



Strasbourg (France)

E-MRS Spring Meeting 2004  
May 24-28, 2004

## SYMPOSIUM P

Filled and nano-composite polymer materials

Symposium Organizers:

Rex Hjeltn, Los Alamos National Laboratory, USA

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Avancés, Le Mans, France

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# E-MRS 2004 SPRING MEETING

## SYMPOSIUM P

Tuesday, May 25, 2004

Morning

- 09:00 INTRODUCTION OF THE SYMPOSIUM  
by all Co-Chairs
- 09:30 Keynote address:  
AROUND FILLED POLYMERS, NANO-COMPOSITES POLYMERS AND MACROSCOPIC PROPERTIES  
**Alain le Méhauté**, L. Nivanen and A. Wang, ISMANS, 44 avenue Bartholdi, 72000 Le Mans, France  
The relation between macroscopic properties of complex structures and their local features is currently an opened question. This is due to the absence of relevance of any continuum model and due to long range correlations introduced by the complex and versatile geometry. We can find such industrial problematic for instance for tires engineering (filled polymers), optimisation of concretes for civil engineering (compound minerals), storage of energy (complex surface), etc. The case of filled polymers is well illustrated by the behaviour of tires which strongly depend on the micro and macrostructure of the filler and their interactions with the matrix. Starting from fractional statistical mechanics and geometrical considerations the contribution will show how the energy of rolling and ageing for example can be absorbed and desorbed through the modification of the statistic distribution and filler geometry. The main question is then the reversibility of geometrical properties.  
The question of all the opportunities opened by the nano-composite properties will be considered from the same point of view. As the transfer of the mechanical momentum is under the control of the statistics of the filler, the statistic of the nano composite will modify the transfer of any extensity (entropy, action, molecule, ion, electron, etc). The main feature pointed out for efficiency will be the characteristic length of the transfer. As the fillers modify the geometry and the statistic at high characteristic length, nano particules modify the metric of internal space time and topology at lower characteristic length. As a consequence, any transfer of physical quantity through this geometry modifies the material at this characteristic length in correlation with the nano structure. The geometry is then modified and this modification leads to entropic or neg-entropic properties directly observed through a change of properties.
- 10:10 **BREAK**

Session I: Theoretical developments and modeling of properties

Session chair: R.P. Hjelm

- P-I.02** 10:40 -Invited- NANOSTRUCTURES IN POLYMERS AND POLYMER/INORGANIC HYBRIDS FROM ADVANCED SOLID STATE NMR  
**H.W. Spiess**, Max-Planck-Institute for Polymer Research, PO Box 3126, 55021 Mainz, Germany  
Nanostructures are important aspects of composite polymers, such as block copolymers and organic-inorganic hybrids generated from them. Advanced solid state NMR techniques recently revealed, however, that conventional homopolymers can also exhibit pronounced nanostructures. There, they arise from orientational correlations between neighbouring chains or from an inherent incompatibility between different functional groups within the repeat unit. The presence of such nanostructures has important consequences for the dynamic behaviour and the properties of these materials.  
The different NMR techniques applied, i.e. spin-diffusion, two-dimensional exchange and double-quantum NMR are introduced and applied to such diverse problems as elucidating the interface in structured polymer-ceramic hybrids from poly (ethylene oxide-block-isoprene) or poly (ethylene oxide-block-n-hexyl methacrylate) and aluminosilicates, the organization of polyelectrolyte multilayers on silica surfaces, the chain order and translational motion in poly (butadiene) melts as well as poly (butadiene-block-polystyrene) and the nanostructure in poly (n-alkyl methacrylates). The NMR-results are compared with the findings of other techniques and related to the properties and function of the materials.
- P-I.01** 11:20 -Invited- A MINIMAL MODEL FOR UNDERSTANDING THE COMPETITION BETWEEN EQUILIBRIUM CLUSTERING AND PHASE SEPARATION IN NANOPARTICLE DISPERSIONS  
**Jack Douglass**, National Institutes of Standards and Technology, Gaithersburg, Maryland, USA  
There is evidence from both experiment and simulation that both synthetic and biological (proteins) nanoparticle systems exhibit dynamic clustering transitions in solution and polymer melts. This problem could be fundamental for understanding and controlling particle dispersion in polymer nanocomposites and this problem is being studied by a variety of methods. In this talk, the Stockmayer fluid (Lennard-Jones particles with a dipolar interaction super-imposed) is specifically considered as a minimal model for this type of clustering transition. The interplay between the dynamic clustering transition and phase separation in this model based on a lattice model of a kind commonly used in polymer science (i.e., Flory-Huggins model).

**P-I.03** 12:00 -Invited-

**A MULTIFRACTAL ANALYSIS OF RUBBER SURFACES**

**Claude Tricot**, Département de Mathématiques, Université Blaise Pascal (Clermont-Ferrand), 63177 Aubière Cedex, France

Pictures taken from compound surfaces show essentially two components : A gray level background similar to fractal noise which results from the mixing of carbon black in polymer; and a uniform distribution of non disintegrated pellets. A suitable filtering allows to separate the two components of the picture, and various tools of the multifractal analysis are introduced to discriminate the level of irregularity. These image analysis technique are used to quantify the dispersion level of black.

12:40

**LUNCH**

Tuesday, May 25, 2004

Afternoon

Session II: Polymer surface interactions and adhesion

Session chair: S. Blazewicz

- P-II.01** 14:00 -Invited- CONTROLLING ADHESION AND MOTION OF NANOPARTICLES WITH SURFACE-ATTACHED POLYMER MONOLAYERS  
**Jürgen Rühle**, IMTEK – Insitute for Microsystem Technology, University of Freiburg, 79110 Freiburg, Germany  
In this contribution we will describe the synthesis of polymer brushes via different routes of surface-initiated polymerisation, namely ATRP and free radical based approaches. Using these techniques we were able to also generate brushes consisting of block copolymers and so-called mixed brushes in which different homopolymers are randomly tethered to a surface. The various approaches allow to control the graft density and molecular weight of the attached polymers as well as the block length of each component of the tethered block copolymer and the graft density of each polymer within a mixed brush. Due to the incompatibility of the polymer blocks or homopolymers microphase separation is observed for all these layers, which expresses itself as topological features on the surfaces. However, by using a selective solvent it is possible to trigger an enrichment of the soluble component on the surface and smooth layers are formed. Subsequent treatments with suitable solvents can be used to switch back and forth between smooth and rough (microseparated) topologies and these changes make it possible to move nanoparticles seeded on top of these layers. First efforts to control this motion will also be described.
- P-II.02** 14:40 -Invited- INTERACTIONS OF PMMA ON A SURFACE ENVISIONED BY MOLECULAR MODELING  
**Armand Soldera**, Département de Chimie, Université de Sherbrooke, Sherbrooke J1K 2R1, Canada  
The way surface interactions could affect thermal behavior of a polymer is of relevant importance in the polymer-nanocomposite studies. A complete description of such microscopic interactions is not yet reached. To give a better understanding of such a behavior poly(methyl methacrylate), PMMA, offers a particular regard since according to the tacticity of its chain, different physical properties are exhibited. Among the properties of interest is the glass transition temperature,  $T_g$ , whose difference between the two configurations is more than 60 degrees. This difference tends to cancel out as the thickness of the PMMA film on a specific substrate decreases. Accordingly the  $T_g$  of the isotactic chain, i-PMMA increases while that of the syndiotactic chain, s-PMMA, decreases. Different attempts have been carried out to explain this different behavior. Molecular modeling was first used to specifically study the molecular reason that give rise to the variation of  $T_g$  in the bulk: differences in energy, internal geometry, local dynamics could thus be envisioned. In this presentation we propose to transcribe those molecular modeling results to explain the general behavior observed for PMMA polymers in confined geometries. However, a perpetual interaction with experimental data has to be carried out.
- P-II.03** 15:20 COMPARED STUDY OF COOPERATIVITY IN POLYMER THIN FILMS AND NANOCOMPOSITES  
T. Anh Tran, S. Said, Y. Grohens, Laboratoire Polymères et Procédés (L2P), Centre de Recherche, BP 92116, Rue de Saint Maudé, 56321 Lorient Cedex, France  
Strong deviations from the bulk concerning chains dynamics and glass transition have been reported. For supported PS thin films, the measurement of  $T_g$  by different techniques (ellipsometry, X-ray reflectivity, dielectric spectroscopy) give evidence of a decrease of  $T_g$  (up to 40 K) which is more pronounced for smaller values of the film thickness. An identical dependence is found for s-PMMA. For i-PMMA contradictory results are obtained according to the techniques used. An increase of the glass temperature is observed with ellipsometry whereas a decrease is recorded with dielectric spectroscopy. Many attempts have been undertaken to explain these observations. One appealing approach is developed by Donth which consists in associating to dynamic heterogeneity measured by NMR a spatial length scale<sup>1472</sup>; This length scale has rapidly been identified with cooperatively rearranging regions (CRR) whose size increases near the glass transition. Thus, on an experimental level it is interesting to measure the size of CRR. A convenient way to do it, is to confine the polymer chains in geometries with size of the order of the CRR. For instance, clays seems to be an interesting system as it is possible to vary the interlayer spacing according to the degree of intercalation and the preparation conditions. Another promising way is to make a direct measurement of the size of CRR from specific heat capacity values. This is the approach we develop in this work. In a first step, we compare the evolution of  $T_g(h)$  in two different systems eg thin films and nanocomposites in order to prove that the same mechanisms are at stake. Then in a second step, we determine the size of CRR for i-PMMA and s-PMMA and discussed the obtained values.

