

SYMPOSIUM T
Polymer Nanocomposites

April 2 – 4, 2002

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SESSION T1: INNOVATIONS IN POLYMER
NANOCOMPOSITES

Chairs: Steven R. Nutt and Max D. Alexander
Tuesday Morning, April 2, 2002
Franciscan I (Argent)

8:00 AM *T1.1

NEW ADVANCES IN CLAY-POLYMER NANOCOMPOSITES.

Emmanuel P. Giannelis, Department of Materials Science and Engineering, Cornell University, Ithaca, NY.

Work in clay-polymer nanocomposites has exploded over the last few years. The prospect of a new materials technology, which can function as low-cost alternative to high-performance composites for applications ranging from automotive to food packaging to microelectronics has become irresistible to researchers around the world. In this talk I will review our current efforts in new nanocomposites for applications ranging from batteries to tissue engineering.

8:30 AM T1.2

OPTIMIZATION OF A NAFION[®] PROTON-EXCHANGE MEMBRANE BY INFILTRATION OF A P₂O₅-SiO₂-ZrO₂ GLASS.

Françoise Damay, Lisa C. Klein, Rutgers University, Dept of Ceramic and Materials Engineering, NJ.

Infiltration of a Nafion[®] membrane by a fast proton conducting silicophosphate gel, belonging to the P₂O₅-SiO₂-ZrO₂ ternary system, is studied to improve the water retention properties of these membranes, widely used in proton-exchange membrane fuel cells. TGA and AFM studies show that the infiltration does not modify the thermal behavior or structure of the Nafion[®] polymer. The composite membranes after a cleaning treatment show a conductivity of ~ 0.1 S.cm⁻¹ at high relative humidity, similar to the conductivity of Nafion[®] in the same conditions. In addition, the composite membranes exhibit significantly improved transport properties at low relative humidity, where dehydration is much slower and less serious than in the Nafion[®] sample. From the increase of the conductivity at 40%RH, the water content, $\lambda = H_{H_2O}/N_{SO_3H}$, is estimated to be $\lambda = 6$ in the composite membranes, compared to only $\lambda = 3$ in the Nafion membranes. This is attributed to the enhanced water retention properties of the phosphosilicate glass, in which the hydrogen of the P-OH group is strongly hydrogen bonded with water molecules.

8:45 AM T1.3

NANOCOMPOSITES INCREASE FUNCTIONS OF

CHONDROCYTES. Jennifer Savaiano, Grace Jun, Sarina Kay, and Thomas J. Webster, Department of Biomedical Engineering, Purdue University, West Lafayette, IN.

The objective of the present in vitro study was to determine functions of chondrocytes (cartilage-synthesizing cells) on composites of nanostructured poly-lactic/glycolic acid (PLGA) and nanophase titania. Substrates were prepared by adding 30 wt. % of either nanophase (less than 100 nm) or conventional (greater than 100 nm) grain size titania (Nanophase Technologies, Inc.) to 70 wt. % PLGA previously dissolved in chloroform. The composite was mixed, cured, and vacuum dried. Some of the polymer fiber sizes were reduced from conventional (i.e., micron) to nanometer dimensions by soaking polymer films in 10 N NaOH for 60 minutes at room temperature. Chondrocytes (Cell Applications, Inc.) were seeded (at a cell density of 3,500 cell/cm²) in chondrocyte growth media (Cell Applications, Inc.) onto the substrates of interest to the present study and were allowed to adhere for 4 hours under standard cell culture conditions (that is, a humidified, 95/5 % air/CO₂, 37°C environment). For proliferation experiments, cells were seeded (at a cell density of 2,500 cell/cm²) in cell culture media and were allowed to proliferate under standard cell culture conditions for 1, 4, and 7 days. After the prescribed time period, cells were fixed, stained, and counted. Experiments were run in triplicate and were repeated at three different times. Compared to conventional-structured composites, chondrocyte adhesion was significantly ($p < 0.1$) higher on composites with nanostructured PLGA fiber dimensions. In fact, chondrocyte adhesion was more than two times greater on composites with nanophase compared to conventional dimensions of individual polymer fibers. In this manner, the present study provides evidence that polymer composites which simulate the nanometer dimensions of the organic components of cartilage enhance functions of chondrocytes.

9:00 AM T1.4

NANOCOMPOSITES WITH CELLULOSE WISKERS IN THERMOPLASTIC MATRICES. Celine Bonini, Laurent Heux, CERMAV-CNRS, Grenoble, FRANCE; Jean-Yves Cavaille, INSA, Lyon, FRANCE.

Nanofillers extracted from the biomass are a possible alternative to inorganic fillers. Cellulose is one of the most abundant biopolymer on

earth. Slender crystalline microfibrils or whiskers are produced by the living species in the form of slender nanometric rods. Their dimensions depend on their origin, ranging from 2 to 50 nm. Aqueous suspension of these cellulose whiskers have been successfully incorporated in latex or hydrosoluble polymers by water casting. An important reinforcing effect has been measured and attributed to a mechanical percolation effect (1). Recently, we have developed a new process with surfactants allowing the dispersion of these cellulose microfibrils in organic solvents (2). New nanocomposites materials has then been processed with various thermoplastic matrices. Atactic and isotactic polypropylene were used with both dispersed and aggregated whiskers to investigate the importance of the dispersion quality. We showed that the fillers-fillers interactions were predominant for the stiffness properties in the case of solvent casted samples. The reinforcing effects at high deformation rate were however particularly sensible to the dispersion quality in solvent casted samples. In the case of extruded ethylen- vinyl acetate (EVA) nanocomposites, the effect of the processing conditions was also important at high deformation rate. (1) V. Favier, H. Chanzy, J.Y. Cavaille, *Macromolecules*, 28, 6365 (1995). (2) L. Heux, C. Bonini, G. Chauve, *Langmuir*, 16, 8210, (2000).

9:15 AM T1.5

POLYMER NANOCOMPOSITE FOAMS PREPARED BY MICROFABRICATION AND SUPERCRITICAL FLUID FOAMING TECHNOLOGY. L. James Lee, Changchun Zeng, Xiangmin Han, David L. Tomasko, Kurt W. Koelling, Dept of Chemical Engineering, The Ohio State University, Columbus, OH.

