

# SYMPOSIUM KK

## Filled and Nanocomposite Polymer Materials

November 27 – 30, 2000

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\* Invited paper

SESSION KK1: DEVELOPMENTS IN MODELING  
OF PROPERTIES – MECHANISMS OF  
REINFORCEMENT

Chair: Michel Gerspacher  
Monday Morning, November 27, 2000  
Gardner (Sheraton)

**8:30 AM \*KK1.1**

SOME MOLECULAR CONCEPTS REGARDING RUBBERLIKE ELASTICITY AND ELASTOMER REINFORCEMENT. J.E. Mark, Department of Chemistry and the Polymer Research Center, The University of Cincinnati, Cincinnati, OH.

Rubberlike elasticity is defined as very high deformability with essentially complete recoverability. It is exhibited only by polymeric materials, and then only when the chains have the required flexibility and mobility, and are connected into network structures. A primary goal in this area is to maximize the mechanical properties of such elastomers, and some of these materials can reinforce themselves by strain-induced crystallization. This type of reinforcement, even when present, generally has to be augmented by the incorporation of particulate fillers such as carbon black or silica. There has long been a need for better molecular insights into how such fillers provide reinforcement, and this has encouraged recent analytical theories and computer simulations. Work in the simulations area is illustrated by some Monte Carlo calculations on one aspect of the problem, specifically determining the excluded volume effects of the filler particles on the network chain configurations. The resulting end-to-end distributions can be used in standard molecular models to generate stress-strain isotherms, which document the nature of the reinforcement obtained.

**9:15 AM KK1.2**

A MESOSCALE STRENGTH MODEL FOR SILICA-FILLED POLYDIMETHYL SILOXANE BASED ON ATOMISTIC FORCES OBTAINED FROM MOLECULAR DYNAMICS SIMULATIONS. D.E. Hanson and A. Redondo, Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM.

We present a novel mesoscale model that describes the tensile stress of silica-filled polydimethylsiloxane (PDMS) under elongation. Molecular dynamics simulations of a single chain of PDMS, interacting with itself and/or a hydroxylated silica surface provide estimates of the microscopic forces required to stretch or uncoil a chain of PDMS, or detach it from a silica surface. For both stretching and detachment, we find that the internal potential energy is linear with the distance the chain end is moved, albeit with differing slopes. From this we conclude that the forces required to stretch a chain or detach it from a silica surface are constants. Using these results, we develop a mesoscale inter-particle strength model for uncrosslinked, silicate-filled PDMS. We assume that most PDMS chains adhere to more than one silica particle, producing a single, continuous network whose strength arises primarily from the forces described above. The strength model includes these atomistic forces, as determined from the simulations, a small entropic component, and a Gaussian probability distribution to describe the lengths of PDMS strands connecting two silica particles and the chain lengths in the free ends. We obtain an analytic stress/strain expression whose predictions agree with experiment. This model also suggests mechanisms to explain the phenomena of hysteresis and permanent set.

**9:30 AM KK1.3**

MOLECULAR MECHANISMS OF FAILURE IN POLYMER NANOCOMPOSITES. Dilip Gersappe, SUNY Stony Brook, Dept of MS&E, Stony Brook, NY.

While a large number of studies on polymer nanocomposites have examined the development of morphology in the material, there is relatively little work that has examined the molecular mechanisms of failure in these materials. Here, we use a Molecular Dynamics simulation to study the processes by which spherical nanofillers can improve the strength of a polymer matrix. We examine systems in which the filler concentration is below the percolation threshold of the system (< 10% by volume). The polymer matrix is modeled as a bead spring chain, with chain lengths that are larger than the entanglement length. We examine the effects of filler size, interaction between the filler and the polymer matrix, temperature and pulling speed on the mechanism of failure in these systems. Our results show that the above the glass transition temperature of the polymer matrix, the mobility of the filler particles controls the response of the nanocomposite to an external load, by increasing the critical yield strength for cavitation in the material. By comparing these results to simulations in which the filler particles are effectively frozen in the matrix, we will show that by changing the mobility of the filler particles it is possible to induce a different mechanism of fracture in polymer nanocomposites. Thus, these results have important implications in the development of guidelines for the fabrication of polymer nanocomposites

**9:45 AM KK1.4**

CURE CHARACTERIZATION AND MECHANICAL REINFORCEMENT WITH POSS-BASED THERMOSETS. Xiaomei Fang and Patrick T. Mather, Institute of Materials Science, University of Connecticut, Storrs, CT.

To develop a better thermosetting system which combines high temperature performance with enhanced fracture toughness, polyhedral oligomeric silsesquioxane (POSS) monomers have been incorporated in traditional thermosetting polymers. In particular, we are focusing our attention on both bismaleimide and epoxy systems. To this end, POSS-diphenylene bismaleimide (POSS-BMI) was synthesized to yield a bulky, main-chain monomer distinct from commonly examined pendant-POSS monomers. Using multiple in-situ cure characterization techniques, we have found that bismaleimide groups in POSS-BMI react with traditional BMIs to provide direct chemical bonding between the bulky POSS polyhedra and the BMI comonomers. Moreover, this direct chemical bonding is shown to play an important role in both mechanical and thermal properties. The thermal cure reaction of POSS-octaglycidyl epoxide (POSS-OG) with 4,4-diaminodiphenyl sulfone (DDS) has also been investigated. Mechanical, rheological, and microstructural properties of these novel POSS-based thermosetting polymer systems will be discussed.

**10:30 AM \*KK1.5**

THEORY AND MODELING OF POLYMER REINFORCEMENT. Manfred Klüppel, Joachim Schramm, Deutsches Institut für Kautschuktechnologie e.V., Hannover, GERMANY.

A molecular based model of hyperelasticity and stress softening of filler reinforced elastomer materials is developed. It considers an advanced concept of rubber elasticity of bulk polymer networks together with a micro-mechanical model of strain induced filler cluster breakdown. The polymer network is described by a non-affine tube model of highly entangled chains, which takes into account that fluctuations in bulk networks are strongly suppressed by packing effects. The evaluation of stress softening is obtained via a strain dependent hydrodynamical amplification of the rubber matrix that refers to an irreversible breakdown of filler clusters with increasing strain. It is shown that the developed concept is in fair agreement with stress-strain data of unfilled NR-samples and carbon black filled SBR- and EPDM-samples. In particular, it is demonstrated that different modes of deformation (uniaxial, biaxial, pure shear) can be described by a single set of material parameters, since these are related to the specific morphological properties of the polymer network and the flocculated filler associates.

**11:00 AM KK1.6**

FRactal SHAPE ANALYSIS OF TIRE DEBRIS PARTICLES AND APPLICATIONS. Marina Camatini, Giovanni F. Crosta, Gaia Corbetta, Stefano Ambrosio, GianPaolo Giuliani, Università degli Studi Milano - Bicocca, Dipartimento di Scienze dell' Ambiente e del Territorio, Milano, ITALY; Simone Cenetti, Claudia Regazzoni, Pirelli Pneumatici S.p.A., Milano, ITALY.

Tire debris is produced by the normal wear of vehicle tire treads. Preliminary results are presented, which aim at characterizing the shape of debris particles by means of fractal analysis. Materials and Methods Silica and carbon black filled styrene-butadiene rubber debris coming from controlled laboratory wear tests is being analyzed. The binarized images of individual debris particles obtained from a white light microscope are processed by an algorithm [1], which determines the length of the perimeter (P) as a function of the chosen unit of length (yardstick, L). The fractal dimension (D) of the perimeter is deduced from the  $\text{Log}[P]$  vs.  $\text{Log}[L]$  plot [2]. Results Some sets of wearing conditions (abrader type, pressure, velocity) yield particles in a homogeneous class, described by one value of D in the explored yardstick range. Example: coarse particles similar to those of [3] have  $D = 1.3$ . Particles produced under different conditions need not be homogeneous: Log-Log plots either yield one value of D or exhibit a corner point at a characteristic yardstick length  $L_c$ . In this case particles have both a textural and a structural fractal dimension. Interpretation Particle morphology is the response to wearing conditions mediated by material inhomogeneities at the micrometer scale of length [3, 4, 5]. These results may provide information about crack initiation and tear dynamics [6] in filled elastomers. Applications Beyond being relevant to the diagnostics of rubber wear processes and to product quality assessment, fractal shape analysis provides a non destructive means, other than analytical electron microscopy [7], of characterizing and identifying tire debris particles in heterogeneous, environmental specimens. With reference to this last application, morphological analysis has to be cross validated by a different method: indeed, the elastomer contents is determined by a purposely developed, high sensitivity technique, which relies on IR absorption spectroscopy. Results from this technique will be presented

as well.

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#### 11:15 AM **KK1.7**

##### INTERCALATION OF UNENTANGLED POLYMER MELTS IN LAYERED NANOSTRUCTURES: A COARSE-GRAINED MOLECULAR DYNAMICS SIMULATION STUDY.

Rishikesh K. Bharadwaj, Systran Federal Corp., Dayton, OH; R.A. Vaia, B.L. Farmer, Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson AFB, OH.

The dynamics of the initial stages of polymer melt intercalation into layered nanostructures have been studied using coarse-grained molecular dynamics simulations. The bead-spring model was used in representing both polymer chains and the sheets comprising the layered nanostructure. The influence of the sheet stiffness, polymer-sheet and sheet-sheet interactions on intercalation behavior was studied. It is found that sheet stiffness plays a crucial role in determining the ability of a layered nanostructure to intercalate. Nanostructures comprised of flexible sheets intercalated spontaneously. Stiff sheets did not intercalate but manifested a sliding behavior, which occurred only when the polymer-sheet interactions were very strong compared to the sheet-sheet interactions. The results from the general model adopted here are discussed in the context of the intercalation phenomenon occurring in aluminosilicates.

#### 11:30 AM **\*KK1.8**

COPING WITH COMPLEX BOUNDARIES. Jack Douglas, Polymers Division, National Institute of Standards and Technology, Gaithersburg, MD.

There are many applications in materials science involving boundaries having complicated shapes and disordered particle configurations. Direct analytic treatment of this type of problem based on a traditional differential equation formulation with suitably prescribed boundary conditions is often intractable and the presence of complex and even "fractal" boundaries makes even finite element calculation difficult. This type of problem is recast in terms of an averaging over random walk trajectories (path integration). Representative calculations include the capacity (or equivalently Smoluchowski rate constant) and electric polarizability tensors of complex conductors, slow viscous flow in complex shaped channels, virial coefficients for the transport properties (thermal and electric conductivity, dielectric constant and refractive index, magnetic permeability,...) for filled materials containing complex-shaped particles having arbitrary property mismatch with the embedding medium, and long-wavelength scattering lengths of complex-shaped objects for electromagnetic and acoustic scattering. The Stokes friction coefficient and the intrinsic viscosity of complex shaped objects is also estimated based an electrostatic-hydrodynamic analogy. The capacity (Stokes friction coefficient) is calculated from the volume swept out ("Wiener Sausage") per unit time of the complex shaped particle undergoing random walk (Brownian) motion. Comparisons with exactly solvable and non-trivial test cases show that the path-integral computations give very accurate results and in many cases they become more efficient with increasing boundary complexity. These methods complement finite element calculations which are often more efficient for problems with simpler boundary geometries.

#### SESSION KK2: ADVANCED NANOCOMPOSITES I

Chair: Patrick T. Mather  
Monday Afternoon, November 27, 2000  
Gardner (Sheraton)

#### 1:30 PM **\*KK2.1**

MULTI-COMPONENT SYSTEMS CONTAINING NANOSCALE DISPERSIONS OF ORGANICALLY-MODIFIED LAYERED SILICATES. Richard A. Vaia, Barry L. Farmer, Janis Brown, Materials and Manufacturing Directorate, Air Force Research Laboratory Wright-Patterson AFB; Weidong Lui, R.K. Bharadwaj, Systran Federal Corporation, Dayton, OH.

Over the last decade, the utility of nanoscopic dispersions of inorganic nanoparticles as additives to enhance polymer and polymer-blend

performance has been established. A variety of fabrication routes, including co-dissolution, in-situ-polymerization, melt processing and mesophase mediated synthesis, are utilized. Recent rheological and processing research has demonstrated that the final, multiscale (hierarchical) morphology of the inorganic, and thus physical properties, depend critically on the fabrication and processing routes. In addition to these factors, the extremely large interfacial area between filler and matrix in true nanocomposites (approaching 500-700 m<sup>2</sup>/g) will result, in multi-component systems (such as polymer blends or thermosets), in segregation of constituents to the interface and subsequent depletion of the 'bulk' composition. These compositional fluctuations and graded-interfaces may be comparable to the distance between filler particles, thus challenging our conventional perception of discrete phases in multi-component systems. Herein, a detailed understanding of the spatial distribution of the various constituents and associated influence on thermodynamic and kinetic (rheological) aspects of the system is crucial. With regard to these issues, in-situ small angle x-ray scattering was used to examine the effect of a mixed medium on the structure and rheology of layered silicate dispersions. Preferential segregation of constituents is considered through spectroscopic measurements. Finally, coarse-grain Kremer and Grest molecular dynamic simulations of a stack of layers in a mixed oligomeric medium are discussed to provide addition insight into the development of the complex interfacial regions. These studies provide insight into the use of nanoparticles as blend compatibilizers, of polar activators for organosilicate rheological control agents and of additives to enhance nanocomposite formation (e.g. H<sub>2</sub>O addition for optimal exfoliated PDMS nanocomposites and incorporation of malic anhydride to produce polypropylene nanocomposites).

#### 2:00 PM **KK2.2**

'GREEN NANO-COMPOSITES' - THE MATERIALS OF THE FUTURE: COMBINATION OF NATURAL POLYMERS AND INORGANIC PARTICLES. Sabine Fischer, Jan de Vlieger, Lawrence F. Batenburg, Hartmut R. Fischer, TNO-Institute for Industrial Technology, Eindhoven, THE NETHERLANDS.

Research in the area of biological renewable materials has shown that the main building blocks of life - carbohydrates, fats, proteins, and their derivatives - could substitute products from traditional non-renewable sources. However its realization will need significant and continuous improvement of those materials. Problems of applications of bioplastics arise not only from the (prize) competition with the highly developed synthetic polymers but also from their, up to now not sufficient property levels. Possibilities to decrease the hydrophilicity and to increase the values of mechanical properties so far are: i) application of coating(s) of the processed bioplastic material with hydrophobic materials; ii) blending with different, hydrophobic, biodegradable synthetic polymers (polyesters) and iii) new ways of reactive extrusion of natural polymers (graft- and co-polymerization, esterification during extrusion process). A new possibility in this direction is seen in the creation of composite materials of thermoplastic organic biopolymer and nanoscopic inorganic particles incorporated on a molecular scale. The presentation will show the results of the first experiments to get nano-scale starch/clay composites. The starch will be fully gelatinized and the modified clay can be dispersed homogeneously on a truly nano-scale. Therefore all requirements of a significant increase in mechanics and a decrease in permeability of this composite material are present.

#### 2:15 PM **KK2.3**

BLOCK COPOLYMERS AS TEMPLATES FOR SELF-ORGANIZING NANOCOMPOSITE ELECTRODES FOR HIGH-POWER, RECHARGEABLE LITHIUM BATTERIES. Patrick E. Trapa, Simon C. Mui, Biying Huang, You-Yeon Won, Donald R. Sadoway, Anne M. Mayes, Dept of Materials Science and Engineering, MIT, Cambridge, MA; Azzam Mansour, Naval Surface Warfare Center, Carderock, MD.

Using block copolymers as templates, nanocomposite electrodes capable of delivering very high currents in rechargeable lithium batteries have been synthesized. Anodes comprising carbon nanotubes connected to a dispersion of metal nanoparticles, all self-assembled within the POEM phase of the diblock copolymer poly[oligo(oxyethylene) methacrylate] - b - poly(laurel methacrylate) doped with lithium triflate, have been characterized in coin-cell battery test configurations. Cathodes comprising carbon nanotubes coated with vanadium oxide were similarly prepared. In charge/discharge tests over hundreds of cycles at rates as high as 4 C these electrodes exhibited high resistance to capacity fade.

#### 2:30 PM **KK2.4**

STRUCTURE CONTROL IN POLYMER-INORGANIC NANOCOMPOSITES FROM BLOCK COPOLYMERS. Adam C. Finnefrock, Gil Toombes, Sol Gruner, Ulrich Wiesner, Cornell

Univ, Ithaca, NY; Ralph Ulrich, Alexander Du Chesne, Max-Planck-Institute for Polymer Research, Mainz, GERMANY.

Nano-structural control at the near-atomic scale of organic as well as inorganic materials is an essential feature of growth phenomena in living organisms. In biological systems it has been achieved through long evolutionary optimization processes and is often the result of a complex interplay between a large number of constituents. Such nano-structural control in the synthetic approach to polymer-inorganic nanocomposite materials is still a challenge. Here the effect of block copolymers as structure directing agents will be discussed.[1] Unprecedented morphology control is achieved by changing from conventional silicon precursors to organically modified ceramic (ormocer) precursors in the block copolymer directed synthesis. The resulting polymer-inorganic nanocomposite materials show a unique type of interface between organic and inorganic components in which one of the blocks is entirely embedded into the inorganic phase.[2] This leads to a two phase system which shows very similar phase behavior as observed in phase diagrams of block copolymers and mixtures with their respective homopolymers. With the help of transmission electron microscopy (TEM) and two-dimensional small angle x-ray scattering (SAXS) we show the existence of a whole range of block copolymer microstructures for the polymer-inorganic nanocomposites. Particular emphasis will be on the analysis of bicontinuous cubic structures in which the polymer phase is the minority component. Calcination leads to mesoporous materials which have potential applications in the fields of catalysis, separation technology and microelectronics.

References:

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#### 2:45 PM **KK2.5**

FIELD-STRUCTURED SUPERPARAMAGNETIC NANOPARTICLE COMPOSITES. James E. Martin, Eugene Venturini, and Judy Odinek, Sandia National Laboratories Albuquerque, NM.

