to modify the CB surface to create certain active sites on its surface and produce new tailored CB grades.
- 16:20 **N-VI.6** **SCANNING FORCE MICROSCOPY STUDY OF NANOSTRUCTURES IN POLY(ESTER URETHANES)**
M.E. Hawley, E.B. Orlor, D.A. Wroblecki, R.P. Hjelm and G.W. Brown, Los Alamos National Laboratory, Los Alamos NM 87545, USA
Segmented poly(ester urethanes) are an important class of structural polymers that derive their desirable mechanical properties from the nanophase separation of immiscible crystalline (hard) and rubbery (soft) segments that make up the polymer. It is well known that the thermoplastic character of polyurethanes is a result of changes in structure that occur on heating and cooling. Phase sensitive atomic force microscopy imaging is sensitive to the differences in mechanical stiffness of the hard (HS) and soft segment (SS) rich domains formed by the segregation of the polyurethane components, as shown in our previous study. The objective of this study is to determine the time- and heat-dependent evolution of the structure of samples with different HS content and cooling rate. Scanning Probe Microscope (SPM) provides near surface information on the time dependent component segregation. Quenching lead to formation of a network of a very hard rod-like micro-phase. More rapid quenching resulted in a more extensively developed structure, consisting of smaller branches emanating ~90 degree from the hard rod-like network. Over an extended period, 100 angstrom wide strand-like nanodomains, seen prior to heating, redeveloped, coalescing into dense mats. Coincident with the appearance of these strands is the formation of a background structure consisting of ~10 nm interpenetrating SS and HS domains with a length scale similar to that observed in small-angle scattering experiments.

SYMPOSIUM N

17:00

N-VI.7

ADDITIVES AT POLYMER SURFACES STUDIED BY TOF-SIMS

P. Bertrand, A. Delcorte, N. Médard, C. Poleunis, Université Catholique de Louvain, PCPC, Croix du Sud, Louvain la Neuve, Belgium

Additives are commonly used in the formulation of commercial polymer materials. They aim at stabilizing and improving different properties by acting as antioxidants, light /UV stabilizers, anti-blocking or anti-static agents, flame retardant, biocides... However their migration and possible segregation at the surface can deeply modify the surface properties required for specific applications such as food packaging, interfacial adhesion and biocompatibility.

To study such phenomena, a surface sensitive analytical technique, providing molecular information is required. Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is ideally suited for that purpose. Nowadays, this technique is intensively used for polymer surface characterization. Characteristic molecular fragment and parent ions can be used for identification of polymer and organic materials (such as additives) present at the surface and the quantitative interpretation of the data is in progress.

The aim of this presentation is to review our recent results in the field.

We prepared samples consisting in pure additives, mixed additives and thin polymer layers containing controlled amounts of selected additives. The SIMS intensity of the characteristic molecular ions was then compared with the bulk concentration. For additive mix (Irgafos 168 - Hostavin N30 system), a good correlation was found, showing that, in that case, no matrix effect disturbs the quantitative interpretation of the SIMS data.

ToF-SIMS allowed us to study antioxidant (Irgafos 168) segregation and crystallisation at a polyester surface. Very low bulk concentrations (~ 1 wt-%) of additive in poly(ethylene terephthalate-ethylene isophthalate) (PETI) thin films were seen to lead to an almost uniform coverage of the polymer surface, indicating a pronounced surface segregation (blooming effect). For a higher concentration (5.5 additive wt-%) ToF-SIMS imaging showed the formation of antioxidant crystals at the top of the additive covered PETI surface. In the range of low additive concentrations (0.3 wt-%), quantification of the additive surface concentration was obtained by using a multivariate statistical data treatment (Principal Component Analysis).

In order to improve the ToF-SIMS sensitivity to additives, we found recently that the deposition of small gold nanoclusters at the sample surface increases significantly the SIMS signal of additives (in negative mode) and leads to the detection of Au-cationized parent molecules in positive mode. This effect is related to an increased ionization probability of the emitted species caused by the metal clusters. This procedure was also seen to improve the sensitivity for oligomers and polymer fragments.

17:40

N-VI.8

DIELECTRIC SPECTROSCOPY AS A METHOD FOR CHARACTERISING CARBON-BLACK/RUBBER MIXTURES

D. Goeritz, Th. Lanzl, Fakultät für Physik, Universität Regensburg, 93040 Regensburg, Germany

A modified dielectric test method is presented with which carbon-black/rubber mixtures have been analysed in the frequency range from 20 Hz to 1 GHz. Two dielectric transitions are found experimentally which can be attributed to Debye relaxations in the aggregates and in carbon-black clusters. Analysis of both transitions, which are described by a closed model function, leads to the following picture for a series of samples with various filler content. Even below the percolation threshold the aggregates form local percolation networks which themselves percolate when the amount of filler is increased. The method permits the average thickness of the rubber layers between the aggregates to be estimated.