**P-II.04** 15:40 POLYMER-FILLER INTERACTIONS IN KAOLIN/NYLON 6,6 COMPOSITES CONTAINING A SILANE COUPLING AGENT  
M. Buggy, G. Bradley and Ann Sullivan, Department of Materials Science and Technology, University of Limerick, Ireland  
The mechanical properties of untreated kaolin filled nylon 6,6 composites are kaolin type (hydrous and calcined) independent. However, A1100 surface treatment leads to a distinction between calcined and hydrous kaolin composites, promoting adhesion only with calcined kaolin. Treated calcined kaolin filled nylon 6,6 exhibits improved strength and elongation properties, which are influenced by the silane loading level relative to the filler surface area. The predicted equilibrium work of adhesion is comparable with the equilibrium work of cohesion of nylon 6,6 with a mixed mode of failure resulting. At high silane loading levels a plastic effect was observed with impact strength decreasing. The wet strength of A1100 treated calcined kaolin composites are almost double that of the untreated condition and are reversible upon drying. As A1100 does not promote adhesion with hydrous kaolin their wet and dry strength properties are relatively unaffected, with the mode of failure being interfacial. Evidence of interfacial chemical bonding was found only in A1100 treated calcined kaolin. It is thought that the interaction is controlled by an acid base interaction between surface free primary amines and carboxylic acid polymer end groups with amide formation at the interface. The distinction between treated calcined and hydrous kaolin composites is due to the availability of surface free amines. Calcined kaolin has a relatively neutral surface on which the amines are not inhibited in their interaction with nylon functional groups. Hydrous kaolin has an acidic surface with Bronsted activity that protonates surface amines inhibiting their interaction with nylon 6,6.

**P-II.05** 16:00 MICROSTRUCTURE OF MONTMORILLONITE BASED NANOCOMPOSITE POLYMERS: AN ATOMISTIC STUDY OF GRAFTED POLYMER – ORGANOMODIFIED NANOFILLERS INTERACTIONS  
F. Tsobnang, B. Minisini, Institut Supérieur des Matériaux et Mécaniques Avancés du Mans, 44 Av. F.A. Bartholdi, 72000 Le Mans, France  
The microstructure of nanocomposite produced by melt blending depends on the type of organomodified nanofillers and the interactions between these later and the polymer matrix. These interactions depend in turn on the hydrophobicity of the constituent. When the polymer matrix is hydrophobic like polypropylene, grafted functional groups are used. In order to understand the influence of chemical composition of grafted groups on polymer-nanofillers interactions, we developed a methodology combining quantum mechanical and molecular dynamics calculations. Quantum mechanics was used to study and select grafted groups. Then, molecular dynamics calculations were carried out on fully atomistic models of nanocomposite grafted polypropylene with organically-modified clay. From these calculations, interaction's energies were evaluated. The improvement of this energy with the maleic anhydride was shown to be in agreement with the experimental results. The methodology and the results will be discussed.

16:20

**BREAK**

Session III: Fillers development

Session chair: M. Gerspacher

**P-III.01** 16:40 -Invited- PLASMA BARBON BLACK - THE NEW ACTIVE ADDITIVE FOR PLASTICS  
**T. Zielilski**, J. Kijelski, Industrial Chemistry Research Institute, Rydygiera 8, 01-793 Warsaw, Poland  
The increase of using and applications of plastics and rubber products in various branches of industry all over the world creates the needs of finding new additives, like plasma carbon black, what could guarantee economical benefical production and better properties and stability of ecological safety products, and new and safe methods of making carbon black itself. The paper presents the new kind of active additive for plastics &#8211; plasma carbon black, produced by plasma conversion of aliphatic hydrobarbon gases, like methane, ethane, ethylene, acetylene, and carrier gases, like argon or helium.  
The high adsorption capacity of the prepared carbon black in respect to nitrogen, iodine and dibutyl phthalate indicated a good absorbability, allowing molecules of various substances, for example stabilizers, easily drive into and settle on carbon black surface. The average bulk density of the plasma carbon black is about 10 g/dm<sup>3</sup>, which is over 10 times lower that the average bulk density of the commercial carbon black. This value makes possible to use few times lower amount of the plasma carbon black in the composition of the cable plastic than the commercial composition. The results of oxidation induction time (OIT) tests showed the much better (57 min) properties of cable polyethylene and HDPE geomembranes (56 min), modified by more than 5 times lower amount of plasma carbon black as a antioxidant in the composition, than commercial cable polyethylene (&#8805;22 min) without any significant differences in mechanical strenght. Special physical-chemical, thermal-mechanical and OIT properties give possibilities to produce special use cable PE and HDPE geomembrane, which are environmentally friendly and oxidation resistant what can elongate the time of use.

- P-III.02** 17:20 -Invited- **IMPORTANCE OF NITROGEN DOPING OF THE CARBONS USED IN THE PREPARATION OF NON-PRECIOUS METAL CATALYSTS FOR PEM FUEL CELLS**  
**Jean-Pol Dodelet**, INRS-Énergie, Matériaux et Télécommunications, Varennes, QC, J3X 1S2, Canada  
 Polymer electrolyte membrane (PEM) fuel cells are efficient and non-polluting electrical power generators based on the electrochemical oxidation of hydrogen and reduction of oxygen. Only Pt and its alloys have been used to date as catalysts in full size applications because non-noble metals corrode in the acidic environment (pH 1) of the fuel cell membrane. Replacing Pt might be possible at the cathode, provided that the alternative catalysts display activity and stability approaching that of Pt. To the present date, N4-Metal macrocycles have been of interest in this respect. It was demonstrated that a heat-treatment of several M-N4 macrocycles (where M is a transition metal ion, especially Co and most especially Fe) adsorbed on a carbon support improves the activity of these catalysts for oxygen reaction reduction (ORR). It is not even necessary to pyrolyze Fe-N4 macrocycles on carbon to obtain catalytic activity for ORR. Catalytic materials are also obtained by pyrolyzing Fe salts or complexes adsorbed on a carbon support in the presence of a nitrogen precursor. We demonstrated that two catalytic sites, labeled FeN4/C and FeN2/C are observed simultaneously in all these catalysts but in different proportions depending upon the nature of the iron precursor. In recent studies we also showed that between these two nitrogen containing sites, the most active one is FeN2/C. Since both catalytic sites contain nitrogen atoms, it is important to dope the surface of the carbons with nitrogen before using them as catalyst supports. Different strategies consisting in nitrogen doping of the carbon supports will be described and compared.
- P-III.03** 18:00 **MORPHOLOGY OF ADSORBED RUBBER ON CARBON BLACK**  
 Richard Hofmann, Dietmar Göritz, Faculty of Physics, University of Regensburg, 93040 Regensburg, Germany  
 The question of polymer chain mobility in thin adsorbed layers has not yet been answered consistently with respect to theory and experiment. As found experimentally, the glass temperature of a self-supporting film depends on its thickness, but there may be uncertainty about the influence of the substrate on the glass temperature and kinetic processes in its environment.  
 Our examinations aim at understanding the state of an adsorbed polymer film by measuring its mechanical properties on a filler surface. In order to understand the reinforcement produced by carbon black in rubber it is important to distinguish whether the adsorbed layer is actually in the glassy state or the rubber is just immobilised. The experiments were carried out using AFM on a model system consisting of highly ordered pyrolytic graphite (HOPG) and polymer.
- P-III.04** 18:20 **CARBON BLACK MODIFICATION BY ATMOSPHERIC PLASMA**  
 N. Tricás(a), S. Borrós(b), R.H. Schuster(a), (a)Deutsches Institut für Kautschuktechnologie e.V., eupener Straße 33, 30519 Hannover, Germany, (b)Institut Químic de Sarrià, Av. Sarrià 390, 08017 Barcelona, Spain  
 The specific surface area, particle structure and surface chemistry of Carbon Black (CB) are the filler properties responsible for the final behaviour of filled polymers. In order to modify CB surface, plasma treatments present interesting advantages compared to the wet chemistry as an example of a completely different chemistry and with a lack of solvents harmful to the environment. Low pressure plasma (cold plasma) is the most common technique to perform this kind of treatment; it is characterized by the low temperature which allows the treatment of any material without causing any damage. On the other hand, this technique presents an important drawback at industrial levels as it requires low pressure to achieve the plasma state. Nowadays a quite new technique based on atmospheric plasma has been developed in order to solve pressure problems while keeping a low enough temperature to treat the materials.  
 In this work an atmospheric plasma reactor has been adapted to treat powder materials. Afterwards Carbon Black was treated with air plasma and nitrogen plasma at different conditions (time and temperature). The effect of the plasma on the filler particles was determined by measuring the pH, the acidic value for different bases (NaOH, BaOH<sub>2</sub>, NaHCO<sub>3</sub>) and the surface tension. To determine the modification in the filler-polymer interaction the bound rubber was determined in CB filled polybutadiene mixtures. The results obtained show that this technique is a very effective method in the CB surface modification especially for its oxidation process which gives to this material very interesting properties.
- P-III.05** 18:40 **CARBON NANOTUBES - POTENTIAL CANDIDATES FOR THE IMPROVEMENT OF MECHANICAL PROPERTIES OF EPOXY MATRICES**  
Florian H. Gojny, Bodo Fiedler, Malte H.G. Wichmann, Karl Schulte, Technical University Hamburg-Harburg, Polymer Composites Section, Denickestrasse 15, 21073 Hamburg, Germany  
 Since the discovery of carbon nanotubes (CNTs) in 1991 by Iijima research activities focussed mainly on the evaluation of nanotube properties themselves. The unique mechanical properties of CNTs, their high strength and stiffness and the enormous aspect ratio exhibit a high potential for several applications. Composites with nanotubes as reinforcing elements should show improved mechanical properties, and an electrical and thermal conductivity together with a low density.  
 The investigation of a functionalisation of the nanotube surface on the dispersion behaviour and the interfacial adhesion is a key issue in the realisation of nanotube reinforced polymers. A mechanical reinforcement of polymers by CNTs can only be realised by finding appropriate methods to achieve a homogeneous dispersion of the nanotubes in the polymer and to strengthen the interfacial adhesion between the CNT and the matrix. Within this presentation the results of the investigation of nanocomposites based on epoxy resin and catalytically grown nanotubes, either functionalised or not will be presented. The DMTA showed strong influence of the nanotube content and functionalisation on the loss modulus and glass-transition temperature T<sub>g</sub>. This effect gives evidences for the relevance of a surface modification of carbon nanotubes to achieve good nanotube-polymer interactions. The results could be substantiated by SEM and TEM observations. The interfacial interaction reduces the mobility of the epoxy matrix around the nanotubes and leads to the observed increase in thermal stability. An improvement of strength and stiffness of the nanotube/epoxy-nanocomposites could already be achieved with low nanotube contents. Furthermore the observed toughening effect will be presented.