Filled polymer composites typically consist of randomly dispersed particles, and so have isotropic properties. It is possible, however, to use electric and magnetic fields to create highly anisotropic chain-like and sheet-like particle structures, provided a sufficient permittivity or permeability contrast between the particle and polymer phases exists, and that the particles are sufficiently large that the induced dipolar interactions exceed the thermal energy. These Field-Structured Composites can have highly anisotropic optical, magnetic, dielectric, and transport properties. In the case of magnetic particles, it is possible to create significant dipolar interactions with single-domain nanoparticles that exhibit superparamagnetism. The magnetic properties of these nanostructured composites are highly anisotropic, due to the collective interactions between these particles. Significant shifts in the blocking temperature occur, as well as in the susceptibility, and these are modeled by a Langevin spin dynamics code. Both experimental and simulation results are discussed, and the origin of the glassy magnetization dynamics is illustrated in calculations on periodic nanoparticle superlattices.

#### 3:30 PM **\*KK2.6**

ALTERNATIVE APPROACHES TO THE FORMATION OF POLYMER-CLAY NANOCOMPOSITES. Thomas J. Pinnavaia, Zhen Wang, Michigan State University, Department of Chemistry, East Lansing, MI.

The preparation of polymer - clay nanocomposites is normally based on the use of onium ion exchanged smectite clays as the reinforcement phase. The organic onium ion is needed in order to make the polarity of the clay nanolayers compatible with the polymer for dispersal in the polymer matrix. However, these reagents are expensive, and, more importantly, they often compromise the performance properties of the reinforced nanocomposite. We are developing several new approaches to dispersing silicate nanolayers in either a thermoset or a thermoplastic polymer matrices by greatly reducing or even eliminating the need for organic modification of the nanolayers. Consequently, one can expect to greatly improve the economics of nanocomposite manufacturing and at the same time improve the performance properties of the nanocomposites.

#### 4:00 PM **KK2.7**

COMBINATORIAL APPROACH TO NANO-FILLED POLYMER FILMS. Vincent Ferreiro, Jack F. Douglas, J.C. Meredith, Archie P. Smith, Eric J. Amis, Alamgir Karim, Polymers Division, NIST, Gaithersburg, MD.

The characteristics of thin polymer films as barrier properties, dewetting, nanomechanical properties or phase separation behavior for a filled polymer blend can be tuned by adding fillers. We investigate the influence of different kind of fillers on the properties of coated homopolymers as polymethylmethacrylate (PMMA), polyethyleneoxide (PEO) and coated polymer blends (PS/PVME, PEO/PMMA). Polymer or blend films with a composition gradient of fillers were prepared in one direction (x direction) and a temperature gradient has been applied in a perpendicular direction (y direction). For each position (x,y) we can follow the influence of filler concentration on the properties of the filled films such as dewetting. We also investigated the nanomechanical properties of filled thin film by a combinatorial way. We choose a filled matrix where the degree of crosslinking of the matrix is function of UV exposure. Then, we prepared samples with a gradient of filler concentration in one direction (x direction) and a gradient of crosslinking in the perpendicular one (y direction). The nano-mechanical properties of coated films for each (x,y) position have been obtained using atomic force microscopy by analyzing force curves.

#### 4:15 PM **KK2.8**

ADVANCED NANOCOMPOSITE POLYMER FILMS FOR BIMORPH GAS SENSORS. G. Gerlach, M. Guenther, G. Suchanek, Dresden University of Technology, Institute for Solid State Electronics, GERMANY; K. Sahre, K.-J. Eichhorn, F. Simon, Institute for Polymer Research Dresden, GERMANY; A. Deineka, L. Jastrabik, Institute of Physics, Acad. Sci. CR, CZECH REPUBLIC.

Thin films of aromatic polymers such as polyimide (PI) find extensive use in aerospace and electronic application. Heterogeneous films with graphite-like surface regions are produced by deterioration of chemical bonding under ion bombardment. The physical properties of these nanocomposite films may be tailored for special sensor applications. In this work, a complex investigation of film composition, microstructure and physical properties of ion beam modified polymer films was carried out in order to optimize gas uptake and gas selectivity. To modify thin films of polyimide and polyethersulfone up to a depth of about 750 nm, 50 to 180 keV boron ions were implanted. The irradiation dose was varied between  $10^{13}$  and  $10^{16}$  B/cm<sup>2</sup>. After implantation, the chemical changes in the surface regions were investigated by Attenuated Total Reflection (ATR)-FTIR spectroscopy and ESCA. Film composition was also analyzed by RBS. The thickness of surface layers, refractive index and extinction coefficient depth profiles were determined by Variable Angle Spectroscopic Ellipsometry (VASE). Anisotropy and uniaxial character of polymer orientation in the spin coated films were obtained by fitting optical functions using a 4x4 matrix formalism. Volume and surface resistivity measurements were performed using evaporated Ag and NiCr/Au electrode configurations consisting of bottom, measuring and guard electrodes as described in IEC 93. Gas uptake  $c_s(\varphi)$  was determined as the actual mass uptake by the polymer film using an enclosed precision balance with an accuracy of about 20  $\mu$ g and described by a Freundlich isotherm  $c_s = c_s^m a x \cdot \varphi^n$ . The application of ion beam modified polymer films in bimorph piezoresistive gas sensors is discussed.

#### 4:30 PM **KK2.9**

OPTICAL PROPERTIES AND WETTING OF FLUORO-POLYMER MULTI WALLED NANOTUBE COMPOSITES. Preethi N. Iyer, Richard Czerw, Eric Gregory, David L. Carroll, Dept of Physics and Astronomy, Clemson University, Clemson, SC; Dennis W. Smith Jr., Dept of Chemistry, Clemson University, Clemson, SC; John B. Ballato, Department of Ceramics and Materials Engineering, Clemson University, Clemson, SC.

We introduce a class of fluoropolymer - carbon nanotube blends for which excellent nano-particle dispersion naturally results from wetting interactions. These polymers, in addition to their wettability, have attractive properties like low transmission losses, low refractive index and low dielectric constants, and are ideal materials for potential use in optical communication devices. Monomers were prepared from their corresponding phenolic precursor, and multi-walled carbon nanotubes (MWNTs) were added by melting the monomer, adding the MWNT's, and sonicating. The composite PFCB polymers were produced from the thermal cyclodimerization of these aryl trifluorovinyl ether monomers. Thin films of the composites were made by curing in a press. The surface energies of the monomers and polymers were evaluated using Neumann's equation. The films were examined by scanning electron microscopy, transmission electron microscopy, and Z-scan spectroscopy. UV-vis and FTIR spectroscopy results will also be presented.

#### 4:45 PM **KK2.10**

NOVEL PROPERTIES OF POLYMER NANOCOMPOSITES USING OXIDE NANOPARTICLES PRODUCED BY A FORCED GAS CONDENSATION METHOD AND ULTRASONIC PROCESSING. B. Ash, J. Nugent, M. Aimi, J. Stone, T. Li, L.S. Schadler, R.W.

Siegel, MS&E Department; D. Rogers, C. Wiegand, T. Apple, B.R. Benicewicz, Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY.

In order to capitalize on the unique combinations of mechanical properties observed in polymer nanocomposites, it is vital to understand the interaction of the polymer chain with the particle surface. The goals of our current work are to characterize the polymer/filler interfacial interactions, tailor this interface, and relate this understanding to the bulk mechanical properties of nanocomposites. We chose a glassy thermoplastic polymer, polymethylmethacrylate (PMMA), as a model matrix and added ceramic nanoparticles produced by forced gas condensation to reinforce the polymer. Particles produced by forced gas condensation are chemically "clean", spherical, and relatively monodisperse compared to nanoparticles produced by fuming or chemical synthesis. Therefore, they provide an excellent stage to characterize the interface and particle-to-particle interactions. A key factor in nanocomposite synthesis lies in the dispersion of the nanoparticles. Excellent dispersion was achieved through the use of silane coupling agents and a series of sonication steps. The interaction between filler and matrix was characterized by solid-state nuclear magnetic resonance (NMR) and infrared spectroscopy techniques. Bulk mechanical testing and thermal analysis were carried out by tensile, scratch, differential scanning calorimetry (DSC), and dynamic mechanical thermal analysis (DMTA) techniques. It was found that for specific volume fractions and dispersions of the nanofiller the modulus, ultimate strength, and strain to failure were simultaneously increased by 20%, 45%, and 25%, respectively, when the interface between polymer and filler was optimized. These gains in mechanical properties contrast a 20°C decrease in the glass transition temperature, indicating a rising volume fraction of mobile polymer, as determined through NMR, DSC, and DMTA. We are currently investigating the interfacial effects of altering the molecular weight of the polymer, both above and below the entanglement length, and tailoring the interface to provide strong and weak interactions.

SESSION KK3: DEVELOPMENTS IN THE  
MECHANISM OF REINFORCEMENT

Chair: Richard A. Vaia  
Tuesday Morning, November 28, 2000  
Gardner (Sheraton)

**8:30 AM \*KK3.1**

**POLYMERS IN CONFINED GEOMETRIES AND THE IMPACT ON SILICA REINFORCED ELASTOMERS.** Gert Heinrich, Continental AG, Strategic Technology, Advanced Materials, Hannover, GERMANY; Thomas A. Vilgis, Univ Strasbourg, Inst Charles Sadron, Strasbourg, FRANCE and MPI für Polymerforschung, Mainz, GERMANY.

Balanced fuel economy - wet grip performance is a strong point of silica reinforced solution polymerized styrene-butadiene rubbers (S-SBR) for treads of high performance tires. We present comparable dynamic-mechanical studies on silica filled S-SBR and emulsion SBR (E-SBR) compounds of otherwise same recipe. At intermediate and larger dynamic amplitudes the observed high hysteresis of E-SBR leads to values of the loss factor  $\tan \delta$  much larger as in the case of S-SBR. This larger hysteresis of E-SBR compounds leads to larger rolling losses as seen in corresponding tire tests. It is known that the higher hysteresis of E-SBR is caused by its macrostructure, primarily by the lower primary chain molecular weight and high degree of branching in comparison with S-SBR. We discuss the observed differences in a new physical model of rubber polymer-silica interaction. The model uses the experimentally supported view that silica exists as clustered into agglomerates and should be considered as a nano-porous system. Therefore, it is tempting to model the polymer-silica interaction as the behavior of branched or linear polymers in small pores. In these cases the restricted geometry in space competes with the connectivity of the polymers and new and interesting physical effects come into play. The connectivity is expressed through the spectral dimension  $D_s$  of the (fractal) polymer objects. We discuss consequences for the penetration of typical (E-SBR and S-SBR) tire tread polymers into typical nano-porous silica fillers. The different penetration effects, in combination with effects arising from the chemical activation of the filler surface, lead to a new mesoscopic view of silica reinforcement. Finally, we briefly discuss some consequences for the mixing process of polymers and their corresponding injection thresholds into the pores. A brief outlook discusses consequences for the model if the polar character of silica surfaces is included into the sophisticated model.

**9:00 AM KK3.2**

**THE EFFECT OF FILLER-FILLER AND FILLER-ELASTOMER INTERACTION ON RUBBER REINFORCEMENT.** J. Fröhlich and

W. Niedermeier, Degussa-Hüls AG, Applied Technology, Hürth, GERMANY.

Although the reinforcement of rubber by active fillers is a well recognized phenomenon, neither the term "reinforcement" has up to now been satisfactorily explained nor has the influence of their basic characteristics been investigated in detail. For a better understanding of the mechanism of reinforcement and furthermore of the properties required for rubber products and their end usage it is absolutely necessary to study the role of carbon black and silica on viscoelastic properties of filled rubber compounds intensively. 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 vulcanizate interaction in the green compound as well as in the vulcanizate over a larger share range. 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 tire performance.

**9:15 AM KK3.3**

**EFFECT OF FILLER NETWORKING ON VISCOELASTIC PROPERTIES OF FILLED RUBBER.** Meng-Jiao Wang, Ting Wang, and Khaled Mahmud Cabot Corporation, Business & Technology Center, Billerica, MA.

The impact of fillers on compound properties, in particular dynamic properties, will be discussed. Based on the strain dependence, temperature dependence and frequency dependence of the viscoelastic properties of filled- and unfilled vulcanizates, this paper will discuss the impact of the filler network, both its strength and architecture, on the dynamic modulus and hysteresis during dynamic strain. The effect of surface modification on filler networking will also be discussed.

**9:30 AM \*KK3.4**

**NETWORK TOPOLOGY, FILLERS, AND TEAR.** Jon V. DeGroot, Jr., Elastomer Technology, Dow Corning Corporation, Midland, MI.

Over the years, much theoretical and experimental work has been done to try to optimize the mechanical properties of filled elastomeric systems. One of the properties of particular importance is tear strength. It has long been recognized that the choice of filler, surface treatment, and structure can significantly alter tear properties. More recent work has suggested that the use of bimodal networks can dramatically improve tear properties. This work examines the role of network topology and filler structure together. Fillers with significantly different structures but similar surface chemistries are considered in various bimodal silicone polymer mixtures. The resulting changes in tear strength will be examined as a function of these variables and compared with current theories.

**10:30 AM \*KK3.5**

**REINFORCEMENT MECHANISM OF FILLED POLYMER AND POLYMER BLEND.** R.H. Schuster.

The effects of particulate materials for enhancement of polymer properties are based on supramolecular organized fractal structure of the fillers (filler network) interpenetrating the polymer network. It will be demonstrated that the formation of the fractal filler network depends on the balance of opposing interactions. On one hand the filler-filler interactions and on the other the filler-polymer interactions. The dynamic-mechanical effect of the filler network in the low strain region are rewritten by an universal scaling law, which considers the cluster-cluster aggregation of filler particles and the fractal nature of the filler network. The contributions of both the surface roughness and the surface energy distribution of the filler to its dispersion and percolation threshold will be discussed in relation to the polymer segment interaction potential. New material properties can be developed by appropriate functionalization of the polymers and/or the fillers.

**11:00 AM KK3.6**

**A POLYMER/CERAMIC COMPOSITE IN WHICH GROWTH SEQUENCES ARE DESIGNED TO YIELD A SUPERIOR MICROSTRUCTURE.** Carolyn Dry, School of Architecture, University of Illinois, Champaign, IL.; Natural Process Design, Champaign, IL.

This polymer/ceramic composite is designed to yield superior strength and toughness due to careful growth sequences. The polymer forms

first and the ceramic uses the effluent of this polymerization reaction to react chemically. Intimate bonds are possible because of the chemicals used. Like bone, the polymer is formed first and acts as a three dimensional template upon which the ceramic forms. Thus the ability to control structure at the smallest nanoscale would be present. Like bone, the fibers form first and the matrix is grown around them. The physical design of the overall system is that of a reaction separation vessel in which the reactant materials are released into a matrix via a series of porous walled tubes which place the chemicals where they are needed. This efficient processing method leaves no waste and requires no heat or mixing. Physical testing showed that the composite produced had superior strength and toughness. SEMs revealed that the bonds were chemical and mechanical depending upon which chemicals were used. It appears that templating is occurring in the ones with chemical bonds. Further research is needed to verify the nature of the templating that develops. Deeper understanding of the chemistry involved is needed to give greater microstructural control at the nanoscale.

#### 11:15 AM **KK3.7**

##### DEVELOPMENT OF SELF-HEALING POLYMER COMPOSITES.

Suresh R. Sriram, Jeffrey S. Moore, University of Illinois at Urbana-Champaign, Dept of Chemistry, Urbana, IL.

Polymer composites being stronger and lighter than metals are used in a wide variety of applications ranging from rust-resistant cars and fuel-efficient airplanes to microelectronics. However, due to thermoset nature of many of these materials, they are susceptible to damage in the form of microcracking. Upon formation of cracks the integrity of the structure is significantly compromised. The inability to precisely locate the hidden damage and assess the integrity has been a reason for the limited use of polymer composites, except in niche applications. We herein, report the development of a polymer composite with the ability to self-heal. Self-healing is accomplished by incorporating a microencapsulated healing agent and an embedded catalyst within a polymeric matrix. When the material is damaged, the microcapsules rupture and release the healing agent into the fracture plane through capillary action. As the healing agent contacts the embedded catalyst, polymerization is initiated and the damage is repaired. We have successfully applied the living ring opening metathesis polymerization (ROMP) to develop a system that would meet the diverse set of requirements of the healing agent including long shelf life, low monomer viscosity and volatility, rapid polymerization rate at ambient temperatures and low shrinkage upon polymerization. Experiments on tapered double cantilever beam fracture specimens have shown as much as 75% self-healing efficiency.

#### 11:30 AM **\*KK3.8**

##### EXTRACTING DISPERSION FROM ROUGHNESS. Claude Tricot, Univ Blaise Pascal, Lab Pure Maths, Aubiere, FRANCE.

The dispersion of Carbon Black in Elastomeric matrices, referred as rubber compounds in the industry, is known to be essential to assure quality performances of the final product. Because of the size, shape and nature of the carbon black this dispersion is very difficult to quantify directly. Since the mono-unit of carbon black, the aggregate of sub-micron size, has a strong tendency to agglomerate in clusters of various sizes the quantification of the filler dispersion has to take into account that size distribution. In the past this distribution was subjectively evaluated using 2D-projections obtained using Microscopic techniques ranging from the Transmission Electron Microscope to the most commonly used Optical Microscope. It is well known that the quantification of such images is widely subjective and therefore other techniques were evaluated. The micro-roughness of a freshly created surface of the rubber compound is measured using a scanning mechanical spectrometer equipped with a diamond stylus (tip diameter of 1 micron). The object of this paper being the mathematical treatment of the obtained data it is assumed that the experimental parameters are well defined and produce reproducible data. Assuming that a pure elastomeric surface, without carbon black is perfectly smooth at the micron scale any roughness encountered in filled samples can be attributed to carbon black agglomerates. Therefore the rougher the surface the less dispersed the filler.

##### Getting a long profile

The profilometer measures 200 profiles  $P_1, \dots, P_{200}$ , of a given surface. Each of them is obtained with 500 datas. The horizontal distance between datas is 2 microns, the distance between  $P_j$  and  $P_{j+1}$  is 5 microns. We thus obtain an array of  $500 \times 200$  datas covering a surface of  $1000 \times 1000$  squared microns. 2-D surface roughness analysis always give less precise results than 1-D profile analysis. To get to a 1-dimensional space, we simply put the 200 profiles end-to-end in order to create a  $2 \times 10^5$  microns profile, determined by  $N = 10^5$  datas. We preserve the continuity of this new profile by inverting the sense of every even-numbered profile, so that the end of  $P_j$  is near the beginning of  $P_{j+1}$ . Let us denote by  $z(t)$ ,  $t \in [0, N]$ , the one-variable continuous function whose graph corresponds to these datas.