SYMPOSIUM N

Friday, June 21, 2002
Vendredi 21 juin 2002

Morning
Matin

Session VII
Session Chair: Rex Hjelm

- 08:30 **N-VII.1** **MICRO-MECHANICS OF STRESS SOFTENING AND INTERNAL FRICTION OF FILLER REINFORCED RUBBERS**
Manfred Klüppel, Deutsches Institut für Kautschuktechnologie e.V., Eupener Straße 33, 30519 Hannover, Germany
Based on a micro-mechanical concept of elasticity and fracture mechanics of fractal filler clusters in elastomers, a constitutive material model of stress softening and filler-induced internal friction of reinforced rubbers up to large strain is developed. The model refers to a non-affine tube model of rubber elasticity, including hydrodynamic amplification of the rubber matrix by a fraction of rigid filler clusters with filler-filler bonds in the unbroken, virgin state. The filler-induced hysteresis is described by an anisotropic free energy density, considering the cyclic breakdown and re-aggregation of the residual fraction of more fragile filler clusters with already broken filler-filler bonds. Experimental investigations of the quasi-static stress-strain behavior of silica and carbon black filled rubbers up to large strain agree well with adaptations found by the developed model. The obtained microscopic material parameter appear reasonable, providing information on the mean size and distribution width of filler clusters, the tensile strength of filler-filler bonds and the polymer network chain density.
- 09:10 **N-VII.2** **NANOCRYSTALLINE Eu³⁺ DOPED YTTRIUM OXIDE DISPERSED ONTO SILICA PREPARED BY DEPOSITION-PRECIPIATION METHOD**
C. Cannas, M. Casu, M. Mainas, A. Musinu, G. Piccaluga, Dipartimento Scienze Chimiche, Cittadella Universitaria, S.S 554 Km 4.5, 09042, Monserrato (CA), Italy
Nanocrystalline (Eu³⁺)Y₂O₃ has been widely investigated, due to its interesting applications in the field of phosphors for lighting and cathode ray tubes. Since free standing nanoparticles are unsuitable for technical applications, it is necessary to employ an optical inert and transparent medium as a host. Amorphous silica is the ideal support both because of its transparency and for the stabilising effect over nanoparticles aggregation. We recently used the sol-gel method in order to obtain a (Eu³⁺)Y₂O₃-SiO₂ nanocomposite. The luminescence spectra of this material indicated that the Eu³⁺ ion is located inside the small (2 nm) Y₂O₃ nanoparticles, while particles with larger size should be produced in order to improve the luminescence efficiency. With the aim of obtaining nanocomposites with the required properties we used deposition-precipitation technique, which consists in the impregnation of mesoporous commercial silica with a solution of yttrium and europium nitrates in presence of urea. Urea hydrolysis implies the gradual and homogeneous deposition of yttrium-europium hydroxides onto silica. (Eu³⁺)Y₂O₃ particles form after calcination of the impregnated system at 900°C. The application of deposition-precipitation method was successful in the formation of (Eu³⁺)Y₂O₃ crystalline particles with mean size of 10 nm, embedded in the silica matrix, as evidenced by XRD and TEM. The nanoparticles do not interact at the interface with silica, as revealed by ²⁹Si NMR/MAS and FT/IR
- 09:30 **N-VII.3** **QUASIELASTIC NEUTRON SCATTERING AS A PROBE OF MOLECULAR MOTION IN POLYMER-FILLER SYSTEMS**
V. Arrighi(a), S. Gagliardi(a), J.S. Higgins(b), A. Triolo(c) and J-M Zanotti(d), (a)Heriot-Watt University, Edinburgh, UK, (b)Imperial College, London, UK, (c)BENSC-HMI, Berlin, Germany, (d)LLB, Saclay, France
The addition of fillers or fibers to polymeric materials leads to improvement in the mechanical properties of the polymer matrix. The reinforcement effect is directly related to the properties of the interphase and depends on the nature of the specific interactions between polymer and reinforcing additive.
Various experimental techniques can be used to establish the effect of active fillers on the mobility of the polymer chains. The experimental results from NMR, dielectric spectroscopy and dynamical thermal analysis indicate that the mobility of chain units adjacent to the adsorbed surface differs considerably from that of the bulk polymer.
The technique of quasielastic neutron scattering (QENS) has been extensively used to study the local motion of polymers above their glass transition temperature. We have used QENS to investigate the dynamic properties of poly(dimethyl siloxane) (PDMS) and poly(vinyl acetate) (PVAc) containing hydrophilic Aerosil particles of two different specific surface areas (average diameter 7 and 20 nm, respectively).
In this paper we demonstrate that QENS is an excellent probe of the reduced mobility of the chain segments in polymer-filler systems. Detailed analysis of the QENS spectra leads to the fraction of chains segments that experience dynamic restrictions due to the presence of fillers. This quantity depends on the specific surface area of the particles, their weight fraction as well as the extent of polymer-filler interactions.
- 10:10 **BREAK**

Session Chair: Manfred Klüppel

SYMPOSIUM N

- 10:30 **N-VII.4** **THERMOPLASTIC ELASTOMERS WITH BLOCK COPOLYMERS**
Holger Schmalz(a), **Volker Abetz**(a), Ronald Lange(b), (a)Makromolekulare Chemie II, Universität Bayreuth, 95440 Bayreuth, Germany, (b)DSM-Research, 6160 MD Geleen, The Netherlands
Thermoplastic elastomers are used in a wide range of applications due to easy processing by conventional methods like injection molding and extrusion. In this field copolyether-esters based on poly(butylene terephthalate) (PBT) hard segments and polyether soft segments are of considerable technological interest. An incorporation of aliphatic soft segments, which should improve the elasticity of the material, was impossible until now due to macrophase separation during the melt polycondensation. We show that the use of poly(ethylene oxide)-block-poly(ethylene-co-butylene)-block-poly(ethylene oxide) triblock copolymers avoids macrophase separation and reveals a new class of polyesters with excellent mechanical properties.
ABC triblock copolymers with two hard domain forming endblocks in a rubbery matrix of B are another way to approach thermoplastic elastomers. Here we will compare polyethylene-block-poly(ethylene-alt-propylene)-block-polystyrene and polystyrene-poly(ethylene-alt-propylene)-block-polystyrene triblock copolymers with similar middle block content. Their morphological and mechanical properties will be discussed.
- 11:10 **N-VII.5** **SiO₂ NANOPOROUS THIN FILMS PREPARED BY PECVD. CONTROL OF THE MICROSTRUCTURE BY MODIFICATION OF THE NUCLEATION AND AGGRAGAION STEPS**
A. Barranco, F. Yubero, J. Cotrino, A.R. Gonzalez-Elipe, Instituto de Ciencia de Materiales de Sevilla, CSIC-Univ. Sevilla, C. Americos Vespucio s/n, 41092 Sevilla, Spain
Preparation of thin films with a controlled porosity is becoming a challenge because of the importance of these type of materials for a wide set of applications. In this paper we report about a new method of deposition of oxide thin films whereby their porosity can be changed continuously from the nanoporous up to the mesoporous. Changing some working parameters of the developed PECVD procedure it is possible the synthesis of thin films with optical quality and nanoporous microstructure or that of thin films with high porosity and specific surface area that scatter the light and can be interesting for sensor or membrane applications. In all cases the synthesis is carried out at room temperature, being the main parameter to be controlled the amount of a organic layer which is deposited to modify the nucleation and initial growth processes of the oxide thin film. Some characterization results by ellipsometry (optical thin films with controlled porosity) or gas permeation (membrane thin films with high porosity) are presented to illustrate the possibilities and potential applications of this method.
- 11:30 **N-VII.6** **NANOSTRUCTURED MAGNETITE CONTRIBUTION TO MICROWAVE ABSORBER CHARACTERISTICS**
I. Nedkov, T. Merodiiska, S. Kolev, R. Kotsilkova, Institute of Electronics, BAS, 72 Tzarigradsko Chaussee, 1784 Sofia, Bulgaria and P. Pissis, National University of Athens, 15780 Athens, Greece
Nanocomposites for microwave applications are a fascinating class of materials both in terms of fundamental interest and practice. These materials are promising for reduction of thickness and obtaining a better effectiveness of the magnetic microwave absorbers. The possibilities for optimization of absorber characteristics in X- and Ku- bands are studied. Experimental investigation of the effect of particles shape and grain size of the fillers on microwave absorption as well as reflection of a single-layer absorbers were carried out. Nitrile butadien rubber and epoxy resin - smectite clay were used as matrixes. Molecular mobility in relation to morphology was investigated by broadband dielectric relaxation spectroscopy (DRS) and thermally stimulated depolarization currents (TSDDC).
- 11:50 **LUNCH**