Wednesday, May 26, 2004

Afternoon

Session IV: Filled elastomeric and structural materials

Session chair: D. Goeritz

- P-IV.01** 14:00 -Invited- MICROSCOPIC ORIGIN OF ENERGY STORAGE AND DISSIPATION IN FILLER REINFORCED RUBBERS  
**Manfred Klueppel**, Jens Meier, Michael Daemgen, Deutsches Institut für Kautschuktechnologie e. V., Eupener Strasse 33, 30519 Hannover, Germany  
A constitutive micro-mechanical model of energy storage and dissipation in filler reinforced rubbers is presented that allows for a proper description of stress softening and hysteresis, as typically observed during the Payne effect. According to this model the free energy density of reinforced rubbers consists of two contributions: (i) a stored energy part considering the extensively strained rubber matrix including hydrodynamic strain amplification by a fraction of hard, rigid filler clusters with virgin filler-filler bonds, and (ii) a dissipated energy part, resulting from the residual fraction of softer filler clusters with already broken, damaged filler-filler bonds, which are successively strained, broken and re-aggregated during every stress-strain cycle. The stress softening effect refers to a stress-induced transition of hard clusters to soft clusters with increasing maximum strain that also impacts the hysteresis contribution. The developed model is shown to be well suited for the description of stress-strain cycles of carbon black and silica filled rubbers under various deformation modes.
- P-IV.02** 14:40 -Invited- THE EFFECT OF FILLER-FILLER AND FILLER-ELASTOMER INTERACTION ON RUBBER REINFORCEMENT  
**Joachim Fröhlich**, Degussa AG, Applied Technology, Harry-Kloepfer-Straße 1, 50997 Köln, Germany  
For a better understanding of the mechanism of rubber reinforcement by active fillers and furthermore of the properties required for rubber products and their end usage it is helpful to study the role of carbon black and silica on viscoelastic properties of filled rubber compounds.  
A detailed analysis of the effects of carbon black morphological parameters, such as surface area, structure, surface activity and porosity was carried out by investigating the Payne effect with the Rubber Process Analyzer (RPA) which allows the evaluation of the strength of the filler network and of the ratio of the filler-elastomer interaction in the green compound as well as in the vulcanizate over a large range of shear deformation. The effect of physical and chemical interactions between rubber and filler was also investigated by comparing carbon black, non modified silica and silica modified with a bi- and a monofunctional silane respectively. These investigations provide a deep insight into the mechanism of reinforcement both for carbon black and silica in the rubber matrix and may enable a further improvement of filled elastomer performance.
- P-IV.03** 15:20 INFLUENCE OF NANO-FILLER SURFACE MODIFICATIONS ON DYNAMIC-MECHANICAL PROPERTIES AND FILLER DISTRIBUTION IN POLYMER BLENDS  
J. Zieger, J. Meier and R.H. Schuster, Deutsches Institut für Kautschuktechnologie e.V., Eupener Str. 33, 30519 Hannover, Germany  
Grades of carbon black and precipitated silica were modified by chemical post-treatment. The changes of surface energy distribution results in significant changes of filler-filler interactions as well as filler-polymer interaction. This was proven by Transmissions-Electron-Microscopy and measurements of filler dispersion and bound rubber as well as by effects demonstrated in the dynamical-mechanical behaviour. The filler distribution in rubber blends was estimated from the amplitude of the loss modulus in the glass transition region. It was shown that the loss modulus is increasing linearly with the filler volume fraction. The slope of this dependency is governed by the strength of the filler-matrix interaction. The filler distribution coefficients derived reflect very sensitively small differences in the interaction potential of the filler towards each blend constituent. Thus, by defined filler surface modification the filler distribution and the supramolecular organization can be carefully adjusted. A tailor-made material behaviour can be reproducibly achieved.
- P-IV.04** 15:40 ELABORATION AND THERMAL STABILITY STUDIES OF COLD PLASMA POLYMERIZED COATINGS  
I. Errifai, C. Jama, R. Delobel, Laboratoire PERF UPRES 1040, ENSCL, BP 108, 59650 Villeneuve d'Ascq, France, L. Gengembre, Laboratoire de Catalyse de Lille CNRS UMR 8010, USTL, 59655 Villeneuve d'Ascq, France, A. Mazzah and R. De Jaeger, LASIR UPR CNRS UMR 8516, USTL, 59655 Villeneuve d'Ascq, France  
In order to improve the thermal stability properties of polymers, a low pressure microwave plasma process has been investigated to graft a polyphosphazene onto polymer surface. The effect of several process parameters on the structure of the coatings are investigated. The graft materials are characterized using X-ray Photoelectron Spectroscopy, Fourier transform Infra red (ATR) and Scanning Electron Microscopy. The fire retardant performance of the treated materials has also been evaluated by the cone calorimeter technique.

**P-IV.05** 16:00 THERMAL STABILITY AND MECHANICAL PROPERTIES OF BIODEGRADABLE POLYLACTIDE/MONTMORILLONITE NANOCOMPOSITE  
Jidong He(a), Cheng Chen(a), Hongliang Kang(b), Man Ken Cheung(a) and Lisong Dong(b), (a)Department of Applied Biology & Chemical Technology, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, P.R. China, (b)State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P.R. China  
Polylactide (PLA) is linear aliphatic thermoplastic polyester, produced from renewable resources with good properties compared to many petroleum-based plastics. Because of excellent biodegradability and biocompatibility, PLA has been used widespread as a biomedical material, which includes bioabsorbable surgical sutures and implants, controlled drug delivery, and tissue culture. However, PLA has some undesirable shortcomings that have prevented its development as a commodity material, such as thermal stability, gas barrier, solvent resistance, and flame retardance. In order to design environmentally benign materials based on PLA that could have complete biodegradability and other properties suitable for various end-use purposes, the nanocomposites of PLA/montmorillonite (MMT) with the composition of 3%, 5%, 7% and 10% (w/w) were prepared by melting intercalation technique, and then their thermal stability and mechanical properties were emphatically investigated.  
Direct evidence of the intercalation of the polymer chains into the silicate galleries is provided by the WAXD patterns. With increasing MMT content, the diffraction peak of MMT becomes stronger and shifts to higher diffraction angle. Hence, the ordered intercalated structure is obtained in each nanocomposites, and the interlayer spacing decreases with the increase in MMT content. TGA curves of PLA and PLA/MMT nanocomposites with different MMT content in air and nitrogen atmospheres show that the thermal stability of PLA/MMT nanocomposites is remarkably improved. This means that the processing range of the nanocomposites is remarkably widened. The layer silicate has an excellent barrier property that prevents against the permeation of various atmospheric gases.

16:20

**BREAK**

Session V: New materials developments

Session chair: R. Schuster

**P-V.01** 16:40 -Invited- TAILORING OF BIOCOMPATIBILITY OF POLYMER – BASED COMPOSITE BIOMATERIALS  
**S. Blazewicz**, AGH University of Science and Technology, al. Mickiewicza 30, 30-059 Cracow, Poland  
Many structural materials have been placed in the human body in attempt to aid the body in repairing processes of diseased hard and soft tissues. By far, the predominantly used materials in the treatment of soft and hard tissue have been and still are metals and pure polymers. Most of tissues, including bone, have complex structure, and due to presence of fibrous components in organic or inorganic matrices their physical and mechanical properties are strongly anisotropic; the tissues have typical composite structure consisting of fibrous components. Thus, a materials that can function intimately with the living tissue, with minimal adverse reaction can not be manufactured as a single metallic or non-metallic phase. The work presents the results concerning new biomaterials that exploit the potential of non-metallic composite materials. Such composites, consisting of reinforcing fibrous elements, bioactive fillers and polymer matrices, are desirable as implant materials as both their biological and mechanical properties can be tailored for a given medical use. In this work we report a study on polymer – based composites considering the development of new biomaterials which can be used as composite internal fixation devices, bone substitutes and support for cellular growth in tissue engineering. Biostable and bioresorbable polymers, specially prepared fibrous constituents (polyacrylonitrile, carbon fibers) and bioactive ceramic fillers were combined to obtain specific set of properties and specific biological behavior. Ceramic nano - powders (calcium phosphate, hydroxyapatite) were used as fillers to prepare bioactive composite biomaterials. Possible applications of composite biomaterials in tissue engineering and in medicine are discussed.