#### Roughness analysis

We choose to work inside the scales  $\tau = 1$  to 100 microns. The size of the carbon black agglomerates fit that scale. A first method to evaluate roughness consists in measuring the *local oscillations*

$$r(z, t) = \sup\{|z(ts) - z(t)|, |s| \leq \tau\}$$

of the function  $z$ . Averaging over the whole interval  $[0, N]$  gives

$$S_\tau^{(\infty, 1)} = \frac{1}{N} \int_0^N r(z, t) dt.$$

We know that for small values of  $\tau$ ,  $S_\tau^{(\infty, 1)} \simeq \tau^\Delta$  where  $\Delta$  is the fractal dimension of the profile. Using logarithmic scales, the graph of  $\log S_\tau^{(\infty, 1)}$  vs  $\log \tau$  is increasing, and its behaviour gives interesting informations on the surface roughness (crossovers, local slopes). More generally, one can use the roughness functions

$$S_\tau^{(\alpha, \beta)} = \left( \frac{1}{N} \int_0^N \left( \frac{1}{2\tau} \int_{-\tau}^{\tau} |z(ts) - z(t)|^\alpha ds \right)^{\beta/\alpha} dt \right)^{1/\beta}$$

where  $\alpha \geq 1$ ,  $\beta \geq 1$ . The choice of  $(\alpha, \beta)$  determines the type of roughness detected. High values of  $\alpha$  emphasize the role of local peak by ignoring intermediary values of  $z$ . High values of  $\beta$  emphasize the most irregular parts of  $z$ . On the contrary,  $\alpha = \beta = 1$  give the same importance to the differences  $|z(ts) - z(t)|$  all along the definition interval. Usual pairs employed are  $(\alpha, \beta) = (1, 1)$ ,  $(2, 2)$ ,  $(\infty, 1)$  (as above), and  $(\infty, 2)$ . The use of double integrals has the effect of smoothening the *roughness curves*  $\log S_\tau^{(\alpha, \beta)}$  vs  $\log \tau$ . Characteristic parameters of these curves allow us to establish a hierarchy between different samples and predict dispersion. We employ the values of  $\alpha, \beta$  that give the most precise evaluations.

#### SESSION KK4: FILLED ELASTOMERIC AND STRUCTURAL MATERIALS - RUBBER-TOUGHENED MATERIALS

Chair: Tamas Ungar  
Tuesday Afternoon, November 28, 2000  
Gardner (Sheraton)

#### 1:30 PM **\*KK4.1**

##### EFFECT OF A NANO-SIZED FILLER ON THE STRUCTURE AND DYNAMICS OF A POLYMER MELT VIA MOLECULAR DYNAMICS SIMULATIONS. Sharon C. Glotzer, Francis W. Starr and Thomas B. Schröder, Polymers Division and Center for Theoretical and Computational Materials Science, National Institute of Standards and Technology, Gaithersburg, MD.

Significant enhancements the properties of polymer materials can be obtained by adding fillers such as carbon black, talc, silica, and other inexpensive materials. The growing ability to design customized nano-fillers of arbitrary shape and functionality provides an enormous variety of property modifications by introducing specific heterogeneity at the nanoscale. However, detailed knowledge of the effects of fillers on a polymer melt at the molecular level is lacking due to the difficulty of directly probing the polymer structure and dynamics in the vicinity of the polymer-filler interface. In this regard, molecular simulations provide an ideal opportunity for direct insight into filled materials. To probe the effects of the filler on the local melt structure and dynamics, we perform molecular dynamics simulations of an idealized polymer melt with chains having an end-to-end distance roughly equal to the facet size of a nanoscopic filler particle. Our findings show a strong similarity to those obtained for ultra-thin polymer films, suggesting that both ultra-thin films and filled-polymer systems might be understood in the same context. Specifically, we show that the glass transition temperature  $T_g$  of the melt, one of the most important processing parameters, can be shifted to either higher or lower temperatures by appropriately tuning the interactions between polymer and filler. A gradual change of the polymer dynamics approaching the filler surface causes the change in the glass transition. We also find that while the bulk structure of the polymers changes little, the polymers close to the surface tend to be elongated and flattened, independent of the type of interaction we study. Consequently, the dynamics appear strongly influenced by the interactions, while the melt structure is only altered by the geometric constraints imposed by the presence of the filler.

#### 2:00 PM **KK4.2**

##### THE SIGNIFICANCE OF PERCOLATION ON THE DYNAMICS OF POLYMER CHAINS BOUND TO CARBON BLACK.

Alan I. Nakatani, Robert Ivkov, Peter Papanek, Catheryn L. Jackson,

National Institute of Standards and Technology, Gaithersburg, MD; Henry Yang, Leszek Nikiel, and Michel Gerspacher, Sid Richardson Carbon Co., Fort Worth, TX.

Neutron time-of-flight (TOF) spectroscopy is used to compare the chain dynamics of pure polyisoprene with polyisoprene bound to the surface of various grades of carbon black fillers. The carbon black is compounded into the polyisoprene at various initial concentrations. By Soxhlet solvent extraction of the polyisoprene/carbon black compounds, the unbound polymer is removed and samples containing only polyisoprene bound to the carbon black surface are obtained. Two types of dynamic behavior of the polymer chains are observed. At low initial carbon black concentrations, the vibrational density-of-states spectrum of the bound polymer is nearly identical to the spectrum of the pure polymer. However, at higher initial carbon black concentrations, the vibrational density-of-states spectrum of the bound polymer is enhanced over the pure polyisoprene, indicating the bound polymer has higher mobility than the unbound polymer. The transition between the two types of dynamics may be related to the different percolation concentrations of the carbon blacks used in this study. Two models are proposed to explain the observed dynamic behavior.

#### **2:15 PM KK4.3**

**NANOFILLER-POLYMER INTERACTIONS ABOVE THE GLASS TRANSITION TEMPERATURE.** Aijun Zhu, Sanford Sternstein, Rensselaer Polytechnic Institute, MS&E Dept, Troy, NY.

The viscoelastic properties of fumed silica/poly(vinyl acetate) composites are examined in detail. The filler has a specific surface area of 380 meters square per gram and an average particle size of 7 nm, thereby giving enormous surface area for interactions at low volume fractions. Volume fractions from 0.005 to 10 percent are considered. Dynamic modulus and loss factor measured in true simple shear are given for temperatures at and above the glass transition. It is found that the frequency dispersion of the glass transition mechanism is continually broadened at both low and high frequencies by the addition of the filler. This suggests that changes in the short relaxation times (high frequency side) reflect a bound polymer layer and that changes in the long relaxation times (low frequency side) reflect the far-field influence on polymer chain entanglements. Above TG, it is also found that the presence of filler results in a lowering of the strain amplitude at which modulus begins to decrease and that the filler increases the ratio of the moduli measured at low and high amplitudes, respectively. To further elaborate on these ideas, experiments using other fillers such as alumina and silane-treated fumed silica are also reported. Complementary studies using NMR spectra are also presented to further delineate the role of polymer-filler interactions on molecular mobility. The phenomena observed have striking similarities to the Payne effect observed in filled crosslinked elastomers, and may assist in determining the molecular mechanisms responsible for the Payne effect.

#### **2:30 PM \*KK4.4**

**DYNAMICS OF FILLED POLYMERS BY NEUTRON SCATTERING.** Valeria Arrighi, Simona Gagliardi, Heriot-Watt Univ, Dept of Chemistry, UNITED KINGDOM; Julia S. Higgins, Imperial College, Dept of Chemical Engineering, UNITED KINGDOM.

Composites in which fibres or fillers are incorporated into a polymeric component exhibit improved mechanical strength compared to the polymer matrix. This reinforcement effect strongly depends on the properties of the interphase and the specific interactions between the polymer and the reinforcing additive. A wide range of experimental methods has been used to assess the effect of active fillers on the mobility of the polymer chains. The experimental results from NMR, dielectric spectroscopy and dynamical thermal analysis reveal that the mobility of chain units adjacent to the adsorbed surface differs considerably from the bulk. We have used quasielastic neutron scattering to investigate the dynamic properties of poly(dimethyl siloxane) (PDMS) and poly(vinyl acetate) (PVAc) filled with silica particles. This technique which probes the motion of the hydrogen atoms has been extensively used to study the local dynamics of polymeric materials. In this paper we demonstrate that QENS provides detailed information on the reduced mobility of chain segments in polymer-filler systems. QENS measurements were carried out on PDMS and PVAc, filled with hydrophilic Aerosil with different specific surface area (average diameter 7 and 20 nm) at constant filler weight fraction. We observe a progressive slowing down of the motion with increasing particle surface area. Detailed data analysis indicates that the QENS spectra of the polymer-filler composites can be described by the sum of two contributions: (a) a quasielastic component due to chains not affected by the presence of the fillers and (b) an elastic term from those chain segments strongly affected by the presence of fillers. The latter depends on the specific surface area of the particles, their weight fraction as well as the extent of polymer-filler interactions.

#### **3:30 PM \*KK4.5**

**INVESTIGATION OF COMPETING METAL ALKOXIDES AS MODIFIERS FOR ANIONIC SOLUTION POLYMERIZATION.** Adel Halasa, Steven K. Henning, Goodyear Tire and Rubber Company, Akron, OH.

Living anionic polymerization has proven to be a useful tool for the production of elastomeric materials. Typically, in the synthesis of solution styrene-butadiene copolymers (SSBRs), polar modifiers are used to randomize the comonomer sequence distribution. When initiating with alkyl-Li, the use of polar modifiers generally leads to increased levels of 1,2 (vinyl) structures in the diene phase of the copolymer<sup>1</sup>. The introduction of alkali metal alkoxides (MOR, where M = Na, K, Rb, Cs) to an alkyl-Li initiated SSBR copolymerization results in a random comonomer sequence distribution<sup>2</sup> and increased vinyl levels. The use of lithium alkoxide has no apparent effect on the resulting diene microstructure<sup>3</sup>, but also does not randomize the incorporation of styrene monomer<sup>4</sup>. This study focuses on the use of different metal alkoxide species as modifiers in anionic polymerizations in order to better understand the nature of the structure of the propagating chain end by investigating the dependence of polymerization kinetics, microstructure, macrostructure, and sequence distribution on the ratio of competing metal alkoxides.

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2. C.F. Wofford, H.L. Hsieh, J. Polym. Sci., Part A-1, 1969, 7, 461.
3. H.S. Makowski, M. Lynn, J. Macromol. Sci. Chem., 1968, A2, 683.
4. Ye. Yu Melenevskaya, V.N. Zgonnik, V.M. Denisov, E.R. Dolinskaya, K.K. Kalninh, Polym. Sci. (USSR), 1979, 21, 2215.

#### **4:00 PM KK4.6**

**MEAN FIELD AND MONTE CARLO MODELING OF MULTI-BLOCK COPOLYMERS.** K.O. Rasmussen, T. Lookman, A. Saxena and T.D. Sewell, Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM.

The (visco-)elastic and nano patterning properties of block copolymers are important in a variety of applications. We study linear multiblock copolymers (which is a model for estane) to examine the effect of block length and polymerization. We investigate structure factor, segregation length scales and micro segregation transitions using a self-consistent mean-field theory. We then compare these results to those (i) obtained using direct Monte Carlo simulations and (ii) by including the effects of fluctuations. The mean field model is further applied to study the dynamics and morphology of three dimensional nano-patterning in block copolymer systems.

#### **4:15 PM KK4.7**

**COMPREHENSIVE STRUCTURAL STUDY OF PRE- AND POST-HEAT TREATED COMPRESSION MOLDED POLYURETHANE SAMPLES OF VARYING COMPOSITION STUDIED BY SCANNING PROBE TECHNIQUES.** Marilyn E. Hawley, E. Bruce Orler, Debra A. Wroblewski and Geoffrey W. Brown, Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, NM.

Only a limited number of structural studies have been performed on polyurethane samples using scanning probe techniques to determine both the microstructure and the corresponding distribution of hard and soft segments within samples. This type of information is needed to better understand the mechanical properties of these materials and to facilitate modeling efforts in this area. In order to address these issues, we have fabricated a series of compression molded samples, i.e. segmented poly(ester urethane), with compositions spanning a wide range of hard to soft segment ratios. Samples were then examined using phase and force modulation scanning probe techniques to obtain the structure as well as map the distribution of hard regions within each sample. The surface of each sample was examined prior to cryo-microtoming sections to obtain the internal structure of the material. Further, samples were heat treated at 100°C for 10 minutes, quenched on a pre-cooled metal block, and reexamined to determine any changes in either the morphology or the hard segment distribution. A number of significant differences were observed between the pre- and post-heat treated samples. Morphological changes can be directly related to the separation of components and to the state of some of the structure. Strand-like structures, possibly due to flow during sample processing by compression molding, seen prior to heating transformed into strings of nanosized ball-like features. Variations in structure from sample to sample can be directly related to compositional changes.

#### **4:30 PM \*KK4.8**

**DENSITY FUNCTIONAL APPROACH TO SELF-ASSEMBLY IN COPOLYMERS.** Shirish M. Chitanvis, Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM.

We have mapped the physics of copolymers onto a time-dependent

Landau-Ginzburg formalism using functional integration techniques. Time in the theory is simply a label for the location of a given monomer along a flexible chain. We derive heuristically within this approach a short-ranged constraint which leads to self-assembly. The structure factor is then computed. The long wavelength limit of the structure factor is used to obtain the elastic moduli of segmented copolymers and compared with experiment. There is a surprising competition between the degree of micro-phase separation and the elastic moduli of the system.

SESSION KK5: POSTER SESSION  
FILLED AND NANOCOMPOSITE POLYMER  
MATERIALS POSTERS I  
Chair: Ramanan Krishnamoorti  
Tuesday Evening, November 28, 2000  
8:00 PM  
Exhibition Hall D (Hynes)

#### **KK5.1**

THE NEW TESTING TECHNIQUE OF MECHANICAL PROPERTY FOR EPOXY/ALUMINUM INTERFACIAL BONDING. Tianbao Du, Jian-Ku Shang, University of Illinois, Dept of MS&E, Urbana, IL.

Polymeric adhesives have been widely used to provide the critical link between different materials. The interfacial reaction plays an important role in determining the durability of the bonding system. A new testing technique based on the piezoelectric ceramic of PZT was designed to study the fatigue behavior of epoxy adhesive bonds. Fatigue crack growth characteristics in epoxy/aluminum interface were studied as a function of stress intensity factor range and cyclic frequency. The testing frequency varies from 50Hz to 1000Hz. SEM and XPS techniques were used to characterize the surface morphology and chemistry change during the fatigue process in order to make clear the failure mechanism. The primary results show that this technique is a suitable accelerated testing approach to the adhesive/metal system and it can be used as an alternative technique to the normal mechanical approach.

#### **KK5.2**

ELECTRICAL AND MECHANICAL BEHAVIOR OF CARBON BLACK-FILLED POLY(VINYL ACETATE) LATEX-BASED COMPOSITES. Jaime C. Grunlan, William W. Gerberich, Lorraine F. Francis, Univ of Minnesota, Dept of Chemical Engineering and Materials Science, Minneapolis, MN.

In an effort to achieve high electrical conductivity at low carbon black concentration, latex has been used as the polymer matrix starting material. Lower carbon black loading produces materials that are easier to process and exhibit better mechanical performance. Composites prepared with a polyvinyl acetate (PVAc) latex exhibit a percolation threshold of 2.5 vol% carbon black, while those prepared using poly(N-vinylpyrrolidone) (PNVP) solution have a more universal value above 14 vol%. By excluding the carbon black from regions occupied by polymeric particles, the dispersion-based composites lead to preferential aggregation of carbon black, as evidenced by SEM, and a lowered percolation threshold. Storage modulus, creep and break strength of the latex-based composites were examined using a dynamic mechanical analyzer (DMA). These mechanical properties were then compared to those of the PNVP-based composite. Higher moduli are obtained at every concentration of carbon black for the PNVP-based composite coatings when all of the composite systems are dried at room temperature. As the drying temperature of the latex-based composites is increased, the films are better able to fully coalesce and the mechanical properties show dramatic improvement. Improved latex coalescence increases the percolation threshold of composite films only one or two percent, leaving far below that of the solution-based system. The final result is composites with low percolation thresholds and good mechanical behavior.

#### **KK5.3**

STUDY ON THE STRUCTURE AND PROPERTIES OF EXFOLIATED GRAPHITE/POLYSTYRENE COMPOSITE PREPARED BY POLYMERIZATION-FILLING TECHNIQUE. Peng Xiao, Kecheng Gong, South China University of Technology, Polymer Structure & Modification Res. Lab, Guangzhou, PR CHINA; Luyi Sun, University of Alabama, Department of Chemistry, Tuscaloosa, AL.

Polymerization-filling technique is a new way to produce polyolefin-based composites with remarkably improved performances. Exfoliated graphite has excellent conductivity which can be obtained by exfoliation of graphite intercalate. As a conductive filler, exfoliated graphite has been incorporated successfully into polymer matrix by mechanically mixing, static melt diffusion mixing or in situ exfoliation

and these composites have many important uses such as electrode material, electrical and thermal conductors, sealing material, et al. In our work, a composite based on exfoliated graphite(EG) and polystyrene was prepared by polymerization-filling technique. The results show that with the augment of the amount of filled EG, the molecular weight of polystyrene in the resulting composite increases and the molecular weight distribution widens. The glass transition temperature of the polystyrene was determined by dynamic mechanical analysis(DMA) and shows the glass temperature of polystyrene increasing to 123.74. The thermal degradation behavior was studied using thermogravimetry (TG) and shows higher thermal stability of the composite than that of pure polystyrene and polystyrene/EG composite prepared by melt-blending. Results of d.c. conductivity of the composites prepared by polymerization-filling technique show that the composites have a percolation threshold in conductivity lower than 2.5wt%.