SYMPOSIUM N

Friday, June 21, 2002
Vendredi 21 juin 2002

Afternoon
Après-midi

Session VIII

Session Chair: Robert Schuster

- | | | |
|-------|-----------------|---|
| 13:40 | N-VIII.1 | <p>RANDOM LASER ACTION IN ORGANIC/INORGANIC NANOCOMPOSITES
 <u>D. Anglos</u>, A. Stasinopoulos, G. Zacharakis, M. Psyllaki, and S.H. Anastasiadis, Foundation for Research and Technology - Hellas, Institute of Electronic Structure and Laser and University of Crete, Department of Physics, 711 10 Heraklion Crete, Greece, R. Das and E.P. Giannelis, Department of Materials Science and Engineering, Cornell University, Ithaca NY 14853, USA
 Laser action is demonstrated in organic/inorganic nanocomposites consisting of (a) surface-modified semiconductor nano- or micro-particles dispersed in an inert polymer matrix; (b) organic laser dyes and scattering particles in an inert polymer matrix; (c) scattering particles in an optically active polymer matrix. All systems feature the simultaneous presence of a component providing gain as well as strong scatterers, whereas the polymer matrix offers ease of material processability in view of potential applications. When excited by a laser pulse of appropriately short duration (ps-ns), the composites give off fluorescence emission, which is strongly amplified as a result of light trapping due to multiple scattering. This laser action is manifested as a dramatic increase in the emitted light intensity accompanied by a significant spectral and temporal narrowing above a threshold value of the pumping laser intensity.</p> |
| 14:00 | N-VIII.2 | <p>POLYACRYLONITRILE AND POLYAMIDE NANOCOMPOSITES FOR CHROMATOGRAPHY
 <u>B.D. Kabulov</u>, <u>O.N. Ruzimuradov</u>, D.T. Satibaldieva, G. Anarbaeva, S.V. Zalyalieva, S.Sh. Rashidova, Institute of Polymer Chemistry and Physics of Academy of Sciences of the Republic of Uzbekistan, 7b, A.Kadiri street, Tashkent, Uzbekistan
 Last time the synthesis of organic-inorganic nanocomposites is very attractive field of polymer chemistry representing scientific and technological interest. These materials, called hybrid, are of interest to use them as chromatography sorbents.
 We developed the method of hybrid sorbent obtaining by radical polymerization in situ of vinyl monomer-acrylonitrile with polyethoxysiloxane (PES) oligomer. The last one was obtained by hydrolysis and condensation of tetraethoxysiloxane (TEOS). The hybrid sorbents homogeneity depends on catalyst quantity that show to the role of physical polymer trap on silica gel formation as well as and hydrogen fixing interaction for polymer homogenous dispersion. From the mixture of polycapromamide in formic acid and tetraethoxysilane at the different relation we got polycapromamide-silica sorbent by sol-gel method. The hybrid sorbents obtained are characterized by microscopy, IR- spectroscopy, X-ray diffraction and chromatography methods.
 It is necessary to note that sol-gel process is poly-side and this is apparently more profitably then other methods of polymer mixing. In the same time this method does not demand organic monomers modification to obtain homogeneous polymeric hybrids. It can appear useful for the synthesis of polymeric hybrids nano- and microcomposites, starting of organic polymers without of high affinity to silica gel because aggregation may be suppressed, if the monomer is polymerized in silica gel matrix "cage". This process is distinguished by simplicity, well controlled and allows to get different organo-inorganic composites at low temperatures including selective hybrid sorbents for modern chromatography methods (HPLC and HPTLC).</p> |
| 14:20 | N-VIII.3 | <p>ZnO/SiO₂ NANOCOMPOSITES OBTAINED BY IMPREGNATION OF MESOPOROUS SILICA
 C. Cannas, M. Casu, M. Mainas, <u>A. Musinu</u>, G. Piccaluga, Dipartimento Scienze Chimiche, Cittadella Universitaria, S.S 554 Km 4.5, 09042, Monserrato (CA), Italy
 This study is focused on the synthesis and characterization of nanocomposites in which ZnO nanocrystals are efficiently incorporated into a SiO₂ matrix. The samples are prepared impregnating a commercial mesoporous silica with zinc nitrate aqueous or ethanolic solutions, employing different times and temperatures of impregnation. The impregnated solids are dried and then calcined in the 500-900°C temperature range. Structural evolution of the samples towards thermal treatments and chemical modifications of the precursor deposited onto silica are studied by TG/DTA, XRD and TEM techniques while the interactions of the zinc oxide with the matrix are investigated employing FT/IR and ²⁹Si NMR/MAS. During thermal treatments the samples evolve toward the formation of nanocrystalline ZnO particles (zincite phase) dispersed onto amorphous silica. XRD and TEM characterizations evidence that the nanoparticle size distribution is strongly affected by the solvent used in the impregnation. A narrower and more homogeneous distribution is obtained using ethanolic instead of aqueous solutions. At the temperature of 700°C the presence of important interactions among particles and matrix appear, which at higher temperatures evolve towards the formation of a zinc silicate phase. This system finds application as a photoluminescent material, due to the presence of anionic vacancy of oxygen in crystalline ZnO, which is known to be improved by reduction of particles size to the nanometric scale.</p> |