Polymer based foams are widely used in many applications, from packaging materials, insulation panels, cushions, to scaffolds for tissue engineering. The estimated value of plastic foam business is 2 billion dollars in 2000. Traditionally foams have been blown with chlorofluorocarbons (CFCs) that have attracted considerable environmental attention due to the ozone depleting reaction that occurs in the upper atmosphere. The Montreal Protocol has laid out a plan to discontinue the use of ozone depleting substances (ODS) and many of the traditional blowing agents have been or are scheduled to be phased out of foam production by 2010. The use of environmentally benign gases such as carbon dioxide (CO₂) as a blowing agent is an attractive alternative for replacing ODS. Recently developed microcellular foams by researchers at MIT and Trexel have drawn a great deal of attention and interest from industry. These microcellular foams have pore sizes less than 10 microns and foam density around 0.5 to 0.8. They are good for structural applications. However, this technology can not produce equivalent materials to the existing ODS containing foams because CO₂ as the blowing agent has lower solubility than CFCs in most polymers. For example, the polystyrene building insulation panels need to have closed cellular structure with pore size ranging from 60 to 100 microns and foam density around 0.05. In order to achieve the optimal thermal insulation. On the other hand, for tissue engineering scaffolds or superabsorbants, a macroporous open cellular structure is required with pore sizes of 100-300 microns and foam density less than 0.1. It is essential to produce CO₂ containing foams of equivalent performance to the wide range of existing foam products because CO₂ is an inexpensive, nontoxic, and unregulated solvent. Furthermore, it would be extremely valuable if improved properties and multiple functions can be added to polymer foams such that they can lead to advanced new products for various applications. This work focuses on novel nanocomposite foams based on a combination of nanoparticle technology, microfabrication technology, and supercritical fluids (SCF) technology. With proper design of the nanoparticle type, content, dispersion, and orientation, the solubility of SCF in the polymer matrix, the rheological properties of nanoparticle containing polymer, and nucleation and foam growth mechanism can be tailored to generate a wide spectrum of foams. They include closed or open cellular structures; macro-(hundreds microns), micro-(<10 microns), or nano-cellular foams; and dual-mode cellular structures.

9:30 AM T1.6

NANOCOMPOSITE POLYURETHANE FOAMS VIA POSS BLENDS. Brock McCabe, Steven Nutt, Univ of Southern California, Dept of Materials Science, Los Angeles, CA; Brent Viers, Tim Haddad, Air Force Research Laboratory, Edwards AFB, CA.

POSS molecules have been incorporated into commercial polyurethane formulations to make nanocomposite foam. This tiny POSS silica molecule has been used successfully to enhance performance of polymer systems using co-polymerization and blend strategies. In our investigation, we use a commercial MDI Poly- urethane resin foam as a model matrix system in order to facilitate fabrication. For the nanofiller, two POSS blend variations, Cp7T7(OH)₃ and iBut7T7(OH)₃ were chosen, and foam samples were synthesized. Structural characterization was accomplished by SEM, TEM, and TGA to determine POSS dispersion, thermal stability, cell structure, and molecular configurations. Performance was assessed by

compression loading experiments and by flammability tests. Measured values were compared with unreinforced PU foam.

10:15 AM *T1.7

CLIMBING THE NANO-LADDER TO COMMERCIAL SUCCESS.

Karl Kamena, Omni Tech International, Midland, MI.

Polymer nanocomposite technologies are beginning to break out of discovery stages and are moving into product development arenas. Commercial applications are being investigated and tested against traditional as well as new competitive product offerings. No question, climbing the nano-ladder is a nano-step by nano-step process. And, no surprise, performance and economics are critical keys to success.

10:45 AM T1.8

ORGANIC/INORGANIC NANOCOMPOSITES FROM FUNCTIONALIZED SILSESQUIOXANES. Jiwon Choi, Ryo Tamaki, Chad Brick, Seunggyoo Kim, Albert F. Yee and Richard M. Laine, Departments of Materials Science and Eng., Chemistry and the Macromolecular Science and Eng. Center, University of Michigan, Ann Arbor, MI; Institute of Materials Research & Engineering, SINGAPORE.

Processing conventional polymer nanocomposites usually requires the addition of organic/inorganic reinforcements into the matrix and these secondary phases often cause problems such as segregation, etc. In our approach with Octasilsesquioxanes [(RSiO_{1.5})₈, cubes] as nanobuilding blocks, organic and inorganic components can be easily incorporated into thermodynamically homogeneous one phase composites. The resulting composites, although one phase, exhibit both enhanced thermal and mechanical properties. In this new category of "nanocomposite", chemical structures of organic phases can be varied at will to mimic the target matrix, generating various kinds of "cubic silsesquioxane-reinforced" nanocomposites. We present here our latest development of epoxy silsesquioxane nanocomposites and imide silsesquioxane nanocomposites.

11:00 AM T1.9

POLYMER NANOCOMPOSITES VIA REACTIVE MELT BLENDING OF THERMOPLASTICS WITH MONOFUNCTIONAL POSS MONOMERS. Sixun Zheng, Frank J. Feher, Jun Xiao, Ren-Zhi Jin, University of California-Irvine, Department of Chemistry, Irvine, CA.

The ability to create well defined, nanometer-scale structures within common thermoplastics offers great potential for enhancing the performance characteristics of thermoplastics. Numerous methods can be envisioned for producing nanostructured thermoplastics, but one of the simplest and most attractive approaches is reactive melt blending of nanostructured chemicals (e.g., POSS) with common thermoplastics. In this paper, we describe a new method for producing thermoplastic polymer nanocomposites via melt processing of thermoplastics (e.g., bis-phenol A polycarbonate or styrene-co-maleic anhydride) with readily available monofunctional POSS monomers. The salient feature of our method is that the POSS is incorporated as both an inert molecular filler and a substituent which becomes covalently attached to the polymer backbone. The synthesis and characterization of these thermoplastic polymer nanocomposites by nuclear magnetic resonance (NMR) spectroscopy, differential scanning calorimetry (DSC) and scanning electron microscopy (SEM) will be described. Implications of our work for the development of other thermoplastic polymer nanocomposites also will be discussed.

11:15 AM T1.10

LAYERED ORGANIC-INORGANIC NANOCOMPOSITES BY CONTROLLED SELF-ASSEMBLY OF POLYHEDRAL OLIGOMERIC SILSESQUIOXANE NANOPARTICLES. Lei Zheng, Sheng Hong, Amiya R. Tripathy, Samuel P. Gido, Richard J. Farris, E. Bryan Coughlin, Polymer Science and Engineering Department, University of Massachusetts, Amherst, MA.