#### **KK5.4**

HIGH DENSITY POLYMER/INORGANIC NANOPARTICLE COMPOSITES WITH IMPROVED MECHANICAL PROPERTIES. M.M.L. Garcia-Curiel, Werner E. van Zyl, Henk Verweij, Laboratory for Inorganic Materials Science, Faculty of Chemical Technology and MESA Research Institute, University of Twente, Enschede, THE NETHERLANDS.

The present study involves the formation of a composite comprising nylon-6 as a matrix and silica nanoparticles as a filler phase. Such hybrid composites show improved mechanical properties such as stiffness, toughness, impact resistance, and hardness when compared with the pure polymer phase. The synthesis method relies on complete dissolution of nylon-6 in appropriate solvents. Silica nanoparticles are then slowly added to the clear solution. This ensures homogeneity is controlled on the molecular level. Finally, the viscous material is moulded or casted and the solvent removed from the transparent gel. The synergetic effect between the silica filler and the polymer matrix resulting in improved mechanical properties will be demonstrated.

#### **KK5.5**

CHARACTERIZATION OF SILICA-BIOPOLYMER AEROGEL COMPOSITES BY SMALL ANGLE NEUTRON SCATTERING (SANS) AND TRANSMISSION ELECTRON MICROSCOPY. Xiangjun Hu, Shuang Ji and William M. Risen Jr., Department of Chemistry, Brown University, Providence, RI; Kenneth Littrell, Intense Pulsed Neutron Source Division, Argonne National Laboratory, Argonne, IL; David Pickles, Sullivan Research Center, Corning Incorporated, Corning, NY.

A new type of silica-biopolymer aerogel composite containing the biopolymer chitosan has been studied with small angle neutron scattering (SANS) and transmission electron microscopy (TEM). A new Small-Particle Mass-Fractal model scattering function, derived from the Teixeira Mass-Fractal scattering function, was used to fit the SANS data. As the content of chitosan in the aerogel was increased, the fractal dimension decreased from 2.9 to 2.5, and the cut off length increased from 3.2 nm to 6.0 nm. This indicates that chitosan reinforces the interparticle connections in the silica and helps to form a more open aerogel structure. It supports a structural model in which there are primary particles that connect with each other closely to form clusters, and these clusters serve as a secondary structural unit to form the chitosan-reinforced aerogel network. This picture is consistent with the TEM measurements, which reveal that there are 1.5 nm wide entities with long dimensions in the 3 to 10 nm range.

#### **KK5.6**

NEUTRON REFLECTIVITY AND SCANNING FORCE MICROSCOPY STUDIES ON REINFORCEMENT OF RUBBERS BY SILICA AND CARBON-BLACK FILLERS. Yimin Zhang, S. Ge, B. Tang, M. Rafailovich, J. Sokolov, Dept. of Mat. Sci. & Eng., SUNY at Stony Brook, NY; D. Peiffer, Exxon Mobil Res. and Eng. Co., Annandale, NJ; J.A. Dias, K.O. McElrath, Exxon Mobil Chem. Co., Baytown, TX; M. Lin, S. Satija, NIST, Gaithersburg, MD.

Carbon black and silica are widely used fillers in rubber industry. In numerous applications the mixture of the two fillers are used to reinforce elastomers. Therefore it is interesting to study the differences between the two fillers on polymer rheology and to determine whether the two fillers are distributed uniformly in the polymer material. NR (neutron reflectivity) data show that the proximity of a planar HF-etched hydrophobic Si surface can slow down the dynamics of a dPB (d6-polybutadiene) film. Carbon black fillers also reduce the dynamics of dPB films. When dPB is reinforced with hydrophobic silica particles, a narrowing of the interface with BIMS (Bromo-isobutylene-co-p-methylstyrene) is observed. When hydrophilic silica particles are used, almost no effect on the interfacial width is observed. Scanning force microscopy shows that when carbon black and silica particles are mixed, annealing causes the film to segregate into two layers. The silica-rich layer is present at the air



interface and the carbon-rich layer is beneath. The results of further studies with SANS and SIMS will be presented.

#### **KK5.7**

**CUBIC POLYSILSESQUOXANES AS PRECURSORS TO THERMALLY STABLE NANOCOMPOSITES.** Ryo Tamaki, Jiwon Choi, Yasuyuki Tanaka, Mike Z. Asuncion, Richard M. Laine, Depts of Materials Science and Engineering, and Chemistry, University of Michigan, Ann Arbor, MI.

Polyhedral silsesquioxanes with the empirical formulas  $(\text{RSiO}_{1.5})_8$  or  $(\text{RMe}_2\text{SiOSiO}_{1.5})_8$  [where R is hydrogen, alkenyl, aryl, propanol, or other functional groups], have proven to be versatile building blocks for synthesizing organic/inorganic nanocomposites with well controlled properties. We have recently explored the possibility of using octafunctional octasilsesquioxanes as repeating units for nano-composites having high surface area, remarkable mechanical properties and high thermal stability. Functional groups include epoxy or methacrylate groups, which will photopolymerize using radical or cationic initiators. The cross-coupling of octa-hydrido and vinyl silsesquioxanes via platinum catalyzed hydrosilation to give controlled porosity polymeric materials was also explored. We are reporting here the synthesis, processing and physical properties of nanocomposites obtained from octafunctional silsesquioxanes containing amide, imide or other links. That offers thermal stabilities in excess of 400°C and good-to-excellent mechanical properties.

#### **KK5.8**

**BEHAVIOR OF AMPHIPHILIC GOLD/POLY(AMIDOAMINE) DENDRIMER NANOCOMPOSITE WITH ALKYL SURFACE GROUP AT THE AIR/WATER INTERFACE.** Kwang-Sok Kim, Young-Soo Seo, Kwanwoo Shin, M. Rafailovich, J. Sokolov, SUNY at Stony Brook, Dept of MS&E, Stony Brook, NY; L. Balogh, U. of Michigan, Center for Biologic Nanotechnology, MI; Binhua Lin, Zhengqiang Huang, U. of Chicago, James Frank Institute and CARS; Hyunjung Kim, Argonne National Laboratory, Argonne, IL.

Poly(amidoamine) (PAMAM) dendrimers are synthesized via Michael addition of methyl acrylate to the ethylene diamine (EDA) core and amidation with EDA of resulting ester. They consist of three structural parts, EDA initiator core, interior layer (generations), and terminal functional groups. PAMAM dendrimers have potential applications as Dendrimer Nanocomposite (DNC) materials for drug delivery, catalysis, and polymerization. Especially, compared to hydrophilic DNCs, amphiphilic DNCs can be spread as Langmuir-Blodgett (LB) films which can lead to whole new area of potential applications. In this study, we used two kinds of DNCs, generation 2 and generation 4. The behavior of DNCs at the air/water surface was investigated by using LB technique and in situ X-ray reflectivity. The surface pressure-area diagram of DNC was affected by the dendrimer diameter, concentration, and PH. The thickness change of the DNC monolayer as a function of surface pressure showed rapid increase of thickness when surface pressure was increased. The LB films of DNCs were deposited on silicon wafers and further investigated by AFM and x-ray reflectivity. These studies showed a comparison of the DNCs in their swollen and collapsed states. This work was funded in part by the NSF-MRSEC program and the Chem. CARS consortium.

#### **KK5.9**

**ELECTROSPINNING OF POLYMERIC NANOFIBERS: ANALYSIS OF JET FORMATION.** Antonio E. Senador Jr., Montgomery T. Shaw and Patrick T. Mather, Institute of Materials Science, University of Connecticut, Storrs, CT.

Producing nanometer-diameter polymeric fibers presents an attractive and robust approach toward the processing of nanocomposites, with applications ranging from clear optical components to toughened structural materials. In this work, we are examining the electrospinning process for the production of nanometer-diameter polymer fibers, giving particular attention to the following key features: jet-initiation, spaying, fiber architecture, and fiber distribution. A wide range of polymer systems and polymer-solvent combinations were studied in order to broaden the applicability of our conclusions to other systems. Specifically, a dimensional analysis was applied to jet-formation data obtained by quantifying the conditions required for the expulsion of fibers from a charged capillary to a grounded collection plate. The relationships between various dimensionless groups were compared with the expressions for the critical voltage that have been proposed for electrospinning of polymer solutions. Additionally, dimensional analysis is being used to quantify the effect of heat and mass transfer variables on the onset of spaying and the resulting morphology. Finally, we report on the influence of surface geometry on fiber orientation distribution in electrospun webs. This work is supported in part by grants from the Univ. of Connecticut Research Foundation (PTM) and Connecticut Innovations, Inc. (PTM and MTS).

#### **KK5.10**

**SYNERGISTIC INTERACTIONS OF POLYMER WITH CLAY.** Gudrun Schmidt, Alan I. Nakatani, Vincent Ferreiro, Paul D. Butler, Alamgir Karim, Charles C. Han, NIST.

The shear orientation of viscoelastic clay-polymer solutions was investigated by means of rheology, flow birefringence and small-angle neutron scattering (SANS). Oscillatory shear showed a broad linear viscoelastic region and flow occurred when a critical strain was reached. With increasing steady shear rate a pronounced minimum in birefringence was observed at a critical shear rate corresponding to the orientation of the polymer-clay system. The polymer chains are in a dynamic adsorption/desorption equilibrium with the clay particles to form a network. The same degree of orientation could be achieved by either constant shear rate or constant stress experiments. SANS measured the shear-induced orientation of polymer and platelets as a function of shear rate. At rest and at low shear rates a diffuse isotropic ring of scattering intensity was observed. With increasing shear rate an anisotropic scattering pattern developed. At higher shear rates, the scattering anisotropy increases due to the increased orientation of the clay platelets in the shear field. Cessation of shear leads to fast recovery demonstrating the system to be highly elastic. As a result of drying, these solutions produce translucent nanocomposite films with microporous membrane character and elastic properties. AFM images the network character and the structural formation of "nanoholes" as a function of polymer concentration.

#### **KK5.11**

**RHEOLOGICAL CHARACTERIZATION OF POSS-GRAFTED COPOLYMERS.** Patrick T. Mather and Seung B. Chun, Institute of Materials Science, University of Connecticut, Storrs, CT.

The rheological and thermal properties of new POSS-grafted homo- and diblock copolymers have been investigated. Here, POSS refers to the inorganic-organic hybrid monomer, Polyhedral Oligomeric Silsesquioxane. We present the preparation details of new POSS-grafted polymers that were synthesized via anionic polymerization of organic (homopolymers or block copolymers) and subsequently grafted with the hybrid component (hydridodimethylsiloxy POSS). The completeness of the grafting reaction was characterized using <sup>1</sup>H-NMR spectroscopy, while the thermal properties of the grafted polymers were measured by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). We report on the significantly altered rheological properties of the grafted polymers, investigated by means of oscillatory shear rheology. Our findings are discussed in light of microstructural characterizations performed using wide-angle x-ray scattering (WAXS) and transmission electron microscopy (TEM). Finally new applications of the grafted polymers are proposed.

#### **KK5.12**

**GROWTH OF POLYISOCYANATES FROM NANOMETER-SIZED SILICA PARTICLES.** Mark Jordi, Thomas Seery, Dave Fleming, Benjamin Stermole, Institute of Material Science, Polymer Program, University of Connecticut, Storrs, CT.

In our research to date, we have prepared polyisocyanate brushes on gold nanoparticles as well as fumed silica substrates. This was accomplished by polymerizing isocyanate monomers from alcohol initiator sites attached to the gold and silica surfaces. The polymerization of isocyanates was mediated by a titanium alkoxide species formed from the reaction of titanium tetrachloride with the alcohol functionalized particles. Our current objective is to expand these studies to include isocyanates that are tethered to the surface of nanometer sized silica spheres. The first step was the preparation of silica spheres followed by attachment of an alcoholic functional group. This process is complicated by the tendency of the particles to aggregate when they are prepared in the nanometer size range. A very complete functionalization or steric hindrance of the remaining silanol groups is required. Complete functionalization is balanced by the need to space the initiator sites to obtain the desired density of surface chains. Kinetics studies of the growth of the isocyanate brushes was conducted using IR and NMR.

#### **KK5.13**

**STUDY OF ZrO<sub>2</sub> NANOPARTICLES FILLED POLYMER ELECTROLYTES BASED ON A THERMOPLASTIC POLYURETHANE.** Paulo V.S. da Conceição, Adelina P. Santos, Cláudia A. Furtado, Centro de Desenvolvimento da Tecnologia Nuclear - CDTN/CNEN - Belo Horizonte, BRAZIL.

Polymer electrolytes for solid state electrochemical devices, as capacitors and lithium polymer batteries, must have a range of critical properties including a adequate ionic conductivity ( $> 10^{-8} \text{ S cm}^{-1}$  at room temperature) and a good mechanical properties up to 100°C to prevent leakage and accommodate volume changes during use. Introducing ceramic powders with nanometer-sized grains to a

polymer electrolyte may improve mechanical strength and conductivity. In this work, composite polymer electrolytes on the basis of a thermoplastic polyurethane/LiClO<sub>4</sub> amorphous system and yttria stabilized zirconia ultrafine powder as a filler are reported. Differential scanning calorimetry (DSC) studies showed that T<sub>g</sub> values for the composites up to 18 wt% of ZrO<sub>2</sub> are lower than the T<sub>g</sub> value of the polymer/salt system. Ionic conductivity was evaluated by complex impedance analysis as a function of temperature. Results indicate that the incorporation of the ceramic filler at low levels increases the ionic conductivity ( $\sigma$ ) of the system, while at the higher concentration tested  $\sigma$  decreases. Better mechanical properties were observed for the ceramic reinforced samples in all concentration range studies.

#### **KK5.14**

**DIRECTLY USING RICE HUSK AS FILLER IN POLYPROPYLENE.** Luyi Sun, University of Alabama, Department of Chemistry, Tuscaloosa, AL; Peng Xiao, Jianhua Song, Kecheng Gong, South China University of Technology, Polymer Structure & Modification Lab, Guangzhou, PR CHINA.

The major inorganic component of the rice husk(RH) is silica (4~20%). In the past, the utilization of rice husk mainly concentrated in the ash of the rice husk, such as using rice husk ash (RHA) as filler in plastics, especially in polypropylene (PP). In this work, rice husk was directly used as filler in PP. Some treatments were applied to the RH. Mixing study was carried out using a laboratory size two-roll mixer. The RH and PP were weighted and mixed proportionally to prepare samples equivalent to 5, 10, 15, 20, 30, 50, 80% loading. Mixing were carried out at mixer temperature at 180° for a period of 5 minutes. The tensile strength of the RH-PP composites increases steadily with increasing filler loading until a certain value. The MI of the composite increases with the increasing filler loading, while the composite maintaining good processing property until 50% loading. This study not only reduces the cost of the PP-based products, but also solves the problem of disposal of rice husks.

#### **KK5.15**

**CARBON-SILICA DUAL PHASE FILLER, A NEW GENERATION REINFORCING AGENT FOR ELASTOMERS.** Lawrence J. Murphy, Yakov Kutsovsky, Meng-jiao Wang and Khaled Mahmud Cabot Corporation, Billerica, MA.

Carbon-silica dual phase fillers (CSDPF) are a new set of colloidal materials, developed to enhance elastomer performance properties over carbon black and silica. These materials are produced by co-fuming hydrocarbon and organo-silicon containing feedstocks. These new materials are nano-composites of carbon and silica, having similar colloidal morphology as carbon black. Electron Spectroscopy for Chemical Analysis, Infrared Spectroscopy and Solid State Nuclear Magnetic Resonance Spectroscopy are used to characterize the chemistry of the carbon and silica phases. These techniques reveal that the silicon in these materials is consistent with silica, and the carbon is similar to the graphitic carbon in carbon black. The amount of surface functional groups available for reaction with silane coupling agents, along with a comparison to carbon black and silica will be presented. The silica and carbon domains are well dispersed as will be illustrated by analytical electron microscopy. The size of the silica domains will be revealed by a combination of wet chemical analysis and pore size analysis, and confirmed by Scanning Tunneling Microscopy. The size of the carbon domains will also be presented as measured by X-ray diffraction.

#### **KK5.16**

**SURFACE CHARACTERIZATION OF CARBON-SILICA DUAL PHASE FILLER BY IGC.** Meng-Jiao Wang, Hairuo Tu, Lawrence J. Murphy, and Khaled Mahmud Cabot Corporation, Business & Technology Ctr, Billerica, MA.

A series of carbon/silica dual phase fillers were characterized by inverse gas chromatography at infinite dilution. It was found that due to their unique surface microstructure, the dispersive component of the surface energy of these dual phase fillers is much higher than that of silica and carbon black. The adsorption energies of a series of hydrocarbon probes and polar chemicals were also measured by means of IGC. Compared with conventional silica and carbon black, the higher adsorption energies of hydrocarbon probes on dual phase fillers suggest relatively stronger interaction with hydrocarbon polymers. The polarity of these new fillers is similar to that of fumed silica, which is much lower than that of precipitated silica.

#### **KK5.17**

**CARBON BLACK METAMORPHOSES IN POLYETHYLENE WITH VARYING IONIC CONCENTRATION.** Vaclav Bouda, Jiri Chladek, Czech Technical University, Dept of Mechanics and Materials Science, Prague, CZECH REPUBLIC.

Carbon is a constituent element of nervous systems, bone cells, muscles, etc. The physiological processes involving carbon are as

diverse as proliferation (reproduction), neural signaling, learning, the growth of bones by biomineralization, and the contraction of muscle cells. Ions such as Na, K, Ca<sup>2+</sup>, Mg<sup>2+</sup> regulate the processes by varying the ionic concentration in a medium. Carbon black (CB) in a polymeric medium was used to model physiological processes. Polyethylene (LDPE) filled with CB was placed between hot electrodes to melt the polymer and induce electrolytic dissociation of various electrode materials by alternating current. The ionic concentration in the LDPE-melt was checked by RBS. Impedance analysis, AFM, and TEM were used to investigate the state of the CB-clusters. We go on to discuss metamorphoses of CB-clusters during the growing ionic concentration. CB-particles in clusters are kept firmly apart in a certain range of ionic concentration by electrostatic repulsive forces. In fact a CB-cluster is in a liquid state. Thanks to the thermal motion and specific distribution of the van der Waal attractive forces of CB-particles, their internal structure gradually reproduces itself into the mutable structure of CB-clusters. A further increase in ionic concentration may meet the critical coagulation concentration (CCC). Contractions of the gaps between CB-particles switch the CB-cluster into a solid and conductive state at CCC. The processes of proliferation, neural signaling, learning, and contraction of muscle cells may be cognate.