SYMPOSIUM N

14:40

N-VIII.4

BIONANOCOMPOSITES ON THE BASE OF CHITOSAN AND TETRAETHOXYSILANE.

B.D. Kabulov, O.N. Ruzimurodov, D.T. Satibaldieva, D. Shakarova, M.Yu. Muhamedjanova, S.V. Zalyalieva, S.Sh. Rashidova, Institute of Polymer Chemistry and Physics of Academy of Sciences of the Republic of Uzbekistan, 7b, A.Kadiri street, Tashkent, Uzbekistan

Nanocomposite materials obtaining by sol-gel process through the interaction of organic polymers with tetraethoxysilane (TEOS) become widespread due to simplicity and effectivity of approach to the development of organic-silica polymeric materials which combine the hardness of silica and polymers functional properties. Nanocomposite materials, in which the organic phase consist of biopolymers are of special interest.

Chitosan is one of such perspective polymers, possessing the regular chain structure and forming true solutions in the dilute water solutions of organic and inorganic acid that allows to get with it an hybrid nanocomposite, using sol-gel process.

We investigated chitosan interaction with tetraethoxysilane, in different relations with the aim to get biocomposite-chitosan-silica sorbent for high performance liquid chromatography.

Reokinetical investigations of hybrid matrix formation under TEOS interaction with chitosan in acidic acid solution was performed on rotation viscosimeter Reotest-2 with the effective viscosity measurements at deformation velocity 656s^{-1} and 70°C . It was shown, that on the structure of product formed, process kinetics and mechanism, proceeding on 2 stages, the structural features of reacting components and they ratio influenced.

The product obtained in above mentioned conditions are characterized by microscopy, IR-spectroscopy and X-ray analysis methods.

15:00

Closing remarks

SYMPOSIUM N

POSTERS

- N/P01** **NONLINEAR OPTICAL PROPERTIES OF THE FULLERENE-DOPED PYRIDINE SYSTEMS BASED ON COANP**
M.M. Mikhailova, St.Petersburg State Technical University, N.V. Kamanina, Vavilov State Optical Institute, St. Petersburg, Russia
Optoelectronics tasks have stimulated a search for new nonlinear materials as effective optical limiting media. For this aim, it has been common practice to obtain optical limiting using fullerenes as effective sensitizers of organic structures. Among the materials studied, the organic systems with highly delocalized pi-electrons hold much promise. 2-cyclooctylamino-5-nitropyridine (COANP) compounds have nonlinear coefficients compared with lithium niobate and DKDP crystals. They have an additional absorption band in the near IR spectral range on doping them with fullerenes. In the present paper the fullerene influence on the spectral and nonlinear optical properties of both thin films and solutions based on COANP has been studied. Using the second harmonic of a pulsed Nd-YAG laser, nonlinear transmission has been observed. Laser radiation attenuation has been found to exceed at least by a factor of 10. Reverse saturable absorption, charge transfer complex formation, and free carrier absorption in COANP-C70 composites have been discussed to explain the optical limiting effect in them. Moreover, the laser-induced change in the refractive index has been found to influence the optical limiting properties too. It has been established that the COANP-fullerene structures could be applied for energy density limiting of more than 4 J/sq.cm and could be used as holographic recording media.
- N/P02** **ANALYSIS OF SIZE-DISTRIBUTION FUNCTION OF METALLIC NANOCCLUSERS IN HYDROGENATED AMORPHOUS CARBON MATRIX**
V.I. Ivanov-Omskii, A.B. Lodygin, S.G. Yastrebov, A.F.Ioffe Physicotechnical Institute, Russian Academy of Sciences, St. Petersburg, Russia
A method is proposed for mathematical processing of TEM images of nanocomposites with large amount of non-uniform noise. The approach is 2D spline filtering of the image using the values of average background intensity. The method has been applied to TEM images of amorphous carbon doped with copper. A size distribution function of copper clusters has been obtained which is in a good accordance with earlier data. A dependence of cluster-to-cluster distance on cluster size has been found. This dependence validates the hypothesis of fluctuation growth of the clusters at lower metal contents and their coalescence at higher contents.
- N/P03** **STRUCTURE AND PROPERTIES OF HIGHLY POROUS (FOAMED) NANOBERILLIUM**
Yu.E. Markushkin(a), N.G. Borisenko(b), A.S. Vorontsov(a), V.V. Gorlevsky(a), V.M. Dorogotvtsev(b), I.M.Kamenskich(a), Yu.A. Merkuliev(b), V.G. Starshina(a), A.K. Shikov(a), A.V. Zabrodin(a), (a)Bochvar Institute of Inorganic Materials, Moscow, Russia (b)Lebedev Physical Institute, Moscow, Russia
Recently much attention has been paid to study laser radiation interaction with low-density undercritical matters. These can be the laser-target outer layers providing symmetric heating and compression of the inner spherical target. It was shown earlier that foamed beryllium-containing materials of less than 0.1 g/cc density and pore sizes of ~ 10 micrometers could be used for the said purposes. Such structures could be obtained in the course of thermal transformation of beryllium hydride (deuteride) as well as mixtures of beryllium hydride and lithium hydride. Heavy elements can be admixed to the low-density beryllium and their distribution can be controlled over the layer thickness. The fine microporous structure of the low-density beryllium was studied using SEM and AFM. The results are discussed. The data on its mechanical and physical-chemical properties are given.
- N/P04** **DYNAMIC HYSTERESIS EVOLUTION IN 1-3 PZT-POLYMER FERROELECTRIC COMPOSITES**
J.-M. Liu, B. Pan, Z.G. Liu, Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, China, K. Li, H.L.W. Chan, C.L. Choy, Department of Applied Physics and Materials Research Centre, Hong Kong Polytechnic University, Kowloon, Hong Kong
The 1-3 type PZT-polymer ferroelectric composites are fabricated using a novel technique. We perform systematic investigation of the dynamic characteristics of the ferroelectric hysteresis loop upon variable amplitude and frequency of the external electric field, using the high-voltage Sawyer-Tower technique. It is revealed that the low-frequency hysteresis dispersion roughly follows the predicted power law, while the high-frequency response shows rapid decaying with increasing field frequency. The mechanisms controlling the dynamic hysteresis are discussed.
- N/P05** **HIGH STRENGTH HIGH CONDUCTIVITY Cu-Nb METAL MATRIX COMPOSITES WITH NANOSCALED MICROSTRUCTURE**
A. Shikov, V. Pantsyrnyi, A. Vorobieva, A. Silaev, N. Khlebova, N. Kozlenkova, I. Potapenko, N. Beliakov, V. Drobyshev, Bochvar Institute of Inorganic Materials, Moscow, Russia
Significant amount of modern research programs require magnetic fields of extremely high intensity. The availability of winding materials with unique combination of high strength and high conductivity has become a limitation factor for the designers of high field pulse magnets. The recent advances in exploration of the mechanism of anomalous increase of strength in two phase metal matrix composite materials with nanoscaled microstructure have provided a basis for the research on technically useful winding wires. The long length wires with rectangular cross sections up to 4x6 mm² having ultimate tensile strength higher than 1150 MPa and conductivity up to 70 % IACS have been successfully designed and fabricated. The present state of microcomposite Cu-Nb winding wire development will be given focusing on the complex interrelations between microstructure, mechanical and physical properties altogether with fabrication issues.