**P-V.02** 17:20 INNOVATIVE, SCRATCH PROOF NANOCOMPOSITES FOR CLEAR COATINGS  
T. Graule, B.B ommer, J. Kürsteiner, O. Trzebiatowski, Swiss Federal Laboratories for Materials Testing and Research (Empa), Ueberlandstrasse 129, 8600 Dübendorf, Switzerland, W. Koch, Nanosys GmbH, 9427 Wolfhalden, Switzerland, B. Schmid, Basler Lacke AG, 5033 Buchs, Switzerland  
The incorporation of inorganic nanoscale particles into an organic matrix is of interest in many applications. Specific combinations of properties in coatings, such as transparency and wear resistance, can be obtained by using nanoparticles. The aim of the project is the development of high-grade transparent lacquers to provide clear coatings for mobile phones, skis, snowboards and helmets. The incorporation of nanoparticles produced by the process of high temperature flame synthesis should improve the scratch resistance while transparency and gloss remain constant.  
Non-aggregated silica nanopowder with an average particle size of less than 100 nm has been produced by the process of flame synthesis. Following surface modification with different silane e.g with reactive coupling groups nanoparticles were dispersed in 2 two-package polyurethane lacquer using high-speed dissolvers and ball mills. Total volume pigment contents of up to 23% were obtained. Nanolacquers with different contents of nanoparticles were applied to glass sheets to analyze scratch resistance and transparency. First results showed a tendency to higher scratch resistance with increasing solids loading.

- P-V.03** 17:40 SYNTHESIS OF NEW MACROAMORCORS BY OZONIZATION OF POLYFLUORIDE OF VINYLIDENE  
A. Serdani, Laboratoire de chimie, Université de Skikda, R. Messmoudi, Faculty of Science, University of Setif, Algeria, A. Djebaili, Laboratoire d'Etude des Matériaux Polymères, B. Boutevin, URA CNRS D 11930, ENS-Chimie- Montpellier, France  
We studied the synthesis of a macroinitiator containing vinylidene polyfluoride (PVDF) obtained by an ozonization reaction. On one hand, we optimized the reaction in order to control the rate of oxydation and on the other hand the ozonized polymer was also proportioned, which enabled us to determine the rate of active oxygen  $T(0^\circ)$  and the rate of hydroperoxydes. We noticed an average of 5.5 10-6 mole/gr, a relatively lower rate  $T(0^\circ)$  compared to those obtained for Polyethylene EP and the Polychloride of vinyl PVC, respectively of 5.6 10-5 mole/gr and 28.10-5 mole/gr. With regard to these two products, the presence of CH and C-Cl bonds sensitive to the action of powerful agents of oxydation such as ozone makes it easy to obtain compounds of oxydation of peroxides type and hydroperoxides compared to the PVDF for which the CF bond which has proven to be stronger. In the same way, this study showed that the technique of ozonization of the powder PVDF, despite of the insufficient rates of oxydation to which it leads, remains the most adequate adapted because it leads to a reduced increase in mass of the product.
- P-V.04** 18:00 SYNTHESIS AND APPLICATIONS OF GRAFT COPOLYMERS FROM OZONIZED POLY (VINYLIDENE FLUORIDE)  
A. Serdani, Laboratoire de chimie, Université de Skikda, N. Bourmada, Faculty of Engineering Science, A. Djebaili, Laboratoire d'Etude des Matériaux Polymères, Z. Skanderi, Department of Chemistry, University of Batna, B. Boutevin, URA CNRS D 11930, ENS- Chimie- Montpellier, France  
The synthesis and the applications of graft polymers prepared from ozonized poly (vinylidene fluoride) -PVDF - are described. The homopolymer was treated with ozone and then copolymerized with monomers such as styrene, acrylic acid, glycidyl methacrylate or methyl methacrylate. The products were used as emulsifiers in polymer blends as promoters for the adhesion of PVDF to composites made of epoxide matrices filled with glass fibres. The mechanical properties of these products are described. The copolymers were characterized by the grafting- rate.
- P-V.05** 18:20 THE USE OF FILLERS AND NANOCOMPOSITES IN FIRE RETARDANCY  
C. Jama, S. Duquesne, M. LeBras, R. Delobel, Laboratoire des Procédés d'Elaboration de Revêtements Fonctionnels, UPRES EA 1040, ENSCL, 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 nanocomposites, with clay mass fraction of 5%, show excellent improvement. Several approaches can be followed to prepare nanocomposites, in particular, melt mixing. In this study, polyolefin-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. 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.
- 18:40-19:00 POSTER'S SHORT ORAL PRESENTATION
- P/P.01** THE SPECTRAL PROPERTIES OF POLYMER DOPED AND COMPOSITE FILMS DEPENDING ON LEVEL OF DYE ASSOCIATION AND AGGREGATION  
Sergey Svechnikov, Petro Smertenko, Larysa Fenenko, V. Lashkaryov Institute of Semiconductors Physics of NASU, 45, prospekt Nauki, 03028 Kyiv, Ukraine, Nikolay Davidenko, Kyiv Taras Shevchenko University NASU, 64 Volodimirskaja str., 01017 Kyiv, Ukraine, Alexandr Ishchenko, Institute of Organic Chemistry NASU, 5 Murmanskaya str., 02094 Kyiv, Ukraine, Michael Hietschold, Falk Mueller, Chemnitz University of Technology, Institute of Physics, 70 Reichenhainer Str., 09126 Chemnitz, Germany  
The spectral characteristics of organic polymer films on the base of poly(N-epoxypropylcarbazole), doped by organic dyes (OD) with various ionic ability were considered. The preservation of rule of reflection similarity was observed up to high dye concentrations (20 mas.%) in polymer. The boundary dye concentration was revealed to take place in polymer films under investigation. This concentration stipulates for the film structure and properties. The dye aggregation takes place at exceeding boundary concentration in polymer. This was confirmed by results of AFM-investigations. It was shown the forming of H-aggregates. The physical models of structures depending on dye association and aggregation level was proposed.
- P/P.02** DONOR-ACCEPTOR INTRACTION IN ORGANIC POLYMER NANOCOMPOSITE FILMS WITH OXIDE OF transition metalS V2O5  
Sergey Svechnikov, Petro Smertenko, Larysa Fenenko, V. Lashkaryov Institute of Semiconductors Physics NASU, 45 prospekt Nauki, 03028 Kyiv, Ukraine, Nikolay Guba, Ludmila Grebinskaja, L.V. Pizarzhevski Institute of Physical Chemistry NASU, 31 prospekt Nauki, 03029 Kyiv, Ukraine, Sener Oktiik, Ozge Tuzun, Mugla University, 48000 Kotekli, Mugla, Turkey  
The nanocomposite films on the base of carbazolcontaining polymers poly(N-epoxypropylcarbazole) and poly(3,6-di-Br-N-epoxypropylcarbazole) with vanadium oxide (V) V2O5 were investigated. Spectral properties of the films was shown to be conditioned by presence of donor-acceptor charge-transfer complexes in them. The sensitization effect of spectral characteristics of polymer by vanadium oxide was considered. The conductivity of mentioned structures in dark and under illumination was investigated. The current-voltage characteristics was analysed and processed by the differential method, their approximations were offered. The conductivity mechanism in organic polymer nanocomposite films with V2O5 is discussed.