#### **KK5.18**

**THE EFFECTS OF NANOPARTICLE FILLERS ON DEWETTING DYNAMICS.** Sarika Sharma, Jean H. Xavier, Samantha Rodriguez, Myriam Rafailovich, Jonathan Sokolov, Henry White, Dept of Materials Science and Engineering at SUNY Stony Brook, Stony Brook, NY; A. Ulman and M. Scotti, Dept of Chemical Engineering, Chemistry and Material Science, Polytechnic University, Brooklyn, NY.

Fillers are added to polymers to improve their mechanical properties such as mechanical strength, UV resistance, thermal degradation, and other radiation stability. The dynamics of dewetting at the interface between the mixture of polystyrene-gold(PS-AU) and polymethylmethacrylate(PMMA) as a function of the gold nanoparticles(fillers) concentration and the molecular weight of the two polymers were studied. The gold was added to the PS film by mixing a fixed weight percentage in the toluene/PS solution used for spin casting. A solution of monodisperse PMMA and toluene was spun cast on a clean silicon wafer. Two other thin films of monodisperse PS were prepared, one contained gold and the other without gold were floated onto different section of the substrate. The film was annealed at 160°C in a vacuum of 10<sup>-3</sup> Torr for various times. The sample was then analyzed by optical microscopy, AFM, and TEM. The diameter of the dewetting holes of PS and PS-Au was recorded as a function of time using optical microscopy. We found that the dewetting velocity increases with filler concentration. Similar results were obtained for free standing films. Due to these results, we propose that fillers decrease the viscosity and the entanglements in the film. Variation of MW, fillers concentration and polymer/filler interaction were also investigated. For ultra thin film gravitational influence is negligible compare to surface interaction. This work was supported by a grant from NASA Microgravity #963225.

#### **KK5.19**

**AFM STUDIES OF FRACTURE SURFACES OF COMPOSITION B ENERGETIC MATERIALS.** Y.D. Lanzerotti, U.S. Army TACOM-ARDEC, Picatinny Arsenal, NJ.

The size of TNT (trinitrotoluene) crystals remain a subject of investigation in melt-cast TNT formulations such as Composition B (59% cyclotrimethylenetrinitramine (RDX), 40% TNT and 1% wax) which are filled with a large percentage of RDX. One method that can be used to examine the size of the TNT crystals is to examine the surface structure that is exhibited after mechanical failure of the energetic material. The mechanical failure of melt-cast Composition B has been obtained by subjecting the material to high acceleration in an ultracentrifuge at 25°C. Failure occurs at about 46,000 g when the shear or tensile strength of the Composition B sample is exceeded. Scanning electron microscopy (SEM) studies of the Composition B fracture surface reveals that the RDX crystals range from 100µm to 1,000 µm, as specified. More sensitive studies of the topography of the fracture surface by AFM reveals that the TNT particle size range from 60 nanometers to 1.0 micron in size.

SESSION KK6: POLYMER SURFACE INTERACTIONS, ADHESION, FILLER SURFACES, AND FILLER-FILLER INTERACTIONS

Chair: Saad A. Khan

Wednesday Morning, November 29, 2000  
Gardner (Sheraton)

**8:30 AM \*KK6.1**

TOF-SIMS FOR SURFACE CHARACTERIZATION OF POLYMERS AND CARBON BLACK FILLERS. Patrick Bertrand, Université Catholique de Louvain, Unité de Physico-Chimie et de Physique des Matériaux, Louvain-la-Neuve, BELGIUM.

Time-of-Flight Secondary Ion Mass Spectrometry is nowadays intensively used for materials surface characterization. In this presentation, based on our recent results, we will emphasize the potentialities of this technique to look at polymer and filler surfaces. First, the basic mechanisms of molecular ion emission under keV ion bombardment will be briefly presented. Then, it will be shown how this molecular information allows us to quantify the surface composition of random styrene-butadiene rubbers (SBR) and of polystyrene blends. For carbon black (CB), ToF-SIMS is seen to be very sensitive to surface functional groups and structure. Moreover, the sensitivity of the technique to macrochain conformation at the surface has been used to look at the rubber - carbon black interaction. For this purpose, model experiments of SBR thin layer adsorption on CB were performed. The ToF-SIMS analyses indicated a change in polymer chain conformation at the surface upon adsorption on CB. This was explained by a preferential interaction between phenyl (and in a weaker manner, vinyl) groups with the CB surface.

**9:00 AM KK6.2**

TOF-SIMS STUDY OF POLYMER NANOCOMPOSITES. Vladimir S. Zaitsev, Department of Physics, Queens College of CUNY, Flushing, NY; Young-Soo Seo, Kwanwoo Shin, Wenhua Zhang, Department of Material Science and Engineering, SUNY, Stony Brook, NY; Steven A. Schwarz, Department of Physics, Queens College of CUNY, Flushing, NY; Jonathan Sokolov, Miriam H. Rafailovich, Department of Material Science and Engineering, SUNY, Stony Brook, NY.

Polymers nanocomposites, particularly polymer-clay composites are attracting more and more commercial interest due to demand for lighter and stronger materials. Though such materials may appear to be homogeneous at the macroscopic level, their components are segregated into microscopic domains. We have used the Cameca Ion-TOF IV SIMS instrument to study microphase segregation in multicomponent polymer and polymer-filler systems. Apparent lateral resolution of the ion image is about  $0.5\mu\text{m}$  and depth resolution is about  $5\text{ nm}$  in the experiment with thin polymer films (less than  $1\mu\text{m}$ ). A series of 2D images of polystyrene-poly(ethylene-co-propylene)-polymethylmethacrylate and polystyrene-poly(propylene-co-ethylene)-poly-methylmethacrylate-organoclay blends were acquired during sample sputtering. A reconstruction of the sample 3D structure from 2D data was performed. Spatial distributions of Si, O, C, and higher mass fragments revealed microphase segregation with dimension on the order of few microns. Component identification in the microphases was attempted. Correction of 3D images is necessary due to surface height variations as observed by AFM. In our study, TOF SIMS imaging has proved to be a very promising tool for investigation of microphase segregation in nanocomposite polymer materials.

**9:15 AM KK6.3**

MOLECULAR STRUCTURE AND WETTING OF HYDROPHOBIC ALKYL SIDE CHAINS LABELED POLYMER SURFACES. Keshav Gautam, Ali Dhinojwala, University of Akron, Dept of Polymer Science, Akron, OH.

Surface sensitive sum-frequency generation (SFG) spectroscopic technique has been used to study the orientation of alkyl side chains of various length at polymer/fluid and polymer/solid interfaces. The SFG spectra at  $21^\circ\text{C}$  for octadecyl side chains/air interface are dominated by methyl asymmetric and symmetric vibrations indicating well ordered methyl terminal groups. The spectroscopic results are in good agreement with water contact angles measured for both these systems. The surface orientational order changes drastically when the system is heated above the smectic to isotropic transition temperature.

**9:30 AM \*KK6.4**

STRUCTURE OF CARBON BLACKS. T.W. Zerda, J. Qian, C. Pantea, TCU, Dept of Physics, Forth Worth, TX; T. Ungar, Eotvos University, Dept of General Physics, Budapest, HUNGARY.

Raman scattering, gas adsorption, and X-ray diffraction were used to characterize structure of different grades of carbon blacks. We studied both raw material as well as samples of various histories of postproduction heat and pressure treatments. Temperatures up to  $3000\text{ K}$  and pressures up to  $5\text{ GPa}$  were applied. We estimated relative concentrations of amorphous carbon versus carbon organized into graphitic crystallites for each of the samples. The sizes of the crystallites obtained by X-ray diffraction and Raman spectroscopy are compared. The distribution functions of crystallite sizes were

evaluated from X-ray diffraction using the modified Warren-Averbach method. Those functions obtained for different grades are compared and discussed. It is shown that the treatment at high temperatures results in increased vertical and lateral sizes of graphitic crystallites. The postproduction pressure treatment, even at the highest pressures used, has little effect on the average sizes of the crystallites. However, as expected, the strain distribution within the crystallites is affected by applied pressure. A model of the mechanism of temperature induced crystallite growth is proposed. It is suggested that the initial growth is associated with alignment of the existing graphitic planes and later by incorporating aromatic carbon into the crystallites. Possible structures of amorphous carbon are suggested.

**10:30 AM \*KK6.5**

MOLECULAR MECHANISMS OF ADHESION AT POLYMER - SOLID INTERFACES. L. Léger, H. Hervet, F. Kalb, C. Tardivat, V. Koutsos, C. Lorens, Laboratoire de Physique de la Matière Condensée, URA CNRS 792, Collège de France, Paris, FRANCE.

We shall present and discuss three series of experiments performed in order to identify the molecular mechanisms responsible for adhesion at polymer -solid interfaces. In the first set of experiments, the concept of adhesion reinforcement through connector molecules has been tested at the interface between silica surfaces covered with end grafted polydimethylsiloxane (PDMS) chains and PDMS elastomer using the JKR microlenses test. We shall discuss how the molecular parameters of the system, i.e. the surface density and the length of the grafted chains and the molecular weight between crosslinks in the elastomer, influence the ability of the connector molecules to enhance adhesion and the kinetics of the corresponding interdigitation process. In a second set of experiments, the ability of a similar interface, silica with surface anchored polymer chains in contact with a polymer melt or an elastomer, to sustain shear stresses will be analyzed, using a near field laser velocimetry technique which provides information on the local velocity at the polymer solid interface. Finally, the effect of block copolymers formed in situ at the interface between two semicrystalline polymers (isotactic polypropylene and polyamide 6) on the adhesive strength will be examined. Specific effects of the local crystallinity close to the interface will be discussed.

**11:00 AM KK6.6**

INTERFACIAL PROPERTIES OF POLYMER NANO-COMPOSITES. W. Richard Chung, Department of Chemical and Materials Engineering, San Jose State University, San Jose, CA.

An experimental study involving manufacturing of polymer nanocomposites using different types of inorganic fillers dispersed in a nylon-6 matrix was conducted. Conventional methods such as sputtering coating, PVD, and hot-melt compounding were used to fabricate custom made samples. The purpose of this project was to study their reinforcing mechanisms and interactions (filler-filler and filler-binder relationships) in a composite structure. Characterization techniques such as scanning electron microscopy and mechanical testing were employed to investigate the interfacial bonding strengths and their reinforcement. The results of this study will be presented to the conference.

**11:15 AM KK6.7**

INFLUENCE OF LAYERED SILICATE FILLERS ON THE PHASE BEHAVIOR OF PS-PVME BLENDS. Koray Yurekli, Ramanan Krishnamoorti, University of Houston, Dept. of Chemical Engineering, Houston, TX; Alamgir, Karim, National Institute of Standards and Technology, Polymers Division, Gaithersburg, MD.

The influence of the addition of organically modified, highly anisotropic layered silicates on the thermodynamic phase behavior of polymer blends and kinetics of phase transitions is of immense interest not only from a scientific standpoint, but also of significant technological interest<sup>1</sup>. It is anticipated that the preferential interaction of one of the components or the strong attraction of both components to the surface of the filler could lead to significant changes in the phase behavior of the blends. Further, the nanoscopic length scale of the filler could also lead to significant changes to the phase separation kinetics and the final morphologies<sup>2</sup>. We are investigating the influence of an organically modified layered silicate (a dimethyl dioctadecyl ammonium modified montmorillonite) on the well-studied polymer blend system deuterated polystyrene and poly(vinylmethylether) (PS/PVME). The layered silicate can be intercalated by polystyrene and forms a disordered intercalate (with some level of exfoliation) with PVME, suggesting that the PVME is more strongly attracted to the silicate surface than the PS<sup>3</sup>. Because of the large surface area associated with the layered silicate materials, we expect to be able to achieve significant changes in the phase behavior and kinetics of phase transformation at extremely low loadings of the nanofiller. We will be presenting the results of light scattering, small angle neutron scattering (SANS), and viscoelastic measurements aimed to probe the effects of the nanofiller on the

phase behavior, separation kinetics and final morphologies of the PS/PVME blend system.

- 1) V.V. Ginzburg, F. Qiu, M. Paniconi, G. Peng, D. Jasnow, A.C. Balazs, *Physical Review Letters* **1999**, *82*, 4026-4029.
- 2) A.S. Silva, C.A. Mitchell, M.F. Tse, H.-C. Wang, R. Krishnamoorti, *Macromolecules* **2000**.
- 3) R.A. Vaia, E.P. Giannelis, *Macromolecules* **1997**, *30*, 7990-7999.

### 11:30 AM \*KK6.8

MODELING THE 3D STRUCTURAL EVOLUTION OF FILLED POLYMER SYSTEMS. Anna C. Balazs, Valeriy Ginzburg, Univ of Pittsburgh, Dept of Chemical and Petroleum Engineering, Pittsburgh, PA.

We develop a new numerical technique to capture the dynamic behavior of filled blends and diblocks in three dimensions. To model the structural evolution of the system, we combine a mesoscopic, coarse-grained description of the polymers with a discrete model for the filler particles. We focus on the case where one of the components or blocks preferentially wets the surface of the particles. In addition, we introduce wetting interactions between the different components and the underlying substrate. Through this model, we determine how the interplay between the polymer-particle wetting and polymer-substrate adsorption affects the overall morphology of the system. Our findings reveal how the characteristics of the underlying surface can be harnessed to tailor the structure of composite films and diblock/particle mixtures.

### SESSION KK7: STRUCTURE-PROPERTY RELATIONS – MATERIALS AGING

Chair: Ali Dhinojwala

Wednesday Afternoon, November 29, 2000  
Gardner (Sheraton)

### 1:30 PM \*KK7.1

COLLOIDAL SILICA GELS AND NETWORK VIA CHEMICAL AND PHYSICAL CROSSLINKS. Srinivasa R. Raghavan, University of Delaware, Department of Chemical Engineering, Newark, DE; Bor-Sen Chiou, Saad A. Khan, North Carolina State University, Department of Chemical Engineering, Raleigh, NC.

We consider the role of polymer-colloid interactions in dictating the rheology of two types of filled systems. In the first case, we discuss how the surface characteristics of colloidal silica in a non-reactive polymer matrix can be varied to develop gels. In particular, we show that there exists a direct correlation between the colloidal interaction parameters and the corresponding rheology. In the second case, we consider the scenario where the polymer matrix is photocurable. In this case, the system may initially be flocculated or a physical gel, formed through physical crosslinks between colloidal particles. As the system undergoes photo polymerization, chemical crosslinks also begin to occur between polymer chains. The role of physical and chemical crosslinks during the photocuring process is investigated using in situ rheology and FTIR. We discuss the role of fillers in the photocrosslinking process and suggest a criterion to determine the chemical gel point and the transition from the dominance of physical crosslinks to chemical crosslinks.

### 2:00 PM KK7.2

MECHANICAL PROPERTIES OF INTERCALATED EPOXY-CLAY NANOCOMPOSITES. Alan J. Lesser, Adam S. Zerda, Univ of Massachusetts, Polymer Science and Engineering, Amherst, MA.

With the growing interest in nanostructured materials for a wide variety of technical applications, an in-depth investigation of the engineering properties of these materials is presented. Intercalated nanocomposites of modified montmorillonite clays in a glassy epoxy were prepared by crosslinking with commercially available aliphatic diamine curing agents. These materials were shown to have improved Young's modulus but corresponding reductions in ultimate strength and strain to failure. These results are consistent with most particulate filled systems. The macroscopic compressive behavior was unchanged, although the failure mechanisms in compression varied from the unmodified samples. The fracture toughness of these materials was investigated and improvements in toughness values of 100% over unmodified resin were demonstrated. Based on length-scale arguments, it is believed that the close packing of the intercalated structure is necessary for toughening of the matrix to occur. In this manner, the silicates can behave in concert to reinforce the matrix. The fracture surface topology was examined using SEM and tapping-mode AFM and a toughening mechanism is proposed.

### 2:15 PM \*KK7.3

THE INFLUENCE OF BLOCK COPOLYMERS ON SILICA-FILLED POLYISOPRENE. Daniel Gurovich, University of Minnesota, Dept of Chemical Engineering and Materials Science,

Minneapolis, MN; Matthew Tirrell, University of California, Dept of Chemical Engineering, Santa Barbara, CA; Christopher Macosko, University of Minnesota, Dept of Chemical Engineering and Materials Science, Minneapolis, MN.

The properties of filled polymeric materials depend on the balance between filler-filler and polymer-filler interactions. The polar surface of silica particles interacts strongly with like polar surfaces, but not with the polyisoprene (PI) matrix. Thus, silica is difficult to disperse in polyisoprene, and the resulting highly concentrated dispersions tend to re-agglomerate upon aging. Polydimethyl siloxane (PDMS) strongly adsorbs to silica surfaces via hydrogen bonds. Therefore, a PDMS-PI block copolymer is expected to anchor to a silica surface via its PDMS block and modify both filler-filler and polymer-filler interactions. In the present work, precipitated silica, polyisoprene, and PDMS-PI copolymer are mixed in different formulations. The dynamic rheological properties of the resulting materials are measured and are used to assess filler-filler networking. In small-amplitude tests, dispersions containing PDMS-PI exhibit lower values of the dynamic storage modulus ( $G'$ ) than those observed in control samples prepared without copolymer additives. The control samples remain stable during several months of storage, while samples containing low molecular weight block copolymers show evidence of an aging process. The rheological manifestations of this aging include a pronounced decrease in small-amplitude  $G'$  with time, accompanied by weakening amplitude-dependence of both  $G'$  and  $G''$ . These suggest a progressive reduction of filler-filler interactions, presumably caused by the development of a block copolymer layer at the filler-polymer interface. The make-up of that interfacial region is investigated by means of magic-angle spinning solid-state proton NMR.