SYMPOSIUM N

- N/P06** APPLICATION OF STRAIN-TIME CORRESPONDENCE AS A TOOL FOR STRUCTURAL ANALYSIS OF NITRILE RUBBER-BASED NANOCOMPOSITES WITH DIFFERENT ORGANOCCLAY LOADINGS
Seung-Yeop Kwak and Seok Jong Han, School of Materials Science and Engineering, Seoul National University, Seoul, Korea
In this study, Nitrile rubber/organoclay nanocomposites with different type of intercalants as a function of different silicate loadings (1, 3, 5, 7, 8, and 10 wt%) were fabricated by mechanical mixing at 100 rpm and temperature of 90 °C for 600 s, followed by the additional static heat imposition for 100 min after mixing. From the tensile measurements with various strain rates ($\dot{\epsilon} = 0.162, 0.0975, \text{ and } 0.0187 \text{ s}^{-1}$) and application of strain-time correspondence principle, master curves on the tensile modulus as plotting with time, t , were constructed. In pure NBR, a master curve was constructed as use of the horizontal shift factor. However, all nanocomposites did not show master curves unless a modulus shift, $G(a)$, experimentally obtained from the vertical shift for the construction of the master curves, was introduced in addition to the horizontal shift. Moreover, the higher magnitude of $G(a)$ for the vertical shift was required to form a master curve as the amount of silicate loading increased up to 7 wt%, implying further intercalation forming physical crosslinking. For the hybrids with silicate loadings in excess of 7 wt%, on the other hand, the strain-time correspondence principle was no longer applicable and the master curve did not form in spite of both horizontal and vertical shift. This indicated that the silicate loading in excess of 7 wt% resulted in an abrupt change on structure, which was postulated to be formation of the percolated network-like structure.
- N/P07** MICROSTRUCTURAL INVESTIGATION OF NIMESULIDE-CROSPROVIDONE COMPOSITES BY X-RAY DIFFRACTION AND THERMAL ANALYSIS
P. Bergese(a), E. Bontempi(a), I. Colombo(b), D. Gervasoni(b), L.E. Depero(a), (a) INSTM and Structural Chemistry Laboratory, University of Brescia, via Branze 38, 25123 Brescia, Italy, (b)Eurand International S.p.A., Physical Pharmacy, via Martin Luther King 13, 20060 Pessano con Bornago Milano, Italy
Dispersion into crospovidone is a widely employed method for enhancing the solubility of poorly water-soluble drugs, since the 3D polymeric network stabilizes the active substance in molecular clusters and nano-crystalline phases. Nimesulide loaded into crospovidone shows two polymorphic modifications: the native material (form I) and another phase (form II) that matches the nimesulide phase reported on the ICDD database and the powder diffraction pattern simulated from the nimesulide crystalline structure recorded in the CSD database. Microstructure and polymorphism of the composites have been investigated as they affect the drug dissolution rate and in-vivo absorption kinetics (i.e. the bio-availability of the drug from its dosage form).
Differential scanning calorimetry (DSC) showed that the low melting form (form II) is metastable. X-ray diffraction (XRD) evidenced that the embedded crystalline phases are made up of nano-crystallites and that no relevant difference of their size exists between the two forms. Absolute quantitative analysis of the composites turned out to be a challenge with both XRD (strong preferred orientation of the sample grains and lack of the crystalline structure of the form I) and DSC (high nimesulide-crospovidone reactivity, which forbids calibration). Nevertheless, a direct correlation between the crospovidone content and the amount of the form II resulted from the analysis of the diffraction peaks intensities.
- N/P08** FAST NONLINEAR REFRACTIVE INDEX OF PURE AND ALLOY METALLIC NANOCLUSTERS IN SILICA GLASS
G. Battaglin, P. Calvelli, E. Cattaruzza, F. Gonella, R. Polloni, B. Scremin, INFN, Dipartimento di Chimica Fisica, Università di Venezia, Dorsoduro 2137, 30123 Venezia, Italy, G. Mattei, C. Maurizio, P. Mazzoldi, S. Padovani and C. Sada, INFN, Dipartimento di Fisica, Università di Padova, via Marzolo 8, 35131, Padova, Italy, F. D'Acapito, GILDA-CRG, ESRF, B.P. 220, 38043 Grenoble, France
The optical third-order nonlinearity of metal nanoclusters embedded in dielectrics has been the object of much theoretical and experimental investigation in the last years, due to the potential application in the field of all-optical switching technology. In this work, fast nonlinear refractive index was measured for composite films, formed by either copper or gold-silver alloy nanoparticles embedded in silica glass. A single 6 ps long pulse from a Nd:YAG laser was used in the Z-scan measurement, allowing to determine the electronic (non-thermal) component of the nonlinear response. Both the analyzed composites exhibit relatively large (and negative for the Au-Ag alloy) nonlinear index. Transmission electron microscopy, optical absorption spectroscopy and extended fine-structure X-ray absorption spectroscopy were also used to characterize the samples. Some figures of merit for the two samples were also evaluated.
- N/P09** STRUCTURAL EVOLUTION OF Cu-Al₂O₃ NANO-SCALE COMPOSITES SYNTHESIZED BY IN-SITU REDUCTION
M.S. Motta, E.A. Brocchi, P.K. Jena, I.G. Solorzano, PUC, Materials Science and Metallurgy, Rio de Janeiro, Brazil
Copper-alumina composites are reported to have high thermal and electrical conductivities as well as an excellent resistance to high temperature annealing. Furthermore, such properties are essentially dependent on the material's microstructure. Conventional and high-resolution transmission electron microscopy (TEM) have shown that the microstructure of the Cu-Al₂O₃ nano-scale composites synthesized by in-situ reduction is formed by a copper matrix, with crystals in the sub-micron scale and a fine dispersion of alumina particles ranging from 10 to 50 nm. The evolution of the microstructure before/after thermal treatment has been presented. The scale of the alumina particles has also been examined by energy dispersive spectroscopy (EDS) and scanning TEM X-Ray elemental mappings, which have also suggested the appearance of other oxide phases in the system, of the form of Cu_xAl_yO_z. This last result is also supported by electron diffraction experiments. Even after cold rolling and annealing at 900°C, dislocations and sub-grain boundaries are still very present in the microstructure. Further research focusing the thermal stability of the Cu-Al₂O₃ composite microstructure resulting from cold rolling and annealing is currently in progress.