- P/P.03** ELECTRONIC STATES ALIGNMENT OF ZNPC, F16ZNPC AND ZNTPP ON SI(111):H IN VIEW OF SILICON/ORGANIC HYBRID MATERIALS FOR PHOTOVOLTAIC APPLICATIONS  
U. Weiler, T. Mayer and W. Jaegermann, Darmstadt University of Technology, Department of Material Science, Surface Science Division Petersenstr. 23, 64287 Darmstadt, Germany  
 Due to its indirect band gap the absorptivity of silicon is low but charge carrier separation and transport properties are good. On the other hand molecular or polymer semiconductors show high absorptivity but charge carrier separation and transport properties are bad. Therefore we developed a new concept for a solar cell composite material consisting of a silicon matrix with embedded organic pigment molecules or clusters. The intention is to absorb light strongly by the organic molecules, followed by injection of the excited electron-hole pairs into the conduction band and the valence band of silicon, respectively. In order to inject both, the photo excited electrons and the holes, the pigment LUMO state should energetically be situated just above the CB and the HOMO just below the VB. Comparing red-ox potentials of ground and excited states of pigments and electron affinity and ionisation energy of Si, ZnPc, F16ZnPc and ZnTPP have been chosen as possible candidates for the composite. We present experimental electronic states line ups of these molecules adsorbed on hydrogen terminated Si(111) surfaces using UPS and SXPS measurements. No chemically reacted species have been formed at room temperature. For ZnTPP the transport gap as well as the optical gap match perfectly the requirements for effective charge injection. For ZnPc the transport gap matches, but the optical HOMO state is found slightly above the Si VB. In the case of F16ZnPc the transport gap matches, but the optical LUMO state is situated slightly below the Si CB.
- P/P.04** THIN FILM COMPOSITES OF NANOCARBONS-POLYANILINE OBTAINED BY PLASMA POLYMERIZATION TECHNIQUE  
Claudia Nastase, M. Ionescu, F. Nastase, and Ioan Stamatin University of Bucharest, Faculty of Physics, 3Nano-SAE Research Centre, Bucharest Magurele MG-11, Romania  
 In many applications are required nanocomposites with functional gradient properties such as proton exchange membranes with catalytic effect, electronic transport with charge accumulation and electromagnetic shielding. Combining the polyaniline, polymerized in plasma with carbon nanoshells and regular nanocarbons is one of the alternative of these requirements. The insertion of the nanometric carbons into polyaniline films has been accomplished by the simultaneous injection in plasma reactor. The composites show specific features consisting of nano-sized carbon particles chemical bonded between the polymer chains. The films obtained were characterized FT-IR, SEM, AFM, XRD, Raman, electrical conductivity and dielectric properties.
- P/P.05** STRUCTURE AND PROPERTIES OF THE PLASMA POLYMERIZED FEROCENNE-PYRROLE FILMS  
Florin Nastase, Claudia Nastase and Ioan Stamatin University of Bucharest, Faculty of Physics, 3Nano-SAE Research Centre, Bucharest Magurele MG-11, Romania  
 Plasma polymerization is a useful method for depositing thin films on substrates. In this work thin polymer films containing ferrocene-polypyrrole have been prepared by plasma codeposition of the ferrocene and pyrrole monomers using an DC plasma reactor and a special technique of injection into reactor chamber. The polymeric films were characterized by FT-IR, AFM, XRD, SEM. The results show that ferrocene units are embedded between pyrrole units giving a very interesting organic-inorganic copolymer with electroactivity properties.
- P/P.06** CONDUCTIVE POLYMER NANO-COMPOSITES  
Marion Wienecke, Mihaela-C. Bunescu, Marlis Pietrzak, K. Deistung, T. Barfels, H. Hansmann, Hochschule Wismar, Institut für Oberflächen- und Dünnschichttechnik, Philipp-Müller-Str., 23952 Wismar, Germany  
 We report about the development of electrically conductive polymer nano-composites by mixing different graphite powders (carbon blacks, C-fibres and carbon nanotubes) with various polymers. Injection moulded polymer composites were analysed by electrical measurements, dielectric impedance, electromagnetic shielding, dynamo-mechanical analysis, and electron microscopy. The normal correlation between the electrical conductivity and the EMI shielding was registered. The shielding efficiency was enhanced by combination of different fillers in the same polymer matrix. The highest value of the shielding was 32 dB, measured for the complex composite material PBT + CNT + graphite. For 20 wt% CNT filled materials conductivities up to 1 S/cm have been measured. The alteration of the mechanical properties at high contents of fillers was improved by using CNT as filling material, for which a minimal impact on the mechanical properties was measured.
- P/P.07** MICROSTRUCTURE OF MONTMORILLONITE BASED NANOCOMPOSITE POLYMERS : AN ATOMISTIC STUDY OF ORGANOMODIFIED NANOFILLERS  
B. Minisini, Institut Supérieur des Matériaux et Mécaniques Avancés du Mans, 44 Av. F. A. Bartholdi, 72000 Le Mans, France  
 The microstructure of nanocomposite produced by melt blending depends on the type of organomodified nanofillers and the interactions between these later and the polymer matrix. In order to understand the influence of the type of organomodified nanofillers, four surfactants and 2 types of montmorillonite are studied by classical atomistic computer simulation. To this end, the dependency of the total energy with respect to the basal spacing was calculated and used to gain insight into the equilibrium distance and the nature of the interactions. The results are fitted to a Morse function allowing to analyse the local behaviour at equilibrium.

Thursday, May 27, 2004

Afternoon

Session VI: Advanced characterization techniques (1)

Session chair: P. Bertrand

- P-VI.01** 08:30 -Invited- STRUCTURE ANALYSIS OF POLYMER/NANOPARTICLE COMPOSITES  
**H. Hasegawa**, Department of Polymer Chemistry, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan  
Quantitative information on the structures of nanocomposite materials is necessary to understand and optimize their properties. Electron microscopy and small-angle scattering are two major techniques to analyze nanostructures. We employed 3D electron tomography to observe the distribution of metal nanoparticles in structured polymers such as block copolymers. Not only the metal nanoparticles can be selectively introduced into one of their microdomains but also the location of the nanoparticles within the microdomains can be controlled. The 3D image data provide the detailed information on the nanostructures.  
On the other hand, small-angle scattering is useful to evaluate the interfacial thickness of polymeric nanocomposites such as elastomers filled with carbon and silica nanoparticles. We examined natural rubber/polyethylene blends filled with carbon black by small-angle neutron scattering (SANS). Combined 3D electron tomography and SANS give the complete information on the nanostructures.
- P-VI.02** 09:10 -Invited- MECHANISTIC MODELING OF THE REINFORCEMENT AND NONLINEARITY IN NANOFILLED POLYMERS ABOVE THE GLASS TRANSITION TEMPERATURE  
**S.S. Sternstein**, Bing Jiang, Materials Science and Engineering Department, Rensselaer Polytechnic Institute, Troy, NY 12181, USA  
Experimental studies on nanofilled polymer melts and elastomers have shown that the filler surface treatment plays a major role in both the initial reinforcement and the subsequent relative dependence of storage and loss moduli on the shear strain amplitude. Thus, the dependence of the loss factor on strain amplitude is a characteristic of the filler surface that is sustained at all filler levels, including those far below the percolation threshold. In addition, the recovery kinetics of both storage and loss moduli have been shown to also depend largely on the filler surface treatment. Based on these observations, we have postulated that the primary source of high reinforcement at low filler volumes is due to the trapping of entanglements at the filler surface and the subsequent non-Gaussian (Langevin) chain statistics that ensue. Imposition of high strain amplitudes results in a release of the trapped entanglements and a concomitant decrease (or non-linearity) of moduli. These effects have now been modeled and this paper will present our initial results. The model consists of two parts, the first being the kinetics of the release process of surface-trapped entanglements that is associated with an imposed shear field, and the second being the reinforcement or modulus increase that is predicted by Langevin chain statistics and specific filler-polymer interactions. Combination of these two parts leads to the overall reinforcement-nonlinearity mechanism.
- P-VI.03** 10:00 MICROSTRUCTURE AND MORPHOLOGY OF NIMESULIDE-CROSPROVIDONE NANOCOMPOSITES BY RAMAN AND ELECTRON MICROSCOPIES  
**P. Bergese**, I. Alessandri and L.E. Depero, INSTM and Structural Chemistry Laboratory, University of Brescia, via Branze 38, 25123 Brescia, Italy, I. Colombo, Eurand S.p.A., Physical Pharmacy Laboratory, via Martin Luther King 13, 20060 Pessano con Bornago – Milano, Italy, N. Coceani, Eurand S.p.A., via del Follatolo 12, 34148 Trieste, Italy  
In drug-polymer nanocomposites the polymeric matrix inhibits the aggregation of the drug molecules, and “freezes” them in molecular clusters and nanocrystallites, which have different thermodynamic properties with respect to the bulk drug. This approach allows to turn soluble (i.e. bioavailable) yet insoluble drugs that demonstrate excellent pharmacological activity (40% of all drugs) and/or to tailor the drug onset of action. Nanocomposite microstructure and its relation to thermodynamic properties are therefore vital from both fundamental and technological standpoints.  
The present work follows our first study on nimesulide-crospovidone nanocomposites, in which the stability order and crystallite size of the embedded nimesulide polymorphs were investigated [1]. Here, further studies on microstructure and morphology are presented and discussed. They were carried out by analyzing cross sections of the nanocomposites by microraman spectroscopy, scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). Nimesulide resulted to be embedded into crospovidone according to two main arrangements: amorphous drug dispersed into the molecular crosslinked network of the polymer, and drug layers, made up of nanocrystallites, segregated onto the popcorn-like surface of the polymer. Results integrate information from the previous study and complete the microstructural picture of the material. Indeed, the adopted investigation strategy is general, and thus it can be relevant in all the research fields concerning nanocomposite polymer materials. [1] P. Bergese, E. Bontempi, I. Colombo, D. Gervasoni, and L. E. Depero, Compos. Sci. Technol. 63, 1197 (2003).