Nanocomposites have drawn considerable attention due to the initial discovery of nanometer-scale reinforcements in the clay/nylon-6 system. Preparations of nanocomposites of layered silicates and polymeric materials often times encounter the problem of unfavorable interactions between the hydrophilic surface of clays and hydrophobic polymers, which results in incomplete dispersal or limited exfoliation. An exfoliated structure is necessary for significant property reinforcement. A novel approach to obtain nanocomposites containing inorganic nanolayers is reported here. Polyhedral oligomeric silsesquioxane (POSS) nanoparticles are used to achieve the nanolayered structure through controlled self-assembly. POSS are a class of well-defined molecules having an inorganic core comprised of Si₈O₁₂ surrounded by eight tunable substituents, i.e. cycloaliphatic groups. From our previous work, it has been realized that POSS nanoparticles are limited to crystallization in a two-dimensional lattice due to the interconnectivity of the polymer chains with the

POSS nanoparticles. In other words, controlled anisotropic crystallization of nanoparticles can generate a nanolayered structure. A new model of layered inorganic clay-like structure has been designed based on this observation. The target is hybrid copolymers of POSS and organic polymers. The organic polymer in our design is used to regulate the POSS crystallization into a two-dimensional lattice. The POSS nanoparticles can then aggregate and crystallize to form a lamellar structure. The concept is demonstrated by a random copolymer of polybutadiene and POSS. The copolymers were synthesized by ring opening metathesis copolymerization of cyclooctadiene and POSS bearing a polymerizable norbornene group. Interestingly, the nanostructure of the PB-POSS copolymer resembles that of the nacre of abalone shell with alternating inorganic crystalline hard layers and soft organic rubbery layers. This controlled self-assembly process, a so-called bottom-up approach, is noteworthy considering the random nature of the copolymers and broad molecular weight distribution (PDI ~ 2). Detailed information of the synthesis and characterizations of these materials will be presented. Their blending with homopolymers and POSS particles will also be addressed subsequently.

11:30 AM T1.11

HYBRID ORGANIC-INORGANIC POLYIMIDE NANOCOMPOSITES. Chris J. Cornelius, Catalysis and Chemical Technologies, Sandia National Laboratories, Albuquerque, NM.

The structure-property relationships of a series of hybrid organic-inorganic polyimide nanocomposite materials were evaluated for physical property enhancements. Changes in tan delta, glass transition temperature, thermal stability, and permselectivity were attributed to the degree of compatibility between the organic and inorganic domains. Concentration of sulfonic acid groups in the polyimide and the type of silsesquioxane coupling-agent modulated the synergistic properties observed in these materials. The morphology exhibited by these materials was evaluated with TEM, SEM, and AFM, which was attributed to the degree of compatibility and concentration of the organic and inorganic domains. Potential applications for these materials are enhanced membranes for direct methanol and hydrogen fuel cells, ion-exchange membranes, and gas separation membranes. These hybrid organic-inorganic polyimide nanocomposites were synthesized with a fluorinated block polyimide containing various concentrations of sulfonic acid groups, and an organically bridged silsesquioxane coupling-agent.

11:45 AM T1.12

ENHANCEMENT OF SCRATCH RESISTANCE OF NANOPARTICLE FILLED GELATIN. Quan Chen, Linda Schadler, Richard Siegel, Rensselaer Nanotechnology Center, Rensselaer Polytechnic Institute, Troy, NY; Glen Irvin, John Mendel, Eastman Kodak Company, Rochester, NY.

Atomic force microscope and scratch testing were employed to investigate the scratch behavior of nanoalumina-filled deionized gelatin. The results showed that the addition of nano-filler improve the scratch resistance substantially. Further tests on the basic mechanical properties were undertaken and the results exhibited increase on both modulus and tensile strength of the nano-filled gelatin films. Optical transmittance measurements of the polymer composite shown that the nano-filled composite had much higher transmittance than micro-filled composites. Both transmission and scanning electron microscope show excellent dispersion of the nano particles in the gelatin matrix.

SESSION T2: CARBON-BASED POLYMER NANOCOMPOSITES

Chairs: Gary L. Hagnauer and Elena Vasiliu
Tuesday Afternoon, April 2, 2002
Franciscan I (Argent)

1:30 PM *T2.1

PROCESSING AND CHARACTERIZATION OF POLYMER NANOCOMPOSITES WITH CARBON NANOPARTICLES OF VARIOUS MORPHOLOGIES. Michael Sennett, Elizabeth A. Welsh, Jeffery B. Wright, David Ziegler, US Army Soldier and Biological Chemical Command, Natick Soldier Center, Materials Science Team, Natick, MA.

A series of thermoplastic polymer nanocomposites were prepared with a variety of carbon nanoparticle reinforcements, including single and multiwall carbon nanotubes, exfoliated graphite nanoparticles and conventional furnace blacks. The structures were characterized using transmission electron microscopy and the effect of particle morphology on the physical properties of the nanocomposites was examined.

2:00 PM T2.2

POLYMER NANOCOMPOSITES OF MULTI-WALLED CARBON

NANOTUBES. Chyi-Shan Wang, William E. Click, Gary E. Price, University of Dayton Research Institute, Dayton, OH; Max D. Alexander, Air Force Research Laboratory, Wright-Patterson Air Force Base, OH.

Carbon nanotubes, both single- and multi-walled, have excellent mechanical, electronic, and thermal transport properties. Their small diameter and large aspect ratio are highly desirable for introducing exceptional properties to organic polymers for advanced structural, electronic, and electro-optical applications. In this paper, we report on a processing scheme capable of dispersing multi-walled carbon nanotubes into nanophase reinforcement in thermoplastic as well as thermosetting polymers. The resulting polymer nanocomposites exhibit a very low conducting percolation threshold and substantially enhanced tensile mechanical properties and abrasion resistance. The data suggest that the carbon nanotubes are uniformly dispersed in the polymer matrix and maintain a large aspect ratio of length to width.

2:15 PM T2.3

CARBON NANOFIBER REINFORCED THERMOPLASTICS FOR ENHANCED CONDUCTIVITY, STRENGTH, AND TENSILE MODULUS. Gary G. Tibbetts, Ioana C. Finegan, Choongyong Kwag; General Motors R and D Center, Warren, MI.

Carbon nanofibers of diameter 200 nm may be used as an additive to thermoplastics for applications requiring electrical conductivity and enhanced mechanical properties. The electrical properties of nanofiber in thermoplastics such as nylon and polypropylene and are very attractive compared with those provided by other conventional conducting additives. Because of the low diameter of the nanofibers used, the onset of electrical conductivity (percolation threshold) can be below 1 volume %. Because of the highly conductive nature of the fibers, particularly after a graphitization step, the composites can reach resistivities as low as 0.15 Ohm cm. These conducting composites may be used for applications such as radio frequency interference shielding, primerless electrostatic painting, and static discharge. In order to make composites having excellent mechanical properties, good adhesion between fiber and matrix is essential. Carbon nanofiber-matrix adhesion was studied after surface treating the fibers using a variety of methods. Among as-grown fibers, those produced with longer gas phase feedstock residence times in the fiber growth reactor were less graphitic but adhered to a polypropylene matrix better, giving improved tensile strength and modulus. Two chemical treatments were found to be somewhat effective in increasing tensile strength, but both decreased the modulus. A modest degree of oxidation was also found to increase adhesion to the matrix and increase composite tensile strength, while extended oxidation attacked the fibers sufficiently to decrease composite properties.