SYMPOSIUM N

- N/P10** **NICKEL-ULTRADISPERSED MOLYBDENUM OXIDE COMPOSITE FILMS**
T. Mozolevskaya, L. Stepanova, Scientific Research Institute of Physical and Chemical Problems of Belarus State University, Minsk, Belarus
The report presents the research results of the preparation possibility and some properties of new type composite films Ni-ultradispersed molybdenum oxide (MO). Crystalline particles, 100 to 250 nm in size, were determined to be formed by successive boiling at first concentrated (0.4-0.5 M), and then dilute (0.1 M) solutions of molybdenum acid, which were prepared by the method of ions exchange. MO particles with crystalline structure were formed also by hydrothermal (5-20 atm) synthesis from dilute (0.1 M) molybdenum acid solutions.
Crystalline MO particles, suspended in the nickel sulfate bath, were able to embed into the metal matrix to produce composite Ni - MoO₃ films. The speed of the composite films plating from electrolytes (content MO particles about 0.5-3 g/L) was found to have no distinctions from speed of nickel films plating, content of MO in the films altered from 2.0-4.0 to 9.0 mass %. Further increase in the MO particles concentration in the plating bath up to 5 g/L is accompanied by the falling the electroplating speed and amount of MO, embedded in composite coatings.
Comparative investigation of the mass loss of Ni and Ni - MoO₃ composite coatings under dry friction conditions showed that films, which contain 4.0 mass % MO particles, about 100-250 nm in size, is characterized by significantly higher wear-resistance than wear-resistance of nickel films.
- N/P11** **CHARACTERIZATION OF SONOCHEMICALLY PREPARED SILVER-SILICA MONOLITHIC MESOPOROUS NANOCOMPOSITE**
Wei Chen(a), Junying Zhang(a), Lei Shi(a), Yan Di(a), Qi Fang(b) and Weiping Cai(b), (a)Structure Research Laboratory, University of Science and Technology of China, PR China, (b)Institute of solid state Physics, Academia Sinica, PR China
Silver nanoparticles loaded within pores of mesoporous silica were in situ synthesis by sonochemical reduction of silver nitrate within pores of silica. The sonochemical reduction was carried out by ultrasonic irradiation in argon atmosphere at room temperature. The composite was characterized by X-ray diffraction(XRD), high resolution transmission electron microscopy(HRTEM)and optical absorption techniques. It has been shown that silver nanoparticles, with a narrow size distribution, are isolated from each other and dispersed in pores, which are less than 10 nm in diameter.
- N/P12** **INTERACTIONS BETWEEN NANO-PATTERNED SURFACES AND LIQUID CRYSTAL MOLECULES**
C.W. Ahn, M. Behdani and T. Rasing, EVSF2, Research Institute for Materials, KUN, Nijmegen, The Netherlands
We will show the results on the improvement of alignment of liquid crystal molecules on nano-patterned substrates. To make nano-patterned surfaces, we used amphiphilic block copolymers. They form a nano-ordered structure by self-assembly on polymer and oxide surface. And liquid crystal molecules were aligned on the nano-patterned substrates. Preferred orientation of liquid crystal molecules is improved by ordering of nano-patterned substrate. The degree of alignment of liquid crystal molecules and nano-patterned substrate were characterized by polarized optical microscope, second-harmonic generation (SHG), atomic force microscope (AFM), scanning electron microscopy (SEM), and X-ray scattering.
Acknowledgements
This research was supported by STW Project No. NNS.4857.
- N/P13** **PREPARATION AND CHARACTERIZATION OF SEMICONDUCTOR NANOCRYSTAL-CONDUCTIVE POLYMER COMPOSITE WITH TUNABLE ENERGY GAP**
P. L'Ecuier, J. Ding and F. Bensebaa, National Research Council of Canada
Functional hybrid materials containing conductive organic polymer and inorganic nanocrystals have been used in a variety of applications including electrocatalysis, solar cell and high frequency electromagnetic shielding[1]. Non-coated CdS nanocrystal have been prepared and stabilized in a conductive co-polymer matrix. The energy gap of both polymer and the semiconductor nanocrystal are tunable. These new materials are under evaluation for photovoltaic applications. Metal and semiconductor nanocrystal and conjugated polymer composite have been considered in the past as potential photovoltaic material with limited success[2]
[1] P. Gomer-Romero, Advanced Materials 13 (2001) 163-167
[2] A. P. Alivisatos, in *Current Challenges on Large Supramolecular Assemblies*, G. Tsoucaris (ed.), 1999, 405-416.
- N/P14** **SYNTHESIS AND CHARACTERIZATION OF PIGMENTED POLYSTYRENE LATEX PARTICLES IN MINIEMULSION POLYMERIZATION**
E. Bourgeat-Lami, S. Lelu, C. Novat, C. Graillat, A. Guyot, LCPP, CNRS-CPE, Bât. 308F, 43, Bd. du 11 Nov. 1918, 69616 Villeurbanne, France
In the last ten years, a variety of encapsulation techniques have been developed to synthesize nanocomposite particles for applications in catalysis, optics and coatings. Miniemulsion polymerization offers several advantages to achieve this goal. In miniemulsion processes, the size of the droplets is controlled by shearing the system in presence of a surfactant and a costabilizer which role is to protect the organic droplets from Ostwald ripening. Since, particle formation occurs predominantly by radical entry into submicronic stable monomer droplets, the polymer particles are the direct copy of the latter. Miniemulsion polymerization is therefore particularly attractive for the encapsulation reaction of any compound that can be satisfactorily suspended into the monomer phase. In the present work, we want to report our preliminary investigations along this line on the encapsulation of copper phthalocyanine blue pigment. This pigment is largely used in the paint industry and displays a high coloration power. The coating of organic pigments by polymers may be of great benefit to improve their properties. The coating is tailored to prevent pigment agglomeration or to protect it from environmental aggressions (UV radiations, pH). Better storage stability, color stability and durability are expected to be obtained after coating. In addition, polymer encapsulated organic pigments can also find applications in water based paints into which they can be readily incorporated.