10:10

**BREAK**

## Session VII: Advanced characterization techniques (2)

Session chair: C. Hasegawa

**P-VII.01** 10:40 -Invited-

### SIMS AND AFM CHARACTERIZATION OF POLYMER NANOCOMPOSITES

**P. Bertrand**(a), L. Kailas(a), B. Nysten(b), J.-N. Audinot(c), H.-N. Migeon(c), Université catholique de Louvain, (a)PCPM and (b)POLY, Croix du Sud 1, 1348 Louvain-la-Neuve, Belgium, (c)Laboratoire d'Analyse des Matériaux, CRP Gabriel Lippmann, avenue de la Faïencerie 162a, 1511 Luxembourg

Materials characterization at the nanoscale is becoming an important issue for the development of new polymer composites. During this lecture, we want to illustrate the possibilities of the ion beam surface techniques in this field. Polystyrene (PS) and Poly (Methyl Methacrylate) (PMMA) blends and block copolymers, prepared as thin films by spin casting, were annealed above their glass transition temperatures for up to one week. Secondary Ion Mass Spectrometry (SIMS) was used to characterize the surface of as-cast and annealed films. ToF-SIMS, in static mode, allowed us to study the uppermost surface composition. Nano-SIMS, in dynamic mode, provided chemical mapping of the surfaces with a spatial resolution of 50 nm. AFM was also used to look at the surface topography. ToF-SIMS analysis indicated differences between blend and copolymer surface composition upon annealing: an increase in PMMA concentration for blends and the opposite for copolymers. Nano-SIMS images revealed a microphase segregation leading to the formation of submicron PS domains. AFM images confirmed complete phase segregation in the case of blends with droplet-like PS domains on top of a PMMA surface layer. Series of two-dimensional (2D) nano-SIMS images were recorded during the sample sputter etching, allowing a three-dimensional reconstruction of the film structure from successive 2D images. For blends, it is seen that the PS domains extend as columnar patterns inside the bulk of the layer, forming a polymer nanocomposite. The influence on the surface composition and topography and on the film structure, of the film thickness (lower than 50 nm), substrate nature and annealing time, are also discussed for blends and copolymers.

**P-VII.02** 11:20 -Invited-

### AFM AND TENSILE MEASUREMENTS STUDIES OF PDMS AND POLY(ESTER URETHANE) COMPRESSION MOLDED SAMPLES

**M.E. Hawley**, Material Science and Technology Division, Los Alamos National Laboratory, USA

Atomic force microscopy (AFM) phase imaging is a powerful technique for studying local variations in nanomechanical properties. This imaging technique depends on monitoring shifts in the phase of an oscillating tip cantilever due to local variations in tip-sample interactions. We have used phase imaging to study both compression molded filled polydimethylsiloxane (PDMS) composites and poly (ester urethanes) samples. Interest in fumed silica PDMS is driven by the need to optimize mechanical properties in these materials and understand aging processes. We focused on filler content, the evolution of stress-strain behavior during multiple tensile measurements, and time. AFM imaging was used to determine filler size, degree of aggregation, and distribution within the PDMS matrix. A tensile stage was used to measure mechanical properties. 35 parts per hundred filler samples were had optimum mechanical properties and a clear Mullins effect was seen. No change was seen in mechanical behavior as a function of time. Poly (ester urethane) studies were directed at determining the distribution of hard (HS) and soft (SS) within the material and the origin of structures observed at the surface. 10 nm strands and large rod-like structures were observed. 23% HS samples and pure polybutylene adipate, the soft segment component, were studied from 30 - 180°C. The strands disappear at 50 - 60°C, while the adipate melted at 62°C, suggesting that the strands are adipate rich. The rod-like structures persist up to 180°C, below the HS melting temperature. Segregated HS and SS domains around 10 nm were observed.

**P-VII.03** 12:00

### DETERMINATION OF THE ELECTRICAL BEHAVIOUR OF SURFACTANT TREATED POLYMER/CARBON BLACK COMPOSITE GAS SENSORS

**K. Arshak**, E. Moore, L. Cavanagh, J. Harris, B. McConigly, C. Cunniffe, G. Lyons, S. Clifford, Electronic & Computer Engineering Dept., University of Limerick, Plassey Technological Park, Limerick, Ireland

Conducting polymer composites, consisting of an insulating polymer phase and a conducting phase, often carbon black (CB), have been utilised in many applications such as gas sensors, pressure sensors, electrical shielding, thermistors and anti-static devices [1-4]. The conductivity of these materials and their response to compression, or expansion can be explained using percolation theory [5, 6]. Nanosized particles are scattered throughout the polymer and when the volume fraction reaches the percolation threshold conduction paths are completed across the composite along which electrical conduction can occur [1]. Volume changes induced in the composites, with compositions around the percolation threshold, have been found to have large effects on the conductivity where compression leads to increased conductivity and, conversely, expansion leads to decreased conductivity [3]. The permeation of gases into polymers and polymer composites leads to swelling of the material [7, 8]. Thus, these materials are ideal candidates for gas sensing where different polymers are sensitive to different vapours depending on the partition coefficient where CP is the concentration of the solute in the polymer composite phase and CV is the concentration of the vapour in the gas phase [9]. However, not many studies have looked at the effects of surfactants on the performance of gas sensors prepared from these types of composites.

**P-VII.04** 12:20

**FRACTOGRAPHIC STUDY OF VINYLIDENE POLYFLUORIDE COPOLYMERS BY SCANNING ELECTRONIC MICROSCOPY**

A. Serdani, Laboratoire de chimie, Université de Skikda, A. Sakri, Faculty of science, University of Setif, Algeria, A. Djebaili, Laboratoire d'Etude des Matériaux Polymères, M. Belloum, Department of Chemistry, University of Batna, B. Boutevin, URA CNRS D 11930, ENS- Chimie- Montpellier, France

This work made it possible to see the emulsifying effect of copolymer synthesised using SEM to examine the surface quality of the prepared alloys fractures. The examination of the stereotypes obtained on various alloys allowed the visualisation of the two involved phases. We observed on the initial mixture a continuous phase made up of PVDF in which polystyren PS nodules were inserted more or less extended forming a heterogeneous system. In addition, we noticed on other films that as the emulsifying rate in the mixture increases, the density of PS nodules as their size decreases significantly. Thus, the role of the emulsifier in these mixtures appears in the phase size reduction and subsequently by an increase in the state of dispersion. When we go on to a higher concentration of emulsifier agent from 3 % to 9 %, the size of the phases decrease from 19 mm to 10 mm, knowing that the initial value in the basic mixture was 24 mm. All these measurements confirm the emulsifying effect of our copolymer.

12:40

**LUNCH**

Thursday, May 27, 2004

Afternoon

Session VIII: Advanced characterization techniques (3)

Session chair: L. Arleth

**P-VIII.01** 14:00 -Invited-

#### MICROSTRUCTURE OF CARBON-BLACKS FROM X-RAY LINE BROADENING

**T. Ungár**(a), J. Gubicza(b), C. Pantea(c) and T.W. Zerda(c), (a)Department of General Physics, Eötvös University Budapest, Hungary, (b)Department of Solid State Physics, Eötvös University Budapest, Hungary, (c)Department of Materials Science, Cristian University, Fort Worth TX, USA

In x-ray or neutron scattering it is well known that smallness of crystallite size, called *coherently scattering domains*, is diffraction order *independent*, whereas lattice distortions are diffraction order *dependent*. The two effects can be separated provided crystallite size and lattice distortions are modelled correctly. The *coherently scattering domains* can be subgrains tilted or twisted by more than a few degrees or small crystallites separated by large angle grain boundaries. Lattice distortions are given by the mean square strain:  $\langle \epsilon_{L,g}^2 \rangle$ , where  $L$  and  $g$  are the Fourier length and the diffraction vector. Both, the size- and the strain effects can be anisotropic, which means that the corresponding broadenings are non-monotonous functions of the  $hkl$  indices. Whole diffraction pattern fitting methods based on physically sound models of the microstructure enable the characterisation of the size and size-distribution of crystallites and lattice strains. Crystallite shape- and strain anisotropy are also obtained from this type of X-ray diffraction peak profile analysis. Carbon blacks subjected to high pressure and high temperature treatments were investigated by the convolutional multiple whole profile fitting (CMWP) procedure. The average crystallite sizes determined by X-rays are in good correlation with Raman spectroscopy results. The X-ray data have shown that heat-treatment increases the average size of graphitic crystallites and that the initial disc shape tends to spheroidisation.

**P-VIII.02** 14:40 -Invited-

#### AFM STUDIES OF CHAIN AGGREGATE STRETCHING AND BREAKING

**S.K. Friedlander**, Department of Chemical Engineering, University of California, Los Angeles, USA

**P-VIII.03** 15:20

#### VOLUME TRANSITION AND INTERNAL STRUCTURES OF SMALL POLY(N-ISOPROPYLACRYLAMIDE) MICROGELS

**Rex P. Hjelm**(a), Xiaohu Xia(b), Lise Arleth(a) Jianzhong Wu(c) and Zhibing Hu(b), (a)Manuel Lujan Jr. Neutron Scattering Center, H805, Los Alamos National Laboratory, Los Alamos NM 87545, USA, (b)Departments of Physics and Chemistry, University of North Texas, Denton TX 76203, USA, (c)Department of Chemical and Environmental Engineering, University of California, Riverside CA 92521, USA

Monodispersed poly(N-isopropylacrylamide) (PNIPAM) nanoparticles, with the hydrodynamic radius  $R_h$  less than 50 nm at room temperature (about two orders of magnitude smaller than those reported previously), have been synthesized in the presence of a large amount of emulsifiers. These microgel particles undergo a swollen-collapsed volume transition in an aqueous solution when the temperature is raised to around 34°C. The volume transition and structure changes of the microgel particles as a function of temperature are probed using laser light scattering and small angle neutron scattering (SANS) with the objective of determining the small particle internal structure, particle-particle and particle-solvent interactions. We find that, within the resolution of the experiments, these particles have a uniform radial cross-linker density on either side of the transition temperature, in contrast to previous reports on the heterogeneous structures of larger PNIPAM microgel particles, but in good agreement with recent reports based on computer simulations of smaller microgels. Furthermore, the particle interactions change across the transition temperature: at temperatures below the transition, the interactions appear to be described by a hard sphere contact potential, although there is evidence for a strong hard-sphere-like repulsive particle interaction; above the volume transition temperature, the potential is best described by an attractive interaction.