3:00 PM T2.4

MORPHOLOGICAL COUPLING DURING DEFORMATION OF CARBON NANOTUBE - POLYURETHANE NANOCOMPOSITES. Richard A. Vaia, Heather Bentley, Max Alexander, Air Force Research Laboratory, Wright-Patterson Air Force Base; William Click, Gary Price, Weidong Liu, Chyi-Shan Wang, University of Dayton Research Institute, Dayton, OH.

Numerous examples are now available demonstrating the potential to provide enhanced properties to various polymers through the addition to the resin of a low-volume fraction of nanoparticles, including layered silicates, nanotubes and inorganic nanoparticles. However, detailed processing - morphology - property relationships are only beginning to be developed because of the ultra-large interfacial area and extremely process-sensitive complex hierarchical morphology of these systems. To begin to develop these relationships, this effort examines the coupling between mechanical deformation, nanoparticle response and concomitant stress-induced polymer crystallization for conducting elastomeric nanocomposites (carbon-nanotube - polyurethane). In-situ x-ray scattering (simultaneous small and wide angle) during deformation indicates that polymer deformation, stress-induced crystallization and nanotube re-orientation occurs at different rates. These observations provide insight into the strain-dependent mechanical and electrical properties of these nanocomposites.

3:15 PM T2.5

CLUSTER ARRANGEMENT ON THE SURFACE OF GOLD CONTAINING AMORPHOUS HYDROGENATED CARBON (α -C:H/Au) NANOCOMPOSITES. Ivan R. Videnović, Verena Thommen, Daniel Mathys, Richard Guggenheim, Peter Oelhafen, Institut für Physik & REM Labor, Universität Basel, Basel, SWITZERLAND; David Babonneau, André Naudon, Laboratoire de Métallurgie Physique, Université de Poitiers, Poitiers, FRANCE.

Amorphous hydrogenated carbon (α -C:H) with embedded metallic clusters has attracted significant attention in the past years due to its wide technological applications ranging from decorative, solar

selective, to biocompatible coatings. Within this type of nanocomposites, the special importance belongs to the gold containing amorphous hydrogenated carbon (α -C:H/Au), due to the apparent lack of reactivity between gold and carbon. That further leads to the absence of chemical shifts of the C and Au core levels in the X-ray photoelectron spectra (XPS), which results in one's ability to use XPS as a tool to investigate size and arrangement of metallic clusters inside the α -C:H matrix.

We report here on the results of the study of the α -C:H/Au samples obtained by simultaneous plasma enhanced chemical vapor deposition of methane and reactive magnetron sputtering of Au target. We have investigated the arrangement of the gold nanoclusters in the surface region of low gold-content α -C:H/Au (that is, <10 at. % Au). The techniques employed embrace in-depth and angle-resolved *in situ* UV and X-ray photoelectron spectroscopy, atomic force and scanning electron microscopy, and grazing incidence small angle x-ray scattering. The results show that by deposition on electrically grounded substrates one obtains rather flat samples (standard roughness below 1 nm) with topmost Au clusters covered with very thin layer of α -C:H, of thickness in nanometer or even subnanometer range. On the other hand, introducing a dc substrate bias voltage results in significant surface roughness increase by formation larger bump structures (up to 13 nm in height). The total amount of gold in the film decreases, while the carbon component appears to be partially graphitized. The results suggest that in this case at the sample surface the smaller and bald Au clusters are sitting on top of these larger structures.

3:30 PM T2.6

PRESSURE TUNING OF TRANSPORT PROPERTIES FOR C-NANOTUBES. F. Chen, K.L. Stokes, Weilie Zhou, Advanced Material Research Institute, University of New Orleans, New Orleans, LA; H. Wang, Polymers Division, NIST, Gaithersburg, MD.

Different weight percent of single- and multi-wall carbon nanotubes were mixed with polyethyleneoxide and polystyrene. Temperature dependence of thermopower (S) and resistivity (ρ) for these samples was measured under hydrostatic pressure upto 1.2 GPa. The pressure changes the transport properties both intrinsically and by changing the inter-tube coupling. The experimental results will be presented and the interplay between these two effects will be discussed. The tuning of the thermoelectrical properties and potential applications of carbon nanotubes will also be discussed.

3:45 PM T2.7

FLAME AEROSOL SYNTHESIS OF SINGLE-WALLED CARBON NANOTUBES AND NANOFIBERS. Randy L. Vander Wal, Gordon M. Berger, Lee J. Hall, NCMR c/o NASA-Glenn Research Center, Cleveland, OH.

Flame synthesis of SWNTs is demonstrated using Fe nanoparticles (introduced by nebulization of an iron (III) nitrate salt solution) within a pyrolysis flame configuration. The roles of the nebulized solution solvent, solution concentration, pyrolysis flame gas composition, and the surrounding flame gases composition are interpreted as reflecting suitable concentrations of reactants without excessive pyrolysis products or deactivating species. The preferential reactivity of the catalyst particle towards CO and not towards C_2H_2 is understood as reflecting nanoparticle restructuring, interactions between coadsorbates and reactant pyrolysis products. Fe is found to exhibit preferential reactivity towards CO for SWNT catalysis with this reactivity being strongly dependent upon catalyst particle size within our flame conditions. H_2 appears to moderate the dissociative adsorption through electronic interactions with coadsorbates, mediated by the catalyst nanoparticle and by maintaining a catalytically clean particle surface. In complimentary experiments, using a similar pyrolysis flame configuration, flame synthesis of Ni catalyzed nanofibers is demonstrated. Ni nanoparticles, formed by thermal decomposition of a nebulized Ni nitrate solution are entrained into a reactive fuel mixture. Though particles sufficiently small to catalyze single-wall nanotubes (SWNTs) are produced, only nanofibers are produced. Using different reactive gas mixtures consisting of CO or C_2H_2 or their combination, Ni nanoparticles exhibited a high preferential reactivity towards C_2H_2 to form nanofibers. These results are interpreted as a result of CO enhancing the dissociative adsorption of C_2H_2 through electronic charge donation mediated by the Ni nanoparticle and physically protecting active sites against blockage by aromatic molecules.

T3.1
THE CORE-SHELL APPROACH TO FORMATION OF ORDERED NANOPOROUS MATERIALS WITH MPEG-b-PDLLA BLOCK COPOLYMERS. Jeong Ho Chang, Yongsoo Shin, Li-Qiong Wang, Gregory J. Exarhos, Pacific Northwest National Laboratory, Richland, WA.