### 3:15 PM \*KK7.4

ROLE OF FRACTAL FEATURES IN THE STRUCTURE-PROPERTY RELATIONSHIPS OF CARBON BLACK FILLED POLYMER. Françoise Ehrburger-Dolle, Erik Geissler, Cyrille Rochas, Lab Spectro Physique, Univ Grenoble, FRANCE; Françoise Bley, Frédéric Livet, LTPCM, INPG, Grenoble, FRANCE; Manuela Hindermann-Bischoff, ICSI, CNRS, Mulhouse, FRANCE; Thomas Rieker, CMM, Univ New Mexico, Albuquerque, NM.

Carbon black is widely used as a filler in order to modify the mechanical or the electrical properties of polymers. Such composites display significant non-linear effects. Moreover, examination of the large number of papers devoted to the physical properties of carbon black filled polymers indicates that each composite, even composites consisting of apparently similar matrices and similar carbon blacks, can behave differently when prepared by different mixing methods. The present work aims to show that these particular behaviors can be related to the fact that carbon blacks used for composites are low dimensionality mass fractals ( $d_f < 2$ ) which can interpenetrate each other to an extent that depends on the filler-matrix surface interaction and on the volume fraction of filler. Small-angle X-ray scattering (SAXS) is a convenient method for studying disordered systems at length scales ranging between a few tenths and a few hundred nm. Therefore, SAXS is particularly advantageous for exploring the morphology of carbon black aggregates and their degree of interpenetration when dispersed in a matrix. Furthermore, the use of an area detector yields 2-dimensional images and hence information about anisotropy of the arrangement of scatterers. It is shown that this arrangement profoundly influences the physical properties of the composites. Analysis of SAXS curves of a rubber grade carbon black (N330) and of composites prepared by dispersion into polyethylene or EPR will be reported. As an example, the behavior of temperature and frequency dependence of the electrical conductivity will be discussed and compared with theoretical models. Finally, consistency between electrical conductivity behavior and information deduced from the scattering curves will be shown.

### 3:45 PM KK7.5

MECHANICAL PROPERTY CHANGES OF A PARTICULATE-POLYMER COMPOSITE DUE TO AGING AT ELEVATED TEMPERATURES FOR SEVERAL MONTHS. Donald A. Wiegand, ARDEC, Picatinny Arsenal, NJ.

A particulate-polymer (binder) composite was subjected to accelerated aging by holding at elevated temperatures for extended periods. The compressive mechanical properties of the aged material are compared to the same properties of material which was held at ambient temperature for the same periods. The compressive strength is in most cases unchanged, but small increases in Young's modulus and small decreases in the strain at the compressive strength were observed due to aging. However, the major change due to this treatment is increased strain softening at elevated measuring temperatures, which is accompanied by increased surface cracking, an increased density change due to compression, and a decrease in the work of deformation. These results indicate enhanced crack growth in aged samples which is significantly more temperature dependent than

the crack growth in unaged samples. The results are discussed in terms of the increased compliance in the strain softening region due to additional crack damage in the aged material. Aging also produced a color change from white to light yellow or beige, a very small weight decrease and a very small non isotropic decrease in dimensions.

#### 4:00 PM **KK7.6**

**RELATING COMPOSITION AND MORPHOLOGY TO THE SOLID-STATE RHEOLOGICAL BEHAVIOR OF DYNAMICALLY VULCANIZED EPDM/I-PP ELASTOMERS.** Kathryn J. Wright, Alan J. Lesser, University of Massachusetts, Dept of Polymer Science & Engineering, Amherst, MA.

EPDM/i-PP thermoplastic elastomers are displacing traditional crosslinked elastomers in many applications. The complex morphology of these systems has been studied and well characterized in other studies. This study investigates the irreversibility of dynamically vulcanized ethylene-propylene-diene monomer (EPDM) / isotactic polypropylene (i-PP) blends, provided by Advanced Elastomer Systems. The dynamic mechanical responses have been examined in terms of the Payne effect as a function of composition, cure state, PP molecular weight, and oil content. The blends that are EPDM rich exhibit the classical Payne effect in the strain range examined. The data can be partially explained using the Kraus model. It is evident that composition contributes more significantly to the irreversibility than the cure state or oil content. An effort to relate the composition and morphology of these systems to their dynamic mechanical response will also be discussed.

#### 4:15 PM **\*KK7.7**

**SOME ASPECTS OF THE REINFORCEMENT MECHANISM IN FILLED ELASTOMERS.** Prof Dietmar Goeritz.

The fillers carbon black and precipitated silica - both as pure filler and mixed into a rubber matrix - are being investigated with a variety of experimental methods. Scanning probe microscopy and scattering methods provide results on the surface structure and the hierarchical structure of the fillers. Both surface and mass fractal characters are shown by the filler particles. These fractal dimensions are depending on the type of filler. The primary particle radius and aggregate size are determined from X-ray scattering curves in the small-angle region. The reinforcing effect of the active fillers is explained in terms of the interaction of the chain molecules with the filler surface. Two mechanisms of chain adsorption are discussed: some of the chains are adsorbed permanently while others depend on strain and temperature. The Payne effect can be described using this model.

### SESSION KK8: POSTER SESSION FILLED AND NANOCOMPOSITE POLYMER MATERIALS POSTERS II

Chair: Alan I. Nakatani  
Wednesday Evening, November 29, 2000  
8:00 PM  
Exhibition Hall D (Hynes)

#### **KK8.1**

**MOLECULAR STRUCTURE OF POLYSTYRENE AT AIR/POLYMER AND SOLID/POLYMER INTERFACES.** K. Gautam, A.D. Schwab, A. Dhinojwala, University of Akron, Dept of Polymer Science, OH; D. Zhang, S.M. Dougal, M.S. Yeganeh, ExxonMobil Corporate Strategic Research Laboratories, NJ.

We have used IR-visible sum-frequency generation (SFG) spectroscopy in total internal reflection geometry to simultaneously study molecular structure of polystyrene (PS) at PS/sapphire and PS/air interfaces. The symmetric vibrational modes of phenyl rings dominate the SFG spectra at PS/air interface in comparison with anti-symmetric vibrational modes at PS/sapphire interface. This indicates approximately vertical orientation of the phenyl rings at the PS/air interface in comparison to nearly perpendicular orientation at the PS/sapphire interface.

#### **KK8.2**

**EFFECT OF LATEX PARTICLE SIZE AND COALESCENCE ON THE PERCOLATION THRESHOLD OF CARBON BLACK-FILLED LATEX.** Jaime C. Grunlan, William W. Gerberich, Lorraine F. Francis, Univ of Minnesota, Dept of Chemical Engineering and Materials Science, Minneapolis, MN.

In an effort to lower the percolation threshold of carbon black - filled polymer composites, latex has been used as the polymer matrix starting material. Composites prepared with a polyvinyl acetate (PVA) latex exhibit a percolation threshold below 2.5 vol% carbon black, while those prepared using poly(N-vinylpyrrolidone) (PNVP) solution have a more "universal" value above 14 vol%. This lowered

percolation threshold for the latex-based system is most likely due the combination of excluded volume and lack of carbon black stabilization during composite film formation. As the drying temperature of the latex - based composite is raised from 20 to 60°C, the percolation threshold increases by approximately 2 vol% due to improved coalescence of the latex. However, at high filler loadings (> 15 vol% carbon black) the better-coalesced composite exhibits a greater electrical conductivity. Maximum achievable electrical conductivity and percolation threshold can be tailored by changing the drying temperature of the composite film. Another way to tailor the percolation threshold involves changing the average particle size of a given latex. Monodisperse poly(methyl methacrylate-co-butyl acrylate) latices were prepared with a range of particle sizes between 0.1 and 1 µm. These latices were filled with carbon black and the electrical conductivities of dried films were measured. It was found that as the ratio of latex particle size to carbon black particle size (~20 nm) increased the percolation threshold decreased substantially over the range of particle sizes tested. These observations agree with results obtained by others using compressed mixtures of polymer powder and conductive filler.

#### **KK8.3**

**THE INFLUENCE OF CLAY ON THE CRYSTALLIZATION OF POLYPROPYLENE.** Yantian Wang, Wenhua Zhang, Mike Gelfer, Miriam Rafailovich, Jonathan C. Sokolov, State Univ. of New York at Stony Brook, Dept. of MS&E, Stony Brook, NY; Dennis Peiffer, Exxon Res.&Eng. Co. NJ; Kungang Zhou, Steven Schwarz, Queens College, NY.

The crystallization of polymers is widely studied due to its important influence on the physical properties of polymers. In the present study, the effect of clay on the crystallization of polypropylene is demonstrated. PP films with different amounts of clay (20%, 10%, 5%, 0) treated with surfactant is spun-cast onto heated silicon substrates. TEM showed that spinning achieved a large degree of exfoliation. To induce crystallization of the films, they are annealed at 178°C, which is just above its melting point, and then gradually cooled to 165°C. We observed that all samples crystallized and the grain sizes of the samples decreased with increasing amount of clay. These results will be correlated with bulk and surface rheological studies.

#### **KK8.4**

**ROLE OF THE CLAY IN INTERFACE FORMATION BETWEEN TWO IMMISCIBLE LIQUIDS.** K. Kaznachev, Dept of Physics & Astronomy, SUNY, Stony Brook, NY; Young-soo Seo, M. Rafailovich, Dept of Materials Science & Engineering, SUNY, Stony Brook, NY.

Styrene (PS, Mw=750) and Methyl siloxane (PDMS, Mw=500) oils are well known immiscible liquids. The liquid-liquid phase separation was investigated using soft x-ray spectromicroscopy. Well defined patterns, whose shape and domain size depends on composition and film thickness were evaluated as a function of temperature in real time. The effect of exfoliated functionalized clays on the domain morphology of the liquids was also studied. Highly irregular domains with discontinuous boundaries were observed. The domain size appeared to shrink with increasing clay concentration indicating that the clays were effective at reducing the interfacial tension in simple liquids.

#### **KK8.5**

**INFLUENCE OF FILLER PARTICLES AND CLUSTERS IN PHASE-SEPARATING POLYMER BLENDS.** Y. Jiang, T. Lookman, A. Saxena, Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM; J.F. Douglas, Polymer Division, National Institute of Standards and Technology, Gaithersburg, MD.

Motivated by recent experiments on filled phase-separating polymer blends, we perform computer simulations to investigate the evolution of compositional morphologies in the presence of solid particles. We study the effects of geometry on the stability of the phase separating pattern and how the morphology accommodates the surface boundary of the particles or particle clusters (such as fractal clusters). These studies can provide guidelines for facilitating the fabrication of filled polymer systems and nanocomposites with desired properties.

#### **KK8.6**

**PHASE SEPARATION OF PS AND PMMA BLENDS UNDER CONFINEMENT.** Y.S. Seo, K.W. Shin, M.H. Rafailovich, J. Sokolov, SUNY at Stony Brook; D.A. Winesett, H. Ade, NCSU.

We have studied the phase segregation of a dPS or PS (Mw=62k) and PMMA (Mw=25k) blend under confinement using AFM and STXM. The result shows that phase segregation is severely hindered by confinement. Uniform cylindrical structures with a very small wavelength form rapidly and appear to be stable even after long annealing times. These cylinders are oriented perpendicular to the Si

substrate and appear to originate from a thin adsorbed uniform layer of PMMA which coats the Si interfaces. Addition of 10% diblock copolymer decreases the wavelength even further, but otherwise does not change the structure of dynamics. Similarly, the addition of functionalized nanoparticles also affect the interfacial structure. The wavelength dependence of the equilibrium morphologies will be discussed. This work is supported by NSF MRSEC program.

#### **KK8.7**

**THE SYNTHESIS OF LIQUID CRYSTALLINE POLYMER ON GOLD NANOPARTICLES.** Qinghong Fu, Thomas A.P. Seery, Institute of Materials Science, Polymer Program, University of Connecticut, Storrs, CT.

Gold nanoparticles with thiol stabilizing layers were prepared with various fractions of end-functional thiols. These alcohol end-groups were further elaborated to norbornene moieties so that Grubbs catalyst could be tethered to the nanoparticle surfaces. The functional thiols were bound to the gold surfaces using either a C-12 or a C-23 hydrocarbon and the catalyst modified nanoparticles were designated as RuGNP12 and RuGNP23 respectively. The tethered organometallic complexes were used to initiate the polymerization from the nanoparticle surfaces. Liquid crystalline polymers were grown from RuGNP23 while syntheses using RuGNP12 failed. We hypothesize that the RuGNP23 provides a less sterically hindered site for initiation than RuGNP12. Polarized optical microscopy showed that the polymer coated gold nanoparticles could still form a nematic mesophase at elevated temperature although the orientation of mesogens is restricted by crowding at the nanoparticle surface. Samples of unbound polymer were also prepared and exhibited similar transition behavior.

#### **KK8.8**

**SHAPE MEMORY AND VOLUME EXPANSION OPTIMIZATION IN POLYMER MICROBALLOON FILLED ELASTOMER FOAMS UTILIZING A TWO STEP PROCESS.** Mark W. Ellsworth, Miguel Morales, James Rinde, Barry Mathews, Tyco Electronics, Menlo Park, CA.

Foamable thermoplastics and liquid elastomers are commonly used as gap filling materials for sealing, vibration and noise isolation, and insulation. One disadvantage to these systems is that the material is crosslinked during the expansion stage, resulting in some loss of shape memory and some partial collapse in the volume expansion prior to complete cure. This problem can be overcome to some extent by using partially cured (B-stage) resins, but the expansion volume in these resins can vary and the volume expansion decreases with storage time as the partially cured resin continues to crosslink before the foaming process is initiated. We have developed materials which are fully cured at low temperature and expanded at high temperature at a later stage with volume expansions in excess of 500%. These composite materials are obtained by blending polymer microballoons into an elastomeric resin and fully curing the resin below the expansion temperature of the microballoons. The unexpanded materials are storage stable and subsequent expansion is initiated by heating the material at the appropriate expansion temperature. Optimum expansion is achieved by balancing the microballoon loading with the modulus and ultimate elongation of the elastomer. The pre-expanded materials can be molded or cut into complex shapes and high dimensional uniformity is retained upon expansion.

#### **KK8.9**

**HIGH PERMITTIVITY, FIBER FILLED POLYMERS AND FOAMS FOR MICROWAVE APPLICATIONS.** John Schultz, Georgia Tech Research Institute, Atlanta, GA.

Artificial dielectric materials with high permittivities and low loss are desired for microwave applications such as novel antennas. Mechanical flexibility, low density, and ease of processing are also often required for practical applications. This combination of properties is possible with composites such as particulate filled polymers or foams. In this work, the microwave dielectric properties of polymers and foams filled with short fiber particulates were studied. Mixtures were made with silicone elastomers, polyurethane foams, and epoxies blended with metallic and ceramic fibers. Stainless steel fibers of two different aspect ratios and lead zirconate titanate (PZT) fibers with a distribution of aspect ratio were used. X-band waveguide, free-space measurements (4-18 GHz), and impedance analysis were used to determine dielectric properties as a function of volume fraction. SEM and optical microscopy were used to investigate the microstructure of the dispersed filler. The high polarizability of the anisotropic-shaped particulate along with the high conductivity of the stainless steel or the high dielectric permittivity of the PZT enabled these filled systems to exhibit high permittivities with low fill fractions. For example, a microwave dielectric permittivity greater than 10 was achieved in a polyurethane foam filled with less than 1 vol% of stainless steel fiber. The measured results were compared with predictions from effective

medium theories. The permittivity was found to depend on dispersion microstructure as well as constitutive properties.

#### **KK8.10**

**POLYCARBONATE TOUGHENING USING RIGID PARTICLE FILLERS.** Maciej Psarski\*, Robert E. Cohen, Massachusetts Institute of Technology, Dept of Chemical Engineering, Cambridge, MA; Ali S. Argon, Massachusetts Institute of Technology, Dept of Mechanical Engineering, Cambridge, MA. \*permanent address: Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Lodz, POLAND.

Bisphenol-A polycarbonate is known among glassy polymers for its superior performance through its ability to undergo extensive plastic deformation in tension, accompanied by considerably high toughness in standard notched Izod tests at room temperature. However, due to its very low fracture toughness, very sharp notch plane strain conditions render polycarbonate an extremely brittle material. In this study, an approach is made to toughen polycarbonate with rigid particle fillers - that can also counteract the usual reduction in stiffness, inherent to rubber toughening - and to gain a fundamental understanding of fracture processes in rigid particle filled amorphous polymers. Fillers used include submicron size zinc oxide and zinc sulfide particles and larger glass beads. The expected toughening mechanism is based on the promotion of plastic flow in thin interparticle matrix ligaments separating the inclusions. Plastic resistance in these ligaments is expected to be lowered due to debonding of fillers from the matrix and creation of a voided structure. The dispersion of the filler in the matrix and filler/matrix interaction, as well as filler characteristics are found to influence strongly the response of the composite to deformation. Even more importantly, it is demonstrated here that intrinsic matrix properties - fracture toughness, flow stress, initial strain hardening behavior, locking stretch - are critical to the ability of the composite to develop the expected tough response. In the case of polycarbonate the above parameters dictate very strict requirements for the filler dispersion and its ability of easy debonding from the matrix.

We gratefully acknowledge the financial support of the Bayer Corporation for this research.

#### **KK8.11**

**CONTROLLABLE IN SITU CONSTRUCTION BY CHAOTIC MIXING OF PERCOLATING NETWORKS WITH POWDER OR FIBER ADDITIVES IN THERMOPLASTIC MELTS.** David A. Zumbrennen, Clemson University, Department of Mechanical Engineering and NSF Center for Advanced Engineering Fibers and Films, Clemson, SC; Shashank Kasliwal and Amod Ogale, Department of Chemical Engineering, Clemson, SC.