**P-VIII.04** 15:40

#### CHARACTERIZATION OF POLYMERS FILLED BY NANO FILLOSILICATES

G. Giannotta, G.L. Marra, **L. Meda**, R. Po, Ist. Donegani Polimeri Europa, via Fauser 4, 28100 Novara, Italy  
Contents of this work are: the comparison of different fillers in the same polystyrene matrix; and the comparison of different polyolefin nanocompounds. The aim of their preparation is to get good exfoliation of inorganic lamellar fillers. The nanofiller dispersion into the polymers is made by a mixer (Haake Rheomix 600) equipped with roller type motors at about 200°C, with residence times ranging from 1 to 12 min. The samples are cryo-milled and compression molded in a shape of 1 mm thick disks. Virgin polymers are: polystyrene (Edistir N1280, Polimeri Europa) and linear low density polyethylene (Flexirene CL10, Polimeri Europa). The nanofillers are commercial modified montmorillonites: Cloisite 15A (Southern Clay) and Dellite 72T and 43B (Laviosa). The typical nanofiller concentration is 5%, but a good filled dispersion can also be obtained by mixing a fraction of maleated polyethylene (Fusabond MB226D, Dupont) to LLDPE with a very low filler content (0.25 %). The characterization techniques used for these samples are: XRD, TEM, XPS. XRD is the election technique to contror the filler exfoliation, by measuring the lamellar d-spacing of crystalline fillers in the polymer. The disappearing of the basal peaks means loss of crystalline order. TEM micrographs show how the filler is dispersed inside polymers. XPS chemical analysis, performed both at the surfaces and in the polymer bulk; lights up the filler segregation into samples.

16:00

**BREAK**

## Session IX: Advanced characterization techniques (4)

Session chair: W. Zerda

- P-IX.01** 16:20 -Invited- MICROSTRUCTURE OF CARBON BLACKS DETERMINED BY X-RAY DIFFRACTION PROFILE ANALYSIS  
**Tamás Ungár**, Jenő Gubicza, Eötvös University, Deptment of General Physics, P.O.Box 32, 1518 Budapest, Hungary, Cristian Pantea and T. Waldek Zerda, TCU, Department of Physics, Fort Worth TX 76129, USA  
The microstructure of carbon blacks is investigated by X-ray diffraction peak profile analysis. Strain anisotropy is accounted for by the dislocation model of the mean square strain in terms of average dislocation contrast factors. Crystallite shape anisotropy is modeled by ellipsoids incorporated into the size profile function. Different grades of carbon blacks, N990, N774 and N134, untreated, heat-treated and compressed at 2.5 GPa have been investigated. The microstructure is characterized in terms of crystallite size-distribution, dislocation density and crystallite shape anisotropy. Heat treatment results in increased vertical and lateral sizes of graphitic crystallites. Postproduction pressure treatment has little effect on the average sizes of the crystallites, however, it affects the crystallite size distribution function. The average sizes of the crystallites obtained by X-ray diffraction agree with those estimated from Raman spectra. Applied pressure affects the magnitude of strain within the crystallites.
- P-IX.02** 17:00 -Invited- DETAILED STRUCTURE OF HAIRY MICELLES FORMED IN PEGYLATED PHOSPHOLIPID SYSTEMS  
**Lise Arleth**, Danish Polymer Centre, Riso National Laboratory, Denmark, Beena Ashok and Hayat Onyuksel, Department of Biopharmaceutical Sciences, College of Pharmacy, University of Illinois at Chicago IL, Pappannan Thiagarajan and Jaby Jacob, Argonne National Laboratory, Illinois, Rex P. Hjelm, Manuel Lujan Jr. Neutron Scattering Center, MS H805, Los Alamos National Laboratory, Los Alamos NM 87545, USA  
Aqueous suspensions of mixed egg yolk phosphatidylcholine (PC) and poly(ethyleneglycol) (PEG) modified distearoyl phosphatidylethanolamine (DSPE) are prepared over a range of DSPEPEG to PC molar ratios ([DSPEPEG:PC] from [100:0] to [30:70]). The mixed micelles are prepared with either DSPEPEG2000 or DSPEPEG5000, where 2000 and 5000 refer to the molar mass of the PEG chains (in units of Dalton). By mixing DSPEPEG and PC considerable latitude in controlling the particle shape is obtained. Particle size, shape and internal structure were studied using small-angle x-ray (SAXS) and small-angle neutron (SANS) scattering. The obtained data were analyzed in a self-consistent way by fitting a molecularly-constrained model to the SANS and SAXS data simultaneously. We find that at high DSPEPEG:PC molar ratios, nearly spherical micelles are formed. As the PC content increases, the micelles gradually elongate and at a DSPEPEG:PC molar ratio of 30:70 rodlike micelles longer than 1000 Å are formed. At all mixing ratios, the PEG forms loosely structured corona that surrounds the dense core of the micelles. The observed growth is driven by a change of the spontaneous curvature of the lipid monolayer with changing mixing ratio. This extra latitude in controlling the particle size and shape makes the system a promising vehicle for intravenous delivery of hydrophobic drugs.
- P-IX.03** 17:40 STUDY OF UNDOPED POLYACETYLENE BY DIFFERENTIAL SCANNING CALORIMETRY (D.S.C)  
**A. Djebaili**, Laboratoire d'Etude des Matériaux Polymères, M. Belloum, Department of Chemistry, University of Batna, Y. Bouzaher, Laboratoire d'Etude des Matériaux Organiques, M.J.M. Abadie, Laboratoire d'étude des matériaux organique, France  
The isomerization of the form cis into trans is done at the temperature of 145 °C lasting 10 min. The sample subjected to a second cycle of heating does not exhibit the presence of exothermic peak, indicating thereby that it is completely isomerized. By subjecting the sample to different heating rates, it is possible to obtain the activation energy corresponding to the exothermic transformation carried out. Different PA were used. We report the results of two polyacétylène samples. The samples were studied in the temperature range from 30 °C to 280 °C and subjected respectively to heating rates of 5, 10, 20, 40 and 80 °C / min. We recorded the temperatures corresponding to the maximum of the exothermic peak (T max) of the isomerization reaction. It is observed that the points related to the two samples are placed on the same Arrhenius line. The study allowed the determination of the activation energy and the collision factor of the isomerization reaction. The results found are close to those obtained in literature by Ito et al and Bernier et al.

Friday, May 28, 2004

Morning

Session X: Advanced nano composites for optical, electrical and magnetic applications(1)

Session chair: F. Tsobnang

- P-X.01** 08:30 -Invited- USING TRIAXIAL MAGNETIC FIELDS TO CREATE OPTIMAL PARTICLE COMPOSITES  
**James E. Martin**, Robert A. Anderson, and Gerald Gulley, Sandia National Laboratories, Albuquerque NM 87185, USA  
Field-structured magnetic particle composites (FSCs) are an important new class of materials that have great potential as both sensors and actuators. FSCs are synthesized by suspending magnetic particles in a polymeric resin and subjecting these to magnetic fields during polymerization. The properties of FSCs are highly dependent on the structure of the particle assemblies, and we have developed methods of creating optimal structures using complex magnetic fields. If a uniaxial magnetic field is used, the particles will form chains, yielding FSCs whose magnetic susceptibility is nearly optimized along a single direction. A biaxial magnetic field, comprised of two orthogonal ac fields, forms particle sheets, yielding FSCs whose magnetic susceptibility is optimized along two principal directions. A balanced triaxial magnetic field can be used to optimize the susceptibility in all directions, and biased triaxial magnetic fields are effective for producing FSCs with a greatly enhanced susceptibility along a single axis. Particle assemblies that optimize the susceptibility also optimize other properties, such as the conductivity, making such materials quite effective as strain sensors, chemical sensors, etc. However, FSCs also have potential as actuators, since magnetostriction depends on the square of the susceptibility. To investigate magnetostriction we have constructed a constant-stress apparatus capable of 1 ppm strain resolution. We have demonstrated field-structured composites with nearly 10,000 ppm strain, and have shown that at large magnetic fields a structural phase transition occurs within the composite. These experimental results are compared to microscopic, self-consistent field simulations of magnetostriction in these complex, disordered materials.
- P-X.02** 09:10 NANOCOMPOSITE ION CONDUCTING MEMBRANES  
L. Pautrot, D. Carrière, P. Barboux, K. Lahlil, Physique de la Matière Condensée, Ecole Polytechnique, 91128 Palaiseau Cedex, France  
Polymer dispersions of colloidal particles and phosphates with large specific surface area (>100 m<sup>2</sup>/g) can yield large concentrations of ionizable OH groups and exchangeable protons equivalent to molar concentration of acids. These acid functions are anchored to the solid particles and cannot be eliminated during operation in electrochemical devices such as fuel cells or electrochromic cells. Therefore, they can offer a cheap alternative to organic polymers with sulfonic acid functions. However, three parameters must be further optimized: the acid strength, the ionic mobility and the stability of these properties towards dehydration. Indeed, the conduction pathway is controlled by the water content since water molecules act as charge carrier in a Grotthus-type diffusion mechanism of the protonic species. Various colloidal particles such as zirconium and cerium oxides as well as fibrous cerium phosphates were first prepared and purified. Their surface was functionalized through grafting of phosphates or phosphonic acids with increased acidity. Different mixtures of grafted species were also used in order to optimize both the charge carrier concentration and the conduction pathway. Then, the particles were dispersed in various polymers, neutral or with amino and imino functions, which can act as proton acceptor sites to further increase the ionization of the surface oxide particle. The resulting materials and membranes have been evaluated by conductivity measurements between room temperature and 200°C under various partial water pressures.
- P-X.03** 09:30 ORGANIC ABSORBER CENTRES IN Si: AN ORGANIC INORGANIC COMPOSITE ABSORBER MATERIAL FOR THIN FILM SOLAR CELL APPLICATION  
T. Mayer, U. Weiler and W. Jaegermann, Darmstadt University of Technology, Department of Material Science, Surface Science Division, Petersenstr. 23, 64287 Darmstadt, Germany  
High photovoltaic conversion efficiency is expected from a combination of the advantages of organic dyes for light absorption and of silicon for charge carrier separation and transport. The team of a joint project wants to find suitable dyes and deposition conditions for the preparation of inorganic-organic composite materials. The composite materials will be prepared by catalytic chemical vapour deposition of  $\mu$ c-silicon from silane and co-sublimation of organic dye molecules. Dye molecules are synthesized and specifically modified to allow for injection of photo-excited electrons and holes from dye orbitals to silicon bands. In our talk the basic idea of the concept of a bulk hybrid material for photovoltaic application will be introduced. Results of preliminary measurements on dye-Si and Si-dye layer models will be presented. Absorption and Raman spectra show that organic dye molecules as ZnPc withstand the deposition conditions of  $\mu$ c-Si. The selection of dyes crucially depends on the alignment of HOMO states versus the bands of the Si-matrix. Therefore the alignments of optical and transport gaps have been deduced for the possible dye candidates ZnPc, ZnPcF16 and ZnTPP on H-terminated Si(111) from photoelectron spectroscopy measurements. Preliminary growth tests on inorganic-organic model composites demonstrate that the absorptivity of dye molecules may be conserved in a compound. Multi-layer Si/dye systems have been characterized by Raman spectroscopy and Time Resolved Microwave Conductivity. The results will exemplify the strategy to challenge the task of producing a new inorganic-organic functional composite material in view of photovoltaic applications.