Work presented here describes an innovative approach for the preparation of ordered nanoporous ceramic materials that involves a self-assembly process at the molecular level based upon MPEG-b-PDLLA block copolymer templates. This approach provides for rapid self-assembly and structural reorganization at room temperature. Selected MPEG-b-PDLLA block copolymers have been synthesized with systematic variation of the chain lengths of the resident hydrophilic and hydrophobic blocks. The size and shape of the micelles that spontaneously form in solution are then controlled by the characteristics of the copolymer template. Formation of nanoporous silica at room temperature with short-preparation time is demonstrated and silica-containing materials evolve with uniform pore shape and wall structure. The formation mechanism of these nanoporous structures obtained by controlling the micelle size has been confirmed using both liquid and solid state ^{13}C and ^{29}Si NMR techniques. This work both proposes and verifies the formation mechanism of nanoporous structures in which the pore size and wall thickness are closely dependent on the size of hydrophobic cores and hydrophilic shells of the block copolymer templates. In this process, the silica precursor becomes bound to hydrophilic regions of the ordered copolymer after hydrolysis at the aqueous solution interface. The core-shell mechanism for nanoporous structure evolution is based upon the size and contrasting micellar packing arrangements that are dictated by the copolymer.

T3.2
ORGANIC/INORGANIC NANOCOMPOSITES WITH COMPLETELY DEFINED INTERFACIAL INTERACTIONS FROM CUBIC SILSESQUOXANES. R.M. Laine, R. Tamaki, J. Choi, C. Brick, S-G. Kim, N. Takamura, K. Park, Departments of Materials Science and Eng., Chemistry and the Macromolecular Science and Eng. Center, University of Michigan, Ann Arbor, MI.

Our goal is to develop structure-property relationships in nanocomposites prepared using octafunctional silsesquioxanes [(RSiO) $_{1.5}$] $_8$, cubes] to establish a complete understanding of the behavior materials that are expected to offer physical properties nonlinearly related to the properties of the component phases. In the studies presented here we have developed cubes with organic functional groups (R = epoxy, methacryloyl, etc) appended to inorganic cubes and polymerized them to give organic/inorganic nanocomposites wherein both components are present at the 1~2 nm scale and discontinuous. Their properties are found to be governed by the nanoarchitecture of the organic tethers as will be discussed here.

References:

1. R.M. Laine, J. Choi, I. Lee, 'Organic-Inorganic Nanocomposites with Completely Defined Interfacial Interactions,' Adv. Mater. 13, 800-3 (2001).
2. J. Choi, J. Harcup, A.F. Yee, Q. Zhu, R.M. Laine, 'Organic/inorganic hybrid composites from cubic silsesquioxanes,' J. Am. Chem. Soc. ASAP Article 10.1021/ja0107201S0002-7863 (01)00720-X.

T3.3
STRUCTURAL CHANGE OF NITRILE RUBBER (NBR)-BASED NANOCOMPOSITES WITH VARIOUS ORGANOCCLAY LOADING AS CHARACTERIZED BY VISCOELASTIC RELAXATION AND MOTION. Seung-Yeop Kwak, Seok Jong Han, Seoul National University, School of Materials Science and Engineering, Seoul, KOREA.

Characterization of viscoelastic nature of polymer-layered silicate nanocomposites is crucial to gain a fundamental understanding of the processability and structure-property relations to deliver them to new value in polymer academia as well as industry. The objective of our study is to characterize the viscoelastic properties and to evaluate the structural change of polymer-layered silicate nanocomposites by means of analyzing the dynamic viscoelastic relaxation and determining the subsequent collective motion. In this study, acrylonitrile-butadiene copolymer or nitrile rubber (NBR)/organoclay (OC) nanocomposites with different type of intercalants, i.e., nonpolar (OC20A and OC25A) and polar (OC30B) as a function of different silicate loadings (1, 3, 5, 7, and 10 wt%), were prepared by melt intercalation process with additional static heat imposition for 100 min after mixing. From dynamic mechanical measurement with shear

oscillatory mode ($\omega = 10^{-1}$ - 10^2 rad/s) and application of time-temperature superposition principle, master curves on the linear viscoelastic data of storage $G'(\omega)$ and loss modulus $G''(\omega)$ were constructed. At low $a_T\omega$ (corresponding to a regime where the pure NBR exhibits liquid-like behavior), both G' and G'' for the nanocomposites exhibited a diminished frequency dependence, which became more dominant as the silicate loading increased. This trend indicated that the material behavior shifted toward the solid-like with increase of silicate loading. The frequency shift factors, a_T , experimentally obtained from the construction of the master curves, were fit by WLF equation. Then, the activation energy, E_a , was obtained at the corresponding temperatures. With further treatment of viscoelastic data by the empirical Havriliak-Negami (HN) fitting function, the single average relaxation time, τ_{HN} , were determined. The E_a and τ_{HN} were shown to provide a unique means to evaluate the structural change on the basis of the molecular mobility. For the hybrids with silicate loading in excess of 7 wt%, E_a and τ_{HN} increased remarkably compared to those of the hybrids below 7 wt% silicate loading. These results indicated that the hybrids with silicate loading in excess of 7 wt% form the percolation of three-dimensional filler network structure. It is concluded that the combined analyses of the activation energy, E_a , and the average relaxation time, τ_{HN} , can provide another method to evaluate the structural change in the nanocomposites of various silicate loading.

T3.4
MECHANICAL CHARACTERIZATION OF POLYCARBONATE BASED NANOCOMPOSITES. D.A. Crowson, S.G. Corcoran, Virginia Tech, Materials Science and Engineering Dept, Blacksburg, VA; Alex J. Hsieh, Army Research Laboratory, Aberdeen Proving Ground, MD.

The mechanical behavior of clay loaded polycarbonate nanocomposites that exhibit a ductile-to-brittle transition, with respect to amount of clay added, has been investigated. The dynamic impact behavior is of particular importance. Quasi-static and dynamic nanoindentation tests have been used to characterize the rate sensitivity of the hardness and elastic modulus of clay loaded polycarbonate nanocomposites. A correlation between these measurements and the dynamic impact behavior will be shown.

T3.5
NANOCOMPOSITE FILMS DERIVED FROM ALKOXYSILANE TERMINATED AMIDE ACID OLIGOMERS AND CARBON NANOTUBES. Joseph G. Smith Jr. and John W. Connell, National Aeronautics and Space Administration, Langley Research Center, Hampton, VA; Kent A. Watson, ICASE, Langley Research Center, Hampton, VA; Craig M. Thompson, NRC, Langley Research Center, Hampton, VA.

Low color polymeric materials with sufficient inherent conductivity for electrical charge dissipation (ESD) are of interest for potential applications on space vehicles. One method of imparting electrical conductivity while maintaining optical clarity is through the use of single wall carbon nanotubes (SWNTs). Both theory and research on SWNTs have shown these materials to be conductive. However, SWNTs are difficult to disperse in a polymer matrix with much work concentrating on overcoming this problem. One potential solution is to chemically react SWNTs with the polymer to aid in the dispersion process. Thus as part of a materials development effort focused on imparting sufficient electrical conductivity to low color polymers for ESD for potential space applications, SWNTs were combined with controlled molecular weight amide acid oligomers terminated with alkoxyisilane groups. The terminal alkoxyisilane groups can presumably react with functionalities located on the ends of oxidized SWNTs such as carboxylic acid or hydroxy groups to aid in the dispersion of the SWNTs in the cured polymer. These materials were prepared by dispersing a sonicated solution of the SWNTs into a solution of a controlled molecular weight amide acid oligomer terminated with alkoxyisilane groups. Thin films were cast from the hybrid amide acid solutions and cured to 300°C in flowing air. The chemistry, physical, and mechanical properties of these materials will be presented.