Two- and three-dimensional chaotic mixing is being used in both batch and continuous flow processes to produce thermoplastic composites with structured distributions of carbon black or carbon fibers. Unlike common processes, initially compact bodies of particles or fibers become stretched and folded recursively so that structure is developed progressively and controllably. Plastics have been rendered electrically conducting at significantly reduced carbon black concentrations [1,2]. Much smaller percolation thresholds have been obtained because percolating structures are essentially constructed in situ in lieu of being the outcome of chance encounters among additive bodies. Solidified specimens contain morphological signatures that have been documented in fluid kinematic studies of chaotic mixing. Because of combined organization and complexity, interconnections between additives arise and extended networks are formed. Percolation characteristics differ from those for materials subjected to random mixing, where more uniform distributions are obtained. For example, electrical resistivity decreases have been measured even for additive concentrations below the percolation threshold due to the rapid development of localized networks. Composites with either isotropic or directional electrical properties have been produced recently by controlling chaotic mixing parameters. Isotropic properties are readily obtained by promoting three-dimensional chaotic mixing conditions. Directional properties can be obtained by selecting flow fields that generate chaotic mixing predominantly in two dimensions. The structured blends can be subjected to additional processing steps, such as injection molding or extrusion to produce electrically conducting parts or fibers. Most importantly, results suggest that chaotic mixing may offer more controllable mixing conditions so composites can be formed with desired internal structures among additives.

References:

- [1] R.I. Danescu and D.A. Zumbrennen, J. Thermoplastic Composite Materials, 11, 299 (1998).
- [2] R.I. Danescu and D.A. Zumbrennen, J. Vinyl Additive Technology, 6, 26 (2000).

#### **KK8.12**

**HIGH CONDUCTIVITY SHAPE STABILIZED THERMAL**

STORAGE MATERIAL. Min Xiao, Peng Xiao, Kecheng Gong, Polymer Structure & Modification Res. Lab, South China University of Technology, Guangzhou, PR CHINA; Luyi Sun, University of Alabama, Dept of Chemistry, Tuscaloosa, AL.

Organic compound such as paraffins, fatty acids, esters etc. have been found to exhibit many desirable characteristics as phase change materials (PCMs) for thermal storage applications. However, they also have undesired properties such as low thermal conductivity, and as all the solid-liquid PCMs do, they also bring us extra problems in encapsulating them. In this work, composites based on different paraffins, styrene-butadiene-styrene triblock copolymer (SBS) and exfoliated graphite (EG) are prepared. These composites exhibit high thermal conductivity and up to 80% of the heat of fusion of the paraffins (depending on the mass percentage of the paraffins in the composite). In these composites SBS serves as a supporting materials for PCMs. PCMs undergo solid-liquid phase change in the SBS network, and there's no leakage of them even in the state of melt. EG in these composites contributes to their high thermal conductivity. The composites have great potential for solar-assisted heat pump system as well as passive solar applications.

#### **KK8.13**

SILICA NANO-PARTICLE FILLED POLY(ETHYLENE-CO-HEXENE)/XYLENE GEL. Howard Wang, Alan Nakatani and Charles C. Han, National Institute of Standards and Technology, Polymer Division, Gaithersburg, MD.

Physical gels form at ambient temperature upon dispersing a few percent of poly(ethylene-co-hexene) or silica nano-particle in xylene. When both polymer and particle coexist in xylene, complications arise from the interaction between the polymer and the particle. To understand the gel structure and gelation transition in the three component mixture, small angle neutron scattering (SANS), light scattering and rheological measurements have been carried out on both polymer/solvent and polymer/filler/solvent systems. Rheological measurement shows that for both systems, a transition region from ca. 80°C to 110°C separates the gel state and the liquid state, with a difference in their storage modulus,  $G'$ , about 6 orders of magnitude. Within the transition regime,  $G'$  decreases exponentially at both low and high temperatures separated by a finite drop of about 2 orders of magnitude at a critical temperature around 95°C. The changes within the transition regime are also revealed in SANS. The distinct scattering behavior at low- $q$  and high- $q$  during transition suggests that there may exist a two-length-scale structure. These observations suggest that particle interaction is screened by the polymer and the effect of the silica filler in this case is mainly to soften the gelation transition by a broad distribution of the polymer chain conformation near the filler surface.

#### **KK8.14**

DIFFUSION INHIBITION AND FRACTURE TOUGHNESS IN CARBON BLACK FILLED POLYSTYRENE. K. Zhou, V. Zaitsev, V. Shapovalov, Y. Strzhemechny, S. Schwarz, Queens College, Dept of Physics, Flushing, NY; H. Kim, Seoul National Univ, Seoul, KOREA; D. Peiffer, Exxon, Annandale, NJ; M. Gelfer, M. Rafailovich, J. Sokolov, Dept of Materials Science and Engineering, SUNY, Stony Brook, NY.

Several studies relating to inhibited mobility in carbon black filled polystyrene are described. Secondary ion mass spectrometry (SIMS) is employed to observe diffusion in polystyrene near a carbon surface prepared by sputter coating a silicon wafer. A thin deuterated polystyrene (dPS) marker layer embedded between normal PS layers is subjected to anneals of varying length. Diffusion profiles are contrasted to similar samples prepared on uncoated silicon surfaces. As opposed to the silicon surface, no dPS segregation is observed at the carbon surface. Diffusion is strongly inhibited at both surfaces. Computer fits reveal a strong depth and time dependence of the diffusion coefficient  $D$ , which increases roughly as the  $3/2$  power of distance from either solid surface while decreasing gradually with annealing time. SIMS is also being employed to monitor diffusion from a dPS layer into a PS underlayer with inorganic filler, and results are correlated to bulk rheology and  $T_g$  measurements for varying filler concentrations. Finally, a strong suppression in fracture toughness is observed as a function of carbon filler concentration, leveling off at 5 wt.%. Fracture toughness recovers after annealing, and correlates with the SIMS diffusion measurements. The results are consistent with long range inhibition of polystyrene diffusion near the filler particle surfaces.

#### **KK8.15**

MECHANICAL AND CHEMICAL PROPERTIES OF BIOMIMETIC NANOCOMPOSITE COATING. Chung-Yi Tsai, Sunita Satyapal, United Technologies Research Center, East Hartford, CT; C. Jeffrey Brinker, The University of New Mexico, Center for Micro-Engineered Materials and Sandia National Laboratories, Advanced Materials

Laboratory, Albuquerque, NM; Harvey H. Michels, University of Connecticut, Storrs, CT.

The combined strength, hardness, and toughness of natural nanocomposites such as sea shells have inspired chemists and materials scientists to develop synthetic "biomimetic" processes for their construction. In recent years, methods for creating self-assembled micelle structures have been developed with the hope to create revolutionary materials for unprecedented applications. However, the success of these materials for any practical application largely depends on their mechanical and chemical integrity and stability. Until now, this area has been largely overlooked. This work reports the mechanical and chemical properties of various micelle structures including alternating organic/inorganic lamellar structure. This work studied the chemical environmental impact on the coating structure by exposing the coating to possible extreme chemical environments. Erosion was another focus of the study. The coatings were subjected to severe conditions they may experience in their lifetime. Structural strength and integrity was also studied using various state-of-the-art methods to determine mechanical response of these coatings as a function of chemical compositions. The result of this work provides a road map for guiding present biomimetic lamellar coatings to possible applications. It can also be a basis for design of future self-assembled micelle structures. The implications of the results will be discussed.

#### **KK8.16**

THE SYNTHESIS OF SILICON-CONTAINING POLYESTER DIRECTLY FROM NATURAL  $\text{SiO}_2$  AND CHARACTERIZATION OF ITS STRUCTURE. Jianhua Song, Kecheng Gong, South China University of Technology, Polymer Structure & Modification Lab, Guangzhou, PR CHINA; Luyi Sun, University of Alabama, Department of Chemistry, Tuscaloosa, AL.

This article described the preparation of a novel silicon-containing polyester by low-temperature solution polycondensation between a novel tetracoordinate silicon and P-phthaloyl chloride [ $p\text{-C}_6\text{H}_4(\text{COCl})_2$ ]. The tetracoordinate silicon ( $\text{Si}(\text{OCH}_2\text{CH}_2\text{O})\text{OCH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2\text{OH})_2$ ) was prepared by the reaction of 2-Chloroethanol ( $\text{ClCH}_2\text{CH}_2\text{OH}$ ) with a high reactive pentacoordinate silicon complex ( $\text{KSi}(\text{OCH}_2\text{CH}_2\text{O})_2\text{OCH}_2\text{CH}_2\text{OH}$ ) which synthesized by Laine et al. This research solved the pentacoordinate silicon complex' instability, sensibility to water and poor solubility, further more, the synthesised tetracoordinate silicon is a key transferring product from pentacoordinate silicon to polymer. FTIR, TGA, DSC, GPC, etc have been used to characterize this silicon-containing polyester. Some attractive properties, such as the high thermal stability, were observed.

#### **KK8.17**

THE INFLUENCE OF HUMIDITY ON THE STRUCTURE OF  $\text{MOS}_2(\text{PEO})_{1,4}$  NANOCOMPOSITES. Philippe Westreich, Datong Yang, Robert F. Frindt, Simon Fraser University, Dept of Physics, Burnaby, BC, CANADA.

Layered nanocomposites of molybdenum disulfide ( $\text{MoS}_2$ ) and poly(ethylene oxide) (PEO) were studied using x-ray diffraction of powder and oriented thin film samples. Thermal gravimetric analysis provided information on the composition of the material. The effects of the molecular weight of PEO and the atmospheric relative humidity on the structure were also investigated. A basal plane spacing of 14.3 Å, corresponding to an expansion of 8.1 Å between  $\text{MoS}_2$  layers, was found for dry samples, in agreement with the literature. At about 30% relative humidity, the expansion increased to 10.6 Å. This increase corresponds approximately to the thickness of one monolayer of water. The layer spacing was constant until around 65% humidity, when the expansion began to increase again, reaching 25 Å near 100% humidity. Coherence lengths in the direction perpendicular to the planes averaged 13 layers, 7 layers, and 3 layers for the dry, 58% humid and nearly 100% humid samples, respectively.

#### **KK8.18**

CRAZE GROWTH MONITORING USING LIGHT EXTINCTION. Tom Krupenkin, Bell Laboratories, NJ.

A method of real-time in situ monitoring of craze and crack growth in homopolymers and polymeric composite materials is suggested. The method is based on the analyses of the light extinction properties of polymer samples. A possibility of craze/crack detection and characterization using this method is demonstrated. The dependence of the apparent absorption spectra of the sample on the crack/craze depth and surface density is analyzed both theoretically and experimentally. Good quantitative agreement is obtained between theoretical and experimental results. Several directions of the future work are briefly discussed.

#### **KK8.19**

EPOXY INFILTRATION INTO NANOPOROUS ALUMINUM

OXIDE. D. Arayasantiparb, M. Libera, Stevens Institute of Technology, Hoboken, NJ; S. McKnight, Army Research Laboratory, Aberdeen, MD.

The mechanical integrity of fiber-reinforced composites is often dominated by nanoscale structuring at polymer-adherend interfaces. To this end, aluminum adherends are typically anodized to create a nanoporous oxide surface. The detailed nanoscale morphology within the oxide-polymer interphase remains unknown, however, because of the challenging length associated with this problem. Whether or not the nanopores are fully filled by polymer remains an open question. This research uses spatially resolved electron energy-loss spectroscopy (EELS) in a scanning transmission electron microscope (STEM) to study the infiltration of an aromatic epoxy resin into a nanoporous aluminum oxide. Imaging by field-emission scanning electron microscopy (FEG SEM) shows that the oxide surface of the as-anodized aluminum consists of columnar nanopores with diameters ranging from approximately 5 nm to 150 nm. Spatially resolved carbon and oxygen EELS profiles from the oxide are anti-correlated indicating that oxide pore walls are separated by pore interiors filled with epoxy. Spatially resolved low-loss spectral data are transformed into a measure of apparent specimen thickness which in turn is related to the mean free paths for inelastic electron scattering characteristic of the epoxy and the oxide. Comparison of such data to simulations based on experimentally-derived oxide topologies indicate that the pores are fully filled. These findings are consistent with models of nanopore filling which balance capillary forces and applied pressure.

#### SESSION KK9: ADVANCED CHARACTERIZATION TECHNIQUES

Chair: Robert Schuster  
Thursday Morning, November 30, 2000  
Gardner (Sheraton)

##### 8:30 AM \*KK9.1

SMALL ANGLE SCATTERING AND THE STRUCTURE OF FILLED AND UNFILLED RUBBERS. Erik Geissler, Anne-Marie Hecht, Lab Spectro Physique CNRS, Univ Grenoble, St Martin d'Hères, FRANCE; Ferenc Horkay, National Institutes of Health, Bethesda, MD.

Random cross-linking in rubbers produces local variations in the elasticity of the network. These variations, whose characteristic size lies in the range 1-100 nm, are revealed when the rubber is swollen in a low molecular weight solvent, owing to the competition between the osmotic pressure of the solvent and the local elastic constraints, which affects the local polymer concentration. Such concentration fluctuations can be measured by small angle X-ray or neutron scattering (SAXS or SANS). The corresponding contributions to the scattering pattern behave differently when the swollen rubber is stretched, and a local Poisson ratio  $\sigma$  can be associated with the network. Values of  $\sigma \approx 0$  are found. The dynamics of the network can be characterized by neutron spin echo observations. In rubbers containing a filler, the distribution of polymer, as well as of the elastic constraints, is modified. Although the analysis becomes more complicated, use of deuterated solvents changes the contrast in SANS measurements, thereby allowing the scattering function of the polymer to be separated from that of the filler. Observations on silica particles in a PDMS rubber yield measurements not only of the surface area of the particles but also of the fraction of the surface area occupied by the polymer.

##### 9:00 AM KK9.2

X-RAY DIFFRACTION STUDY ON CRYSTALLITE SIZE DISTRIBUTION IN CARBON BLACKS. T. Ungar, J. Gubicza, G. Ribarik, Dept of General Physics, Eötvös University, Budapest, HUNGARY; T.W. Zerda, Zerda, Dept of Physics, Texas Christian University, Fort Worth, TX.

In x-ray or neutron scattering the size of crystallites, called the coherently scattering domains, is diffraction order *independent*, whereas lattice distortions are diffraction order *dependent*. The two effects can be separated providing information on the crystallite sizes and lattice distortions. The coherently scattering domains include dislocation cells or subgrains tilted or twisted by few degrees or small crystallites separated by large angle grain boundaries. The physical interpretation of the crystallite size obtained from line broadening needs a deep insight into the state of the material and usually requires TEM investigations. Lattice distortions are given by the mean square strain  $\langle \varepsilon_{L,g}^2 \rangle$ , where  $L$  is the Fourier length and  $g$  is the diffraction vector. strain  $\langle \varepsilon_{L,g}^2 \rangle$  is almost never a constant, neither as a function of  $L$  nor as a function of  $g$ . The  $g$  dependence is further complicated by strain anisotropy. This effect can be accounted for by the anisotropic contrast effect of dislocations. The Williamson-Hall plot and the Warren-Averbach method have recently been modified so

that  $K^2$  ( $K = 2\sin\theta/\lambda$ ) is replaced by  $K^2\bar{C}$ . For example, in the case of FWHM:  $\Delta K_{1/2} \cong 0.9/D + (\pi M^2 b^2/2) \rho^{1/2} K^2 \bar{C} + O(K^4 \bar{C}^2)$ , where  $D$ ,  $\rho$  and  $b$  are the apparent crystallite size, the average dislocation density, and the modulus of the Burgers vector of dislocations, respectively.  $M$  depends on the effective outer cut-off radius of dislocations. The average contrast factors of dislocation  $\bar{C}$ , which included different characters of dislocations and elastic constants of the crystals have been compiled for the cubic and hexagonal crystals. The method has further been developed in order to enable the fitting of a complete set of diffraction profiles for the cubic or hexagonal crystals. Information on the dislocation structure and character, as well as the crystallite size distribution functions were obtained for different grades of carbon blacks.

##### 9:15 AM KK9.3

SPATIAL GRADIENTS IN PARTICLE-REINFORCED POLYMERS CHARACTERIZED BY X-RAY ATTENUATION AND LASER CONFOCAL MICROSCOPY. R.R. Lagasse, K.R. Thompson, Sandia National Labs, Albuquerque, NM.

The goal of this work is to develop techniques for measuring spatial gradients in particle concentration within filled polymers, such as encapsulants for microelectronic devices. A high concentration of filler particles is added to such materials to tailor physical properties such as thermal expansion coefficient. It is shown that sedimentation and flow-induced migration of particles produces concentration gradients that are most severe near material boundaries. Therefore, techniques for measuring local particle concentration should be accurate near boundaries. Particle gradients in an alumina-filled epoxy resin have been measured with a spatial resolution of 0.2 mm using an x-ray beam attenuation technique. However, an artifact related to the finite diameter of the beam reduces accuracy near the specimen's edge, where the gradient is most severe. This edge-artifact is eliminated by measuring local particle concentration using microscopy coupled with image analysis. This is illustrated by measuring concentration profiles of glass particles having 40 micron median diameter using images acquired by a confocal laser fluorescence microscope. The mean of the measured profiles of volume fraction (0.35-0.5 in different experiments) agrees with the expected value within 3%. Also, an asymmetry in the shape of the measured profiles agrees qualitatively with simple theory for sedimentation of monodisperse particles. Extending this microscopy technique to smaller, micron-scale filler particles used in microelectronic encapsulants is illustrated by measuring local concentration in an epoxy resin containing 0.4 volume fraction of 2 micron silica particles. These local concentration measurements on the small silica particles were derived from scanning electron backscatter micrographs.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

##### 9:30 AM \*KK9.4

CONTROL OF INTERFACIAL CHEMISTRY AND MORPHOLOGY IN NANO-STRUCTURED REINFORCING FILLERS. G. Beaucage, D. Kohls, G. Skillas, Dept. of Materials Science and Engineering, University of Cincinnati, Cincinnati, OH; H. Kammler, S.E. Pratsinis, Eidgenössische Technische Hochschule (ETH) Zurich, SWITZERLAND; I. Noda, C.A. Marcott, M.M. Satkowski, A.E. Dowrey, Procter & Gamble Corporation, Cincinnati, OH.