SYMPOSIUM N

- N/P15** OPTIMIZATION OF THE DESIGN IN GENERATING OF COMPOSITE PLATES UNDER COMPRESSION WITH ANALYTIC AND EXPERIMENTAL STUDY
Ayari Fayza, Institut Supérieure des Etudes Technologique de Rades, BP 342, Le Belvédère, 1002 Tunis, Tunisie, Ali Zghal, Ecole Supérieure des Sciences et Techniques de Tunis, 5 Av. Taha Husein BP 58, Bab Mnara, 1008 Tunis, Tunisie
This paper addresses the effect of the plate geometry and the mechanical characteristics on the buckling behavior of rectangular plates made of advanced composite materials. In this finding we include the effect of loading paths, fiber orientation of composite materials. In addition, we go treated the analytic resolution of the problem of a plate bifurcation with two types of loading, simple and combined compression. For sake of simplicity this survey himself restrained to the case of the simply supported- four edges plate. An experimental study is used to validate the analytic one. In fact, a methodology is discussed in order to optimize the experimental investigations with the extensively used carbon reinforced composites (CFC) plates. We have analyzed the effect of variation in aspect ratio with a monotonic loading path, and the (Bifurcation Load Factor), is studied for various boundary conditions. Laminated square plates of size 200 mm *200mm are used for this purpose under uni-axial compression. The comparative study of analytic and experimental results show, a significant agreement in stress and buckling loads.
- N/P16** ELECTRICAL AND STRUCTURAL INVESTIGATIONS ON NANOTUBE FILLED POLYMER COMPOSITES
Marion Wienecke, Mihaela-C. Bunescu, Marlis Pietrzak, K. Deistung, M.Mischker, H.Hansmann, Hochschule Wismar, Institut für Oberflächen- und Dünnschichttechnik, Philipp-Müller-Str., 23952 Wismar, Germany
Aiming at the development of an electrically conductive polymer for EMI shielding, we investigated different filled polymer systems by electrical measurements, dynamo-mechanical analysis, electron microscopy and measurements of electromagnetic shielding. The fillers we used were various graphite, carbon blacks, C-fibres and carbon nanotubes (Applied Sciences). Thus, we compare micro- and nano structured polymer composites. Systems were created with varying filler contents in different matrix materials. In order to get dispersion especially for the high aspect ratio materials we used ultrasonic bath. Injection moulded PMMA compounds were investigated. As our results reveal, higher contents of graphite and C-fibres, necessary for percolation, strongly decrease the mechanical properties of the composites. On the other hand nanotubes have minimal impact. Aiming at high conductive materials necessary for EMI shielding, we investigated the percolation properties of the filler-matrix systems. Therefore we prepared comparable mixtures in epoxy and wax by hot pressing. For 20 wt% nanotubes filled materials we realized conductivities up to 1 S/cm, sufficient for EMI shielding. SEM and TEM analysis were used for microstructure characterization.
- N/P17** TOF-SIMS STUDY OF THERMALLY INDUCED COMPATIBILIZATION PROCESSES IN POLYESTER-BASED POLYMER BLENDS
A. Auditore(a), F. Samperi(b), C. Puglisi(b), A. Licciardello(a), (a)Dipartimento di Scienze Chimiche, Università degli Studi di Catania, V. Andrea Doria 6, 95125 Catania, Italy, (b)Istituto per la Chimica e la Tecnologia dei Materiali Polimerici, Consiglio Nazionale delle Ricerche, Viale Andrea Doria 6, 95125 Catania, Italy
Surface evolution caused by thermal processing of PC/PET and PC/PBT blends prepared by melt mixing has been studied by ToF-SIMS, one of the most powerful surface analysis tools in terms of sensitivity, amount and localization of chemical information supplied. Existing data on bulk systems show that thermal treatment induces transesterification reactions, leading to the formation of copolymers, and reactions involving the loss of small molecules from the resulting copolymer. Little is known about the effects of such reactions on surface composition. ToF-SIMS measurements performed on blend samples melt mixed at 270°C for different times show that, parallel to the changes in the bulk, modifications of the surface composition take place. Copolymer formation, presence of intermediate systems, rearrangement of repeating units upon thermal treatment, and also the influence of catalysts can be recognized from the evolution of SIMS spectrum. In addition, surface-specific processes, such as segregation and/or recovery of initial surface-segregation, are observed and described. The results obtained from the melt mixed system are compared with those of a parallel ToF-SIMS study involving “in situ” thermal treatment of blends of variable relative composition, prepared as thin films.
- N/P18** CATALYTIC CONVERSION OF HYDROCARBONS IN ZEOLITES FROM FIRST PRINCIPLES
Lubomir Benco(a), Thomas Demuth(a), Francois Hutschka(b), (a)Institut fuer Materialphysik and Center for Computational Materials Science, Universität Wien, Austria, (b)Totalfinal, Centre Européen de Recherche et Technique, Harfleur, France
Conversion of hydrocarbons over zeolites is important industrial process used in the production of petrol. The microscopic steps of the conversion, however, are still not fully understood. In order to examine reaction pathways we have performed static and molecular dynamics DFT calculations on gmelinite zeolite and linear saturated and unsaturated hydrocarbon molecules. The conversion can proceed through the through the chemisorption of olefins at the inner surface of the zeolite. The desorption of chemisorbed species produces unstable protonated molecules. The protonated hydrocarbons are long-lived being stabilized in the zeolite surroundings. They are considerably deformed and at increased temperatures (~700K) high mobility of the H atoms along the molecular chain is observed. The relocation of the H atom can lead to the formation of structures with maximum stabilization of the positive charge, such as molecules with tertiary C atoms and cyclo-structures of hydrocarbons. The back donation of the proton to the zeolite framework can cause collapse of the linear protonated molecule, as well. Both cracked and isomerized products can be formed upon the back donation. Depending on the O...H-C contact established between the molecule and the framework the H atoms are removed from different C atoms thus starting either cracking or isomerization of the hydrocarbon molecule.