**P-X.04** 09:50 OPTICAL AND ELECTRICAL INVESTIGATIONS OF PPV/SiO<sub>2</sub> AND PPV/TiO<sub>2</sub> NANOCOMPOSITES  
S.H. Yang, P. Le Rendu, T.P. Nguyen, Laboratoire de Physique Cristalline, Institut des Matériaux Jean Rouxel, 2 rue de la Houssinière, 44322 Nantes cedex 3, France  
Composites made by incorporation of SiO<sub>2</sub> or TiO<sub>2</sub> nanoparticles into poly(p-phenylene vinylene) (PPV) have been fabricated and their optical and electrical properties have been investigated. Compared to PPV, composites with SiO<sub>2</sub> exhibited a large blue shift of the absorption band while those with TiO<sub>2</sub> showed comparable absorption characteristics. Photoluminescence (PL) spectra showed a similar blue-shift trend only for composites with SiO<sub>2</sub>. An increase in intensity of the shoulder at 514 nm was also observed when the SiO<sub>2</sub> concentration increased. Raman spectra showed a decrease of the 1547/1625 cm<sup>-1</sup> band ratio for composites with SiO<sub>2</sub> nanoparticles as compared to that obtained in PPV film and in composites with TiO<sub>2</sub> nanoparticles. The optical measurements suggest that SiO<sub>2</sub> nanoparticles reduced the conjugation lengths of PPV chains, while TiO<sub>2</sub> nanoparticles did not. In the case of SiO<sub>2</sub> composites, the reduction of conjugation lengths was enhanced on increasing the oxide concentration or on decreasing the particles size. FT-IR spectra showed that both types of particles reduced the formation of carbonyl groups in PPV main chains. Current-voltage characteristics measured in ITO-composite-MgAg diodes exhibit different electrical behavior depending on the particle size and the nature of the used oxide. The composite-electrode contact morphology, the polymer-particle contact and the change in the polymer chain length are the possible explanations for these changes in behavior of the diodes.

10:10

**BREAK**

Session XI: Advanced nano composites for optical, electrical and magnetic applications(2)  
Session chair: J. Martin

**P-XI.01** 10:40 OPTICAL PROPERTIES OF POLY(2-METHOXY, 5-(2'-ETHYL-HEXYLOXY)-PHENYLENE VINYLENE) DEPOSITED ON POROUS ALUMINA SUBSTRATES  
P. Le Rendu, S.H. Yang, T.P. Nguyen Laboratoire de Physique Cristalline, Institut des Matériaux Jean Rouxel, 2 rue de la Houssinière, 44322 Nantes cedex 3, France, H.R. Khan, Materials Physics Department FEM, Katharinenstraße 17, 73525 Schwäbisch Gmünd, Germany  
Thin films of poly(2-methoxy, 5-(2'-ethyl-hexyloxy)-phenylene vinylene) (MEH-PPV) were deposited on alumina-1%Mg substrates with different pore sizes from 18 to 78 nm to study the effects of the size on the optical properties of the polymer. The photoluminescence (PL) spectra of the composite systems showed a peak located at 454 nm, which is attributed to the porous alumina contribution and a peak located in the 590-600 nm region, which is attributed to the polymer. A blue shift of the polymer PL spectra was observed when the pore size decreases. Raman spectra recorded on the samples did not show significant changes compared to that of the polymer, suggesting that the structure of the polymer was preserved. The modifications observed in the PL spectra are attributed to the nanosize effect of the pores.

**P-XI.02** 11:00 POLYMER REFRACTIVE INDEX VARIATION USING NANOSCALED CERAMICS OR ORGANIC DYES FOR APPLICATIONS IN POLYMER WAVEGUIDES  
J. Böhm(a), J. Hausselt(a,b), E. Ritzhaupt-Kleissl(a), T. Hanemann(a), (a)Forschungszentrum Karlsruhe, Institute for Materials Research III, P.O. Box 3640, 76021 Karlsruhe, Germany, (b)Institute for Microsystem Technology, University of Freiburg, Germany  
Plastic Optical Fibers (POF) become more and more important because of their advantageous properties like high flexibility and their cost advantage in comparison to glass fibers. Industrial applications in the automotive sector, in telecommunications and others lead to an increased request for POF in the near future. The refractive indices of core and cladding have to be modified in order to get total reflectance. Thus, there is a strong demand for refractive index adjustable polymers with improved transmission properties in the visible and the NIR range. A large refractive index mismatch between plastic optical fibers or polymer waveguides and semiconductor based optoelectronic devices results in an enhanced Fresnel coupling loss at the interface. Therefore, an adjustment of the polymer's refractive index should reduce the total optical loss in a microoptical system. The dispersion of nanoscaled inorganic fillers in reactive polymer resins allows the modification of the polymer's refractive index to lower or larger values depending on the ceramic used. Due to agglomeration effects, however, scattering increases the optical damping depending on the stirring method. The addition of electron rich organic dyes instead of inorganic fillers results in a significant viscosity reduction in the reactive resins, in a pronounced increase of the refractive index up to 1.54, and in excellent optical transmission data in the NIR-range. A linear increase of the refractive index as a function of the filling content can be determined. Anyway, the transmission behaviour of organic filled test items is nearly independent of the filling content. Transmission values are nearly the same as those of unfilled PMMA.

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| <b>P-XI.03</b> | 11:20 | <p>IMPACT OF SYNTHESIS CONDITIONS ON THE ELECTRIC CONDUCTIVITY OF ORIENTED AND DOPED POLYACETYLENE</p> <p>A. Djebaili, Laboratoire d'Etude des Matériaux Polymères, <u>M. Goumadi</u>, Faculty of Science, University of Ouargla, Algeria, M. Belloum, Department of Chemistry, University of Batna, Y. Bouzahr , Laboratoire d'Etude des Matériaux Organiques, M.J.M. Abadie, Laboratoire d'Etude des Matériaux Organique, France</p> <p>We carried out measurement on a set of oriented polyacetylene films synthesized horizontally and vertically. For every type of a film and for a different thickness. We determined the d.c conductivity as a function of temperature in the range 120 K - 430 K. In the case of the two types of films analysed, the values of the activation energies <math>E_a</math> obtained experimentally are in the same order of magnitude regardless film thickness (<math>E_H = 0.47</math> eV and <math>E_V = 0.49</math> eV).The respective values of the collision factor <math>A</math> were obtained by extrapolation. It is worth noticing that extrapolation of <math>A</math> at 300 K instead of <math>T = 300</math> K; confirm the overall behavior of the curves. The conductivity measurement for <math>T = 300</math> K; corresponding to oriented undoped polyacetylene samples, show different behavior which is related to the deposition procedure of oriented polyacetylene vertically or horizontally, hence exhibiting morphology difference. The experimental conditions leading to optimal conductivity are determined.</p> |
|                | 11:40 | Closing remarks  |
|                | 12:00 | <b>LUNCH</b>   |