T3.6
TEM OBSERVATION OF SURFACE GRAPHITIZATION AND INTERIOR MICROSTRUCTURE CHANGE ON FURAN-RESIN-DERIVED CARBON. Junji Yamanaka, McMaster Univ, Dept of Materials Science and Engineering, Hamilton, ON, CANADA; Eiichi Yasuda, Tokyo Institute of Technology, Center for Materials Design, Materials and Structures Laboratory, Yokohama, JAPAN; George C. Weatherly, McMaster University, Dept of Materials Science and Engineering, Hamilton, ON, CANADA; Yasuhiro Tanabe, Tokyo Institute of Technology Center for Materials Design, Materials and Structures Laboratory, Yokohama, JAPAN.

Furan-resin-derived carbon structures have attracted interest as a component in carbon based composite materials. We investigated the

microstructures of furan- resin-derived carbon after high-temperature heat treatments by transmission electron microscopy. We observed that graphitization occurred at the surface even although furan-resin-derived carbon is a non-graphitizable carbon. On the other hand the interior of the specimens exhibited a cage-like structure. The specimens heat-treated at higher temperatures exhibited a well-developed cage structure, as evidenced by the number of stacked layers and the periodicity. The raw material used in this study was fulfuryl-alcohol condensate, Hitafuran 302, commercially available from Hitachi Chemical Co., Ltd. After curing and post-curing process, the resin (furan-resin) films were carbonized. The specimens were carbonized at 1273 K for 1800 s under Ar flow. Then, the specimens were subjected to high-temperature heat treatments at a temperature from 1773K to 3273K for 1800s under Ar. For cross-sectional observation of the surface, we buried the specimens in an epoxy resin and sectioned the specimens into thin films using an ultra-microtome. To observe the interior of specimens, we crushed specimens using mortar. The surface graphite layer was approximately 20 or 30 nm in thickness in the specimen heat-treated at 3273 K for 1800 s. Atomic stacking in the layer was parallel to the specimen surface. The interior of the specimen was not graphitic but a cage structure. The interior of the specimen heat-treated at 1773K or lower temperatures exhibited an amorphous structure while the specimens heat-treated at higher temperatures exhibited a cage structure. In the case of the 3273K treatment, about 10 graphene layers formed the cage structure and the cage periodicity was approximately 6nm.

T3.7

ELECTROPHYSICAL PROPERTIES OF COMPOSITES BASED ON POLYACETYLENE AND SINGLE-WALLED NANOTUBES. Oleg Efimov, Elena Krinichnaya, Galina Kozub, Institute of Problems of Chemical Physics, Chernogolovka, RUSSIA; Igor Chmutin, Anatolii Ponomarenko, Institute of Synthetic Polymeric Materials, Moscow, RUSSIA; Aleksandr Gusev, Russian Federal Nuclear Centre, Sarov, RUSSIA.

The present work was aimed at the synthesis of composite materials based on polyacetylene and conductive filler, namely, SWNT and the study of their electrophysical properties in the 20-150°C range. SWNTs used in the present study were prepared by the arc-discharge technique using a Co/Ni mixed catalyst (70 w/w. % tube content after purification). The tubes have diameters ranging from 1.2 up to 1.8 nm. Calculated density is equal 0.94 g/cm³. It was found that percolation threshold of polyacetylene- nanotubes composites is about 3 v/v. % and the composites with filler concentration higher than 6 v/v. % have conductivity of 10⁻¹ - 100 · 10³ S/cm. For composites comprising 12 v/v % of nanotubes, conductivity is almost constant in the 20 - 110 °C temperature range. The value of $\sigma(T)/\sigma(200C)$ grows up to 1.35 during heating from 110 up to 150°C and then increases up to 1.5 during cooling down to room temperature.

T3.8

STRUCTURE AND PROPERTY RELATIONSHIP OF POLYMER-CARBON NANOTUBE COMPOSITES. Heather Bentley, Max D. Alexander, Jennifer Stuckey, Air Force Research Laboratory, Wright-Patterson Air Force Base, OH; Chyi-Shan Wang, William E. Click, University of Dayton Research Institute, Dayton, OH.

A class of vapor-grown multi-walled carbon nanotubes is investigated for forming a nanocomposite material with organic polymers. The polymer nanocomposites are achieved by dispersing the carbon nanotubes into a thermoplastic or thermosetting polymer using a solution method. Tensile mechanical properties, electrical conductivity, and thermal transport property of the resulting polymer nanocomposites are characterized as a function of carbon nanotubes concentration. Their morphological properties are determined by techniques such as high resolution scanning electron microscopy to understand their structure and property relationship.

T3.9

LOW PERCOLATION THRESHOLD IN ELECTRICALLY CONDUCTING METAL POWDER-PMMA-MATRIX COMPOSITES POLYMERIZED WITH GAMMA RADIATION. Victor H. Poblete, CChEN, Santiago, CHILE; Mariela Alvarez, Mauricio E. Pilleux, Universidad de Chile, IDIEM, Santiago, CHILE.

Filled polymer composites prepared with low concentrations of a metallic powder filler are of technological interest if metallic conductivity is achieved in the composite with low metal concentrations (<10 vol.%). If a low metal incorporation is achieved, the otherwise insulating organic matrix can maintain its mechanical properties while exhibiting a high conductivity, thus allowing its use in technological applications where a high conductivity polymer is required (e.g., conductive adhesives, electromagnetic shielding, etc.). In this work, polymethyl methacrylate (PMMA) composites were prepared and characterized using 4-30 vol.% of Cu powders (3.25-4.5 μm) or Ag powders (10 μm) strongly mixed with the monomer prior

to polymerization. The polymerization process of the PMMA matrix was induced by means of an appropriate dose of gamma radiation. The optimum dose for complete polymerization was 19 kGy for an 8 h exposure time. The electrical resistivity was analyzed as a function of the metal concentration and of the temperature, and typical values for a 10 vol.% composite at room temperature were 0.41 Ω·m for Cu and 30 Ω·m for Ag. The resistivity exhibited a linear increase between 4 and 30 vol.%. The Cu-metal concentration required to exhibit a conductivity in the order of 1 Ω·m is much lower than the values reported in the literature (≈30 vol.%) for equivalent Cu-polymer systems. Further studies are being performed to evaluate the mechanical properties of the composites and the use of nanosized fillers.

The authors wish to acknowledge the support provided by Fundación Andes.