SYMPOSIUM N

N/P19

SYNTHESIS AND CHARACTERIZATION OF COLLOIDAL PbSe NANOCRYSTALS

A.Sashchiuk, E.Lifshitz, Technion, Department of Chemistry, 32000 Haifa, Israel

The controlled synthesis of colloidal PbSe nanocrystals (NCs) with narrow size distribution is described. Two different methods for synthesis PbSe NCs are applied. 1- TOPO-TOP capped PbSe NCs are prepared from trioctylphosphine (TOP) selenide and lead 2 ethyl-hexanoate under inert gas at 150°C, 2- tributylphosphine (TBP) capped PbSe NCs are prepared from TBP selenide and lead 2 ethyl-hexanoate under inert gas at room temperature. Finally a relatively simple synthetic route to make PbSe/PbS core/shell NCs is presented. HRTEM, X-ray energy dispersion spectroscopy (EDS), absorption and photoluminescence (PL) spectroscopy were used to characterize the samples. The absorption spectra of these colloidal PbSe NCs exhibit few distinct exciton bands, when the lowest energy exciton is blue-shifted with a decrease in the NCs size. The absorption spectra of PbSe/PbS core/shell NCs is red-shifted with increase in the PbS shell thickness. PL characteristics of these materials are also discussed. These non-linear optical properties of different size (in the range of 2.0-7.0nm) of colloidal PbSe NCs embedded in polymer thin films can be of use for difference applications in photonic and opto-electronic devices.

N/P20

AB INITIO INVESTIGATION OF FILLER – MATRIX INTERFACE IN NANO COMPOSITE POLYMERS: STRUCTURE, ENERGETICS AND BONDING OF ORGANIC MODIFIERS

F. Tsobnang, B. Minisini, Institut Supérieur des Matériaux du Mans, 44 Avenue F.A. Bartholdi, 72000 Le Mans, France

Organic modifiers play a key role in the synthesis of nano composites polymeric materials with improved properties. In this study we investigated at ab initio level, their energetics, structure and bonding of tetraalkylammonium cations with nano particles of montmorillonite (MMT). The study has been performed with the density functional theory code VASP, which uses pseudo-potentials and a plane-wave basis set. Bonding are described qualitatively and quantitatively using fundamental descriptors including interaction energy, electron's density and density of states.

N/P21

ATOMISTIC INVESTIGATION OF FILLER – MATRIX INTERFACE IN NANO COMPOSITE POLYMERS

B. Minisini, F. Tsobnang, Institut Supérieur des Matériaux du Mans, 44 Avenue F.A. Bartholdi, 72000 Le Mans, France

In the past few years, several experimental studies have shown that addition of suitable nano fillers in polymers can enhance their mechanical, rheological chemical and thermal properties. Understanding the filler – matrix interaction is a challenging issue for materials science as well as a key step toward the design of new materials with tailored properties. The goal of this work is to describe qualitatively and quantitatively the filler – matrix interface at molecular level in the system Poly n-butylacrylate – organo modified montmorillonite. Investigations are carried out with a molecular static and dynamics. The study will be focussing on the evolution of the interaction's energy and polymer's topology versus the tetraalkylammonium nature.

Acknowledgements

This work is supported by Région des Pays de Loire.