Complex materials such as nano-composite elastomers offer a significant challenge to materials scientists involved in structure/property relationships. These systems are often characterized to a large extent by disorder making statistical characterization techniques, such as small-angle scattering, extremely valuable. This talk will focus on our efforts at drawing a correlation between small-angle x-ray, neutron and light scattering and static and dynamic mechanical measurements chiefly through a dimensional analysis. Mention will also be made of application of a relatively new correlation technique between dynamic mechanical measurements and infrared spectroscopy whereby chemical groups involved in dynamic response can be identified, "2-d IR". 2-d IR is especially valuable in identifying surface functionality that is involved in the dynamic response of a reinforced elastomer.

At Cincinnati, and with our collaborators at ETH in Zurich, we have developed unique facilities for the synthesis of ceramic oxides ranging in primary particle size, continuously, from the molecular to the micron scale. We have also achieved a large degree of control over branch content and mass scaling, demonstrating control over the two structural dimensions of importance to reinforcement, the chemical and the mass fractal dimension. We have controlled, to a large extent, the "degree of aggregation" and larger-scale agglomeration phenomena. Through novel processing approaches we have produced surface modified nano-structured oxides on the kilograms/day scale. Simultaneously our groups have developed expertise in the processing and engineering of elastomer compounds in order to understand relationships between dynamic mechanical properties and



nano-structure.

The work reported here will focus on a comparison of the structural and mechanical behavior of a parallel series of reinforcing fillers with similar nano-structure, carbon (Columbian Chemical), fumed silica (ETH), carbon coated silica (ETH), and silica coated carbon (Cabot). The purpose of this comparison is to investigate the roles of interfacial chemistry and aggregate bonding on reinforcement. This work is supported through a combination of industrial and NSF (CTS) funding most recently under CTS-0070214.

**10:30 AM \*KK9.5**

THE GENERALIZED FRACTIONAL STATISTICS A NEW TOOL FOR COMPLEX MATERIAL ANALYSIS. Alain Le Mehaute, Laurent Nivanen, Qiuping A. Wang.

Some thermo-mechanical properties and phase transitions of nanocomposites will be enlightened with the help of the fractal geometry. A statistics of thermo-mechanical variables, which takes into account the fractality, leads to a generalized thermodynamics. It will be shown that the traditional concepts such as normalization, expectation value, entropy calculation, and so on must be revisited. Such a work based on geometrical analysis of the statistics, leads to a new set of axioms. New normalization and new expectation value conditions arise naturally from this analysis. Combined with a non extensive entropy expression, the generalized formalism recovers most of the specific equations suggested by different issues in fractional statistics

**11:00 AM KK9.6**

STATE OF DISPERSION OF REINFORCING SILICA IN A SILICONE ELASTOMER, AS INVESTIGATED BY TRANSMISSION ELECTRON MICROSCOPY. Rex J Field, Joachim Floess, Stephane Rouanet, Cabot Corporation, Aerogel Product Line, Tuscola, IL; Jeanne Cambray, Cabot Corporation, Analytical Technical Centre, Billerica, MA.

Commercial silicone rubbers typically contain nanometre- and micrometre-sized particles dispersed within them, these particulates being much-responsible for the mechanical properties required for commercial success. Fumed silica has long been used for the reinforcement of higher-performance silicone rubber compositions, but other silica-based materials, such as high-porosity aerogels, which possess quite different structures from that of fumed, can function as well. Such aerogels are becoming available commercially, and the object of the work presented here was to examine and so compare the state of dispersion of a typical, reinforcing-grade fumed silica, with those of some novel high-porosity aerogels. Thus model HCR silicone compositions were prepared, and their mechanical properties characterized. Thin sections of the cured rubbers were then obtained a by cryo-microtome method, and examined by transmission electron microscopy. Much of the fumed silica was seen to have been dispersed to give sub-micron sized features in the rubber, although a number of larger aggregates or fragments were seen to remain in the micron-size range. The high-porosity hydrophobic aerogel of high surface area was, in contrast, seen to have been dispersed to give even smaller, finer features in the rubber, and to show very few super-micron features or fragments of "poorly-dispersed" aerogel. The state of dispersion of the hydrophilic aerogel of similar porosity and surface area to the hydrophobic one was different again, showing many poorly-broken down fragments with diameters of 5  $\mu\text{m}$  or so. The visual appearance of the compound reflected this poorer state of dispersion.

**11:15 AM \*KK9.7**

DYNAMICS OF CLAY-POLYMER NANOCOMPOSITES MEASURED WITH INELASTIC NEUTRON SCATTERING. Robert Ivkov, NIST Center for Neutron Research, MD; Peter Papanek, Univ. of Penn./NIST; Ramanan Krishnamoorti, Univ. of Houston, TX.

Clay-polymer nanocomposites have recently received attention as a new class of composite materials that are useful in several applications. These materials make possible studies into the structure and dynamics of polymers in severely confined geometries. We present neutron filter-analyzer spectroscopy and neutron time-of-flight spectroscopy results on the dynamics of polyethylene oxide (PEO) intercalated into fluorohectorite (FH) clay. We compare the spectra obtained from two samples of intercalated materials, with PEO mass fractions of 0.18 and 0.30, with those obtained from bulk PEO and pure FH clay. We also report conclusions regarding the structure of the polymer chains in the intercalated materials that can be inferred from the spectroscopic data.

SESSION KK10: ADVANCED NANOCOMPOSITES II

Chair: Rex P. Hjelm

Thursday Afternoon, November 30, 2000

Gardner (Sheraton)

**1:30 PM \*KK10.1**

NANOFILLER MODIFICATION OF PHASE STABILITY IN PS/PMMA BLENDS. Gending Ji, Florence Clement and Emmanuel P. Giannelis, MS&E Dept, Cornell University, Ithaca, NY.

Nanocomposites synthesized by intercalation of polymers in layer inorganics have been shown to exhibit improved mechanical properties, outstanding diffusional barrier properties as well as flame and solvent resistance. In this talk we will present our recent work on how the same inorganic nanofillers affect the phase boundaries and the morphological development of phase separated structures. We will show that nanofillers, which are miscible with both polymers, have a similar effect as copolymers in promoting better wetting and adhesion between the two polymer phases.

**2:00 PM KK10.2**

INFLUENCE OF LAYERED SILICATES ON ORDERING OF BLOCK COPOLYMERS. Ramanan Krishnamoorti, Cynthia A. Mitchell, University of Houston, Department of Chemical Engineering, Houston, TX.

The influence of adding layered silicates to the ordering in block copolymer melts has been studied using a combination of radiation scattering, electron microscopy and dynamic viscoelastic measurements. The kinetics of the ordering of block copolymer lamellae and spheres can be dramatically altered by the addition of even 0.4 vol. % layered silicate with lateral dimensions exceeding 0.5 microns. However, for layered silicates with lateral dimensions of 300 Å, or for the development of hexagonal closed packed cylinders, the addition of the nanoscopic filler has negligible effect. On the other hand, in each of these cases the grain size of the ordered domains were considerably decreased in the presence of the filler, suggesting the potential of the layered silicates to disrupt the formation of ordered structures.

**2:15 PM KK10.3**

POLYSTYRENE POLY(METHYL METHACRYLATE) POLY(ETHYLENE-PROPYLENE) CLAY POLYMER COMPOSITE. W. Zhang, Y. Wang, H. White, M. Rafailovich, J. Sokolov, D. Gersappe, Dept Mat Sci Eng, State University of New York at Stony Brook, NY; D. Peiffer, Exxon Res. and Eng. Co. Annandale, NJ; A. Winesett, H. Ade, Physics Dept, North Carolina State University, Raleigh NC; Y. Shnidman, Chemistry Dept, Polytechnic University, Brooklyn, NY.

Exfoliated clays were introduced to polystyrene/poly(methyl methacrylate)/poly(ethylene-propylene)(PS/PMMA/PEP) polymer blends to study the effect of phase behavior. Polymers and Clay were co-dissolved in toluene and dispersed under ultra sound for 1h. Thin films then spun cast and studied by Scanning Force Microscopy, Scanning Transmission X-ray Microscopy, and Transmission Electron Microscopy. TEM pictures show fully exfoliated clay in the blend. AFM and STXM data show that the spun cast films are all initially phase segregated. In the absence of clay, annealing increases the segregation, and micron size of domains are observed. The addition of clay promotes mixing and the domains are observed to shrink with time. After annealed for 3 days the domains became smaller than the STXM Resolution (100nm) and could no longer be detected. It is proposed that the clay platelets are adsorbed to the interfaces between domains and form insitu grafts. Due to the large aspect ratio of the platelet the grafts can localize a high concentration of polymer at the interface without competition from micelle formation. Hence exfoliated clays can be potential compatibilizers for general polymer blend systems.

Funded part by NSF-MRSEC Program and the Procter & Gamble Co.

**2:30 PM KK10.4**

FABRICATION OF NEW MESOPOROUS DIMETHYL-SILOXANE-INCORPORATED SILICA NANOCOMPOSITES. Taeghwan Hyeon, Jin Joo, Jinyu Hyeon-Lee, Seoul National University, School of Chemical Engineering, Seoul, KOREA.

We will present the synthesis of new mesoporous elastomeric dimethylsiloxane-incorporated silica materials. These mesoporous materials were synthesized from the co-condensation of TEOS and diethoxydimethylsilane (DEDMS) in the presence of surfactant self-assemblies. They exhibited high surface areas of  $\sim 1000 \text{ m}^2/\text{g}$ , regular  $\sim 2.5 \text{ nm}$  pores, thick walls of  $> 2.8 \text{ nm}$ , high hydrophobicity, and high mechanical strength. We expect that these mesoporous PDMS/SiO<sub>2</sub> nanocomposites can find applications in catalysis, adsorption technology, and the fabrication of low dielectric materials for ULSI devices. Synthesis, characterization and application of these mesoporous organic/inorganic nanocomposites will be discussed in the presentation.

**2:45 PM KK10.5**

PHENOLIC/LAYERED SILICATE NANOCOMPOSITES:

SYNTHESIS AND CHARACTERIZATION. Derrick Dean, Rhamat Ullah, Center for Advanced Materials, Tuskegee University, Tuskegee, AL; Gary Price, University of Dayton Research Institute, Dayton, OH; Richard Vaia, Air Force Research Laboratory, Dayton, OH.

Phenolic/layered silicate clay nanocomposites have been investigated in this study. The nanocomposites were synthesized by dispersing the clays into the resole intermediates, followed by curing. A commercial resole was compared to a phenol-formaldehyde resole, which was synthesized in the laboratory. In the latter case, the effect of dispersing the clay during resole formation was compared to dispersal after the resole was formed. In all cases studied, including the commercial resole, a mixture of intercalated and exfoliated morphologies were found by wide angle x-ray diffraction. Incorporation of the resoles into the clays was controlled by controlling the pH. Thermo-oxidative properties were observed to increase for increased clay loadings. Flammability studies will be reported.

**3:30 PM \*KK10.6**  
NANOCOMPOSITE SYSTEMS FOR CATALYTIC APPLICATIONS. Jackie Y. Ying, Massachusetts Institute of Technology, Cambridge, MA.

Unique organic-inorganic nanocomposites can be obtained by self-assembly processes using surfactants and block co-polymers as supramolecular templating agents. Upon removal of the organic templates, well-defined nanoporous materials can be achieved with tailored pore size and structure. This talk describes the synthesis of microporous and mesoporous transition metal oxides and silicates of interest for catalytic applications. These novel nanoporous materials have been used to fixate metalloporphyrins for effective epoxidation and hydroxylation reactions without leaching problems. We have also devised vapor grafting techniques to create highly dispersed Pd coating on nanoporous supports for carbon-carbon coupling reactions, with activities that rival even the best homogeneous Heck catalysts.

**4:00 PM KK10.7**  
POLYMERS CROSS-LINKED BY NANOMETER-SIZED OXOMETALLATE CLUSTERS. Ulrich Schubert, Gregor Trimmel, Bogdan Moraru, Nicola Hüsing, Guido Kikelbick, Institut für Anorganische Chemie, Technische Universität Wien, AUSTRIA.

A variety of oxometallate clusters of different size and shape with the general composition  $M_xO_y(OH/OR)_z(OMc)_w$  ( $M = Ti, Zr$ ;  $x = 4-8$ ;  $OMc =$  methacrylate;  $w = 6-12$ ) are obtained in high yields by reaction of  $Ti(OR)_4$  or  $Zr(OR)_4$  with an excess of methacrylic acid. The clusters can be considered structurally well-defined titania or zirconia nanoparticles (diameter 1 - 2 nm) the surface of which is covered by the methacrylate groups. Radical polymerization of 0.5 - 2 mol% of the clusters with methylmethacrylate, methacrylic acid or styrene leads to the formation of inorganic-organic hybrid polymers with the clusters as the inorganic component. This process also offers the possibility to prepare optically transparent films. The clusters reinforce and cross-link the organic polymers. By varying the cluster proportion and the solvent, the structure of the polymers (powder, glassy, gel-like) can be controlled. The swelling behavior in organic solvents and the thermal decomposition of the polymers is distinctly changed by incorporation of the functionalized clusters relative to the undoped polymers. The swelling rate of the cross-linked polymers decreases with the proportion of the oxometallate clusters. Thermal depolymerization typical of the undoped polymers is distinctly suppressed.

**4:15 PM KK10.8**  
NANOSTRUCTURES FROM POSS-GRAFTED BLOCK COPOLYMER PRECURSORS. Seung B. Chun, Patrick T. Mather, Institute of Materials Science, University of Connecticut, Storrs, CT.

A new method to prepare novel nanocomposites has been studied using polyhedral oligomeric silsesquioxane grafted polyisoprene-block-polystyrene copolymers (POSS-g-PI-block-PS). To begin PI-block-PS copolymers (IS) were synthesized via anionic polymerization in tetrahydrofuran (THF) as a solvent.[1] The PI block in IS block copolymers in this study had ca. 94 mole% of pendant vinyl groups (3,4- and 1,2-addition), which can react with hydride substituted POSS (that is, hydridodimethylsiloxy POSS) to form a grafted block copolymer following standard hydrosilylation techniques.[2] Due to the immiscibility between POSS-grafted PI block and PS block, the grafted block copolymer features a microdomain structure that we seek to exploit. The block length ratio of PS block in the grafted block copolymer was varied in the range of 0.1 to 0.35 in order to develop PS microdomains (cylinders or spheres) in the matrix of grafted block copolymer. When exposed to oxygen plasma, films of the grafted block copolymer lose the organic portion (PS microdomains) allowing formation of a well-defined nano-porous film/coating, demonstrated using both TEM and AFM methods. We discuss, in summary, approaches to exploit these structures in the

areas of sensors, microfluidics, and nanocomposites.

[1] G. Mao, J. Wang, S.R. Clingman, C.K. Ober, J.T. Chen, and E.L. Thomas, *Macromolecules* 1997, 30, 2556

[2] C. Pugh, J.-Y. Bae, J. Dharia, J.J. Ge, S.Z.D. Cheng, *Macromolecules* 1998, 31, 5188.

**4:30 PM KK10.9**  
ERBIUM-DOPED SILICA COLLOID/POLYMER NANOCOMPOSITE OPTICAL WAVEGUIDES. L.H. Slooff, M.J.A. de Dood, T. van Dillen, D.L.J. Vossen, A. van Blaaderen, and A. Polman, FOM-Institute AMOLF, Amsterdam, THE NETHERLANDS.

Rare earth doped polymer thin films can find many applications in planar optical amplifier technology. Direct doping of polymers with rare earth ions results in segregation of the rare earth ions. We have shown previously that an organic cage-like molecule surrounding the rare earth ion can overcome this problem, but the organic C-H bonds in the complex resulted in additional quenching of the rare earth luminescence. In this paper we report on a new nano-composite material, in which rare-earth doped nano-colloids are embedded in a polymer thin film. The 340 nm-diameter silica colloids are made by wet chemical synthesis using ethanol, water, ammonia and tetra-ethoxy-silane. Next, the colloids are deposited on a Si substrate and erbium is introduced using 350 keV ion implantation, followed by thermal annealing. The silica particles are an excellent host for the Er ions: sharp photoluminescence spectra centered around 1.54  $\mu\text{m}$  are observed, with a luminescence lifetime as long as 17 ms. The luminescence quantum efficiency is studied using experiments in which the colloids are embedded in liquids with different refractive index. The decay rate decreases with increasing index, due to an increase of the local optical density of states around the Er ions. From the data the quantum efficiency is determined to be as high as 70%, slightly depending on Er concentration. We will show that colloid/polymer films with good optical quality can be obtained. The critical process parameters for the fabrication of optical waveguides with a high density of colloids will be discussed. Finally, prospects for the optical gain performance of these nano-composite materials will be discussed.

**4:45 PM KK10.10**  
MICROSTRUCTURE AND MAGNETIC PROPERTIES OF  $CoFe_2O_4$  NANOCLUSTERS WITHIN BLOCK COPOLYMERS. Sufi R. Ahmed and Peter Kofinas, Department of Materials and Nuclear Engineering, University of Maryland, College Park, MD.

The overall goal of this research is to explore techniques for the development of novel binary magnetic oxide nanoclusters uniformly distributed within a polymer matrix. These metal oxide doped polymer nanocomposites are confined within the self-assembled nanoscale structure exhibited by block copolymers templates. We have synthesized  $CoFe_2O_4$  doped diblock copolymers of various molecular weights and investigated the effect of metal doping on the microstructure and magnetic properties of the self-assembled nanoclusters formed after the microphase separation of the block copolymer. The diblock copolymers were synthesized by ring opening metathesis polymerization of norbornene and norbornene trimethylsilane. Transmission electron micrographs of microtomed thin sections of these nanocomposites show that the metal oxide nanoclusters have ellipsoidal shape and are uniformly distributed inside the polymer matrix. A SQUID magnetometer was used to study the magnetic properties of the polymeric nanocomposites at applied fields up to 5 Tesla and at a temperature range from 300 K to 5 K. The magnetic properties of the nanocomposites vary depending on the block copolymer composition, and type of oxide that is nanoconfined within the polymer matrix. Mossbauer spectroscopy was used to study the structure of the nanoconfined metal oxide and confirmed the synthesis of  $CoFe_2O_4$  nanoclusters exhibiting an inverse spinel structure. This study provided a better understanding of the nucleation, growth and distribution of metal oxide nanoclusters within block copolymers and indicated ways to control the magnetic properties of polymeric based nanocomposite materials.