T3.10

A COARSE-GRAINED MOLECULAR DYNAMICS SIMULATION OF NANOSCALE RIGID RODS IN A POLYMER MELT. Anuchai Sinsawat, University of Virginia, Dept of Materials Science and Engineering, Charlottesville, VA; R.A. Vaia and B.L. Farmer, Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson AFB, OH.

Nanometer-sized rods have demonstrated great potential for use in nanocomposite structures. This type of material exhibits unique mechanical and electrical properties due to dimensional and interfacial effects. Similar to conventional composites, their mechanical properties can be significantly influenced by the degree of orientation and mixing of the components. As a result, the alignment and dispersion of such rods in nanocomposites is a subject of considerable interest. By using computational simulations, the influence of the rigidity of the rods, the spacing between rods, and different variety of polymer-rod interaction parameters have been investigated. The model system consisted of arrays of needle-like rigid rods immersed in a sea of polymer chain. Both polymers and rigid rods are represented by a bead-spring model where chains of spheres are connected by the anharmonic FENE potential. From the calculations, it was observed that polymer chains located within the vicinity of the rods tend to be more extended compared to those in the bulk. The preliminary results suggest that the rigidity of the rods plays an important role in the degree of alignment of the rods in the polymer melt. The mixing of rods and polymers occurs at an early stage of the dynamics, but complete dispersion of the rods in the polymer melt requires long simulation times.

T3.11

PREPARATION AND CHARACTERIZATION OF COMPOSITE POLYMER. G.M. Mastoi, M.A. Kazi Institute of Chemistry, University of Sindh, Jamshoro, Sindh, PAKISTAN.

A schiff base polymers have been prepared and their composite materials have been synthesized. The DTA and TGA study indicate that they are highly heat resistant polymers. The composite materials were also tested for joinings. Various physical and chemical properties are also discussed in detail.

T3.12

ASSESSING EXFOLIATION IN ORGANOCCLAY-POLYMER NANOCOMPOSITES. Michael P. Balogh, Deborah F. Eckel, Chemical and Environmental Science Laboratory, General Motors Research and Development Center, Warren, MI; Paula D. Fasulo, William R. Rodgers, Materials and Processes Laboratory, General Motors Research and Development Center, Warren, MI.

Organoclay-polymer nanocomposites offer improved material properties at very low filler loadings. This improvement in properties requires the organoclay to be at least well dispersed if not exfoliated. Conventionally, the dispersion and exfoliation of the organoclay in the polymer matrix is evaluated using transmission electron microscopy (TEM) and x-ray diffraction (XRD). This presentation will examine the use of TEM and XRD for evaluating and quantifying the dispersion and exfoliation of the organoclay filler in polymeric nanocomposite materials. Data from organoclay-reinforced nylon, polyolefins and thermoplastic urethane will be presented.

SESSION T4: POLYMER-LAYERED SILICATE NANOCOMPOSITES

Chairs: Richard A. Vaia and Anna C. Balazs
Wednesday Morning, April 3, 2002
Franciscan I (Argent)

8:00 AM *T4.1

WHAT IS THE VALUE OF NANO IN NANOCOMPOSITES?

After the pioneering and promising work of the co-workers of Toyota (1) on nylon-6 clay hybrids, nanocomposites have attracted great interest in the academia as well as in industry. The hybrid structure of inorganic layered silicates well dispersed in standard polymers, possess a unique combination of properties. In nature an abundant amount of minerals can be found that fulfill the requirements of stiff layered platelets with a thickness of about one and a diameter of a few hundred nm. Montmorillonite is probable the best choice due to the ability to swell in water and to replace sodium ions by organic compounds. Due to the consequential increase of the hydrophobic behaviour, intercalation of polymers between the clay layers and exfoliation of the clay in polymeric matrices becomes much easier. A substantial improvement of the product properties was noted, in stiffness, strength, barrier properties, etc.. Although each of these improvements is without doubt of great value for practical applications, they are simply not enough to create a breakthrough due to the lack of competitive advantage. There are many more simple and cheaper minerals or fibers that can offer similar properties. Thus, the question arises, are nanocomposites a hype or a breakthrough? The challenge is to focus our investigations on the unique properties of nanocomposites that are unattainable with other fillers. Therefore it was important for us to compare the properties of nanocomposites with microcomposites. In those cases where the advantage is minor it makes no sense to push these materials forward. Part of the lecture will be dedicated to show the similarities of nano and micro materials. However, in certain special areas the advantage is evident and we must focus our efforts on these areas more specific in the future. (1) A. Okada et al., *Polym. Prepr.* 28, 447 (1987).

8:30 AM *T4.2
MINIMIZING THE ORGANIC MODIFIER IN THE PREPARATION OF POLYMER-CLAY NANOCOMPOSITES. Thomas J. Pinnavaia, Peter LeBaron, Costas S. Triantafyllidis, Michigan State University, Department of Chemistry, East Lansing, MI.

Epoxy nanocomposites containing 6 wt. % of exfoliated silicate nanoparticles have been prepared from EPON 826 resin and the Jeffamine diamine D-230 in the presence of mixed-ion exchanged forms of the naturally occurring montmorillonite clay and the synthetic clay fluorohectorite. The replacement of only 35% of the inorganic exchange cations by onium ions on the basal surface of the clay was sufficient to form a lipophilic mixed ion homostructure. The nanolayers of the resulting homostructure could be readily exfoliated into the polymer matrix. The preferred onium ion modifier was the diprotonated form of Jeffamine D-2000. Substantial improvements in the storage modulus were realized without sacrificing the glass transition temperature or thermal stability of the glassy polymer. Thus, substantial cost savings are possible for the preparation of clay nanolayer reinforced epoxy polymers without compromising performance. Similar savings in organic modifier can be anticipated in the design of other polymer - clay nanocomposites through the use of mixed ion clay homostructures.

9:00 AM *T4.3
EXPLORING THE MORPHOLOGICAL BEHAVIOR IN A MODEL POLYMER-LAYERED SILICATE NANOCOMPOSITE SYSTEM. Frederick Beyer, Army Research Laboratory, Polymers Research Branch, Aberdeen Proving Grounds, MD; Mary Kurian, Arnab Dasgupta, Mary E. Galvin, Department of Materials Science & Engineering, University of Delaware, Newark, DE.

Despite the great quantity of experimental work being undertaken on the physical properties and formation of polymer-layered silicate nanocomposites, little work has been directed toward understanding the underlying thermodynamic relationships between the components in these materials. Specifically, little is known about the manner in which the interactions between the polymer matrix, organic surfactant modifier, and layered silicate clay mineral affect morphological and physical behavior. However, recent years have seen a growth in the effort given to understanding on a theoretical basis the morphological behavior of these systems. In this on-going work, the predictions of the Balazs mean-field model for these systems are systematically probed. A series of model surfactants based on polystyrene have been synthesized, and exchanged with the naturally occurring interlayer cations in montmorillonite. The modified clay is then hand mixed with polystyrene homopolymer, formed into a pellet with contact pressure, and then annealed at both 125°C and 165°C for varying lengths of time. Previously, we have shown that at high levels of exchange (approaching 100%), surfactant length and homopolymer length have no effect on the morphological behavior of the system, which forms phase separated morphologies in all cases. Here, these data as well as data exploring the effects of annealing temperature, surfactant coverage, and mixtures of surfactants on the morphological behavior of this model system will be presented.

9:30 AM *T4.4
MECHANICAL BEHAVIOR OF INTERCALATED POLYMER LAYERED-SILICATE NANOCOMPOSITES. Alex J. Hsieh, U.S. Army Research Laboratory, Weapons and Materials Research Directorate, APG, MD.

The effect of layered-silicates on the mechanical response encountered in a host polymer matrix under various loading conditions is being investigated. Polycarbonate (PC) nanocomposites consisting of organo-modified montmorillonite clay were melt-processed. Good particle dispersion and adequate interphase bonding are noted in these intercalated nanocomposites. Incorporation of nanoclay increases the modulus of PC but significantly affects its ductility. For example, PC nanocomposites containing 5 wt.% clay reveal a brittle mode of failure upon tensile loading, while those with 2.5 wt.% or less of nanoclay display a slight decrease in the elongation of break or ductility. The latter nanocomposites also exhibit stress whitening, which is consistent regardless of the loading conditions. Stress whitening is attributed to the light scattering of crazes or microvoids formed as a result of an increase in the yield strength of PC, which may suppress PC from shear yielding in these nanocomposites. Material parameters critical to the high strain-rate impact behavior are being investigated, and their dependence upon the clay loading is also being determined. Comparison of the effect of clay loading upon the mechanical response in a brittle matrix, poly(methyl methacrylate), is also included. Based on these experimental findings, a hard/ductile hybrid system is proposed for optimization of impact performance.

10:15 AM *T4.5
POLYMER NANOCOMPOSITES FORMED BY MELT PROCESSING. T.D. Fornes, P.J. Yoon, D.R. Paul, University of Texas at Austin, Dept. of Chemical Engineering and Texas Materials Institute, Austin, TX.

Polymer-layered silicate nanocomposites formed from the organically modified clay mineral montmorillonite offer some greatly improved properties over those of the matrix polymer, owing to the nanoscale reinforcement and constraints of the polymer, provided the one nanometer thick, high aspect ratio aluminosilicate layers can be individually dispersed or exfoliated into the polymer matrix. Formation of such nanocomposites by conventional melt processing and fabrication techniques is likely to be the most economical and versatile approach for wide-scale use of this technology. This presentation provides a progress report on research whose goal is to understand the mechanism of organoclay exfoliation and to characterize the structure and properties of the resulting composites. A variety of approaches are being used to determine how nanocomposite formation and performance are affected by processing parameters, organoclay structure, and the nature of the matrix polymer (rheological properties, interactions with the organoclay, etc). The focus of this presentation will be on nylon 6 as the matrix polymer; however, the ultimate goal is to develop a more general picture for a wider spectrum of thermoplastic matrices. For a fixed set of near-optimum processing parameters, the effects of nylon 6 melt viscosity and organoclay structure on nanocomposite structure (from TEM and X-ray scattering) and mechanical properties will be described. The measured mechanical properties will be compared with those predicted by conventional composite theory.

10:45 AM T4.6
CARBON FIBER-REINFORCED COMPOSITES WITH EPOXY NANOCOMPOSITES AS MATRICES. Chenggang Chen, Brian P. Rice, Khali Lafdi, University of Dayton Research Institute, Dayton, OH; David Curliss, Air Force Research Laboratory, Materials and Manufacturing Directorate, WPAFB, OH.

Polymer nanocomposites have great potential to enhance the performance of polymers used for composite matrices. In this research, a low-cost nanocomposite composed of organoclay (I30E), Epon 862 and curing agent W was successfully introduced into the carbon fiber IM7 to make a composite. The SEM EDAX data of the cross section of carbon fiber composite showed that there was no filtration effect of the IM7 fiber to the nanoclays. C-scan and optical microscopy indicated that the composite panel was in good quality. Small-angle x-ray scattering and transmission electron microscopy were used to characterize the morphology of the composite. The thermal expansion coefficient of the composite for the nanocomposite as the matrix was measured to be lower than that for neat epoxy resin as matrix. The mechanical properties were also measured as well.

11:00 AM T4.7
ELASTOMERIC NANOCOMPOSITE BARRIER COATINGS. H.A. Goldberg, C.A. Feeney, D.P. Karim, M. Farrell, InMat LLC.

InMat LLC has developed an aqueous, non-hazardous, layered silicate - clay nanocomposite coating with a unique combination of barrier

properties and flexibility. Using butyl rubber as the matrix, and very high aspect ratio vermiculite filler, flexible coatings with gas permeability 30-300 times lower than butyl rubber have been produced. These coatings have been shown to be undamaged by strains up to 20%. There are several technical requirements for producing a coating that has both low permeability and good flexibility that will be discussed. In order to assure that the nano-dispersed silicate clay does not agglomerate, one must control both the solid content and electrolyte balance. The nano-dispersed clay in InMat formulations is locally ordered. This mesoscopic structure of the formulation is important to the formation of good coatings with good barrier properties. Finally, control over the interactions between the nano-dispersed silicate and the butyl rubber is critical in producing a coating that remains flexible under all environmental conditions. This technology enables one to get the barrier properties equivalent to 1-2 mm of butyl rubber with coatings that are 10-30 microns thick, and applications resulting from this will be discussed. The first commercial application of this technology (sold under InMat's trademark Air D-Fense) is in Wilson's new Double Core tennis ball. This ball will hold its air pressure at least twice as long as any other pressurized tennis ball. This technology will lead to significant improvements in a variety of tires. InMat's technology can also lead to thinner, more effective protection against chemical warfare agents.

11:15 AM T4.8

PHYSICAL PROPERTIES OF OPTICALLY TRANSPARENT FILMS OF POLYMER-LAYERED SILICATE NANOCOMPOSITES. Elena Vasiliu, Department of Chemical and Materials Engineering, University of Dayton, Dayton, OH; Chyi-Shan Wang, Department of Chemical and Materials Engineering, University of Dayton and University of Dayton Research Institute, Dayton, OH; Richard A. Vaia, Air Force Research Laboratory, Wright-Patterson Air Force Base, OH.

Polymeric materials with optical clarity and significantly improved thermal and mechanical properties have great potential for advanced applications in optics and windows. In this paper, we report on physical properties of optically transparent polymer-layered silicate nanocomposites based on poly(methylmethacrylate) and polycarbonate. These polymer nanocomposites are prepared through a solution method. Their optical transparency arises from a high degree of exfoliation of the organically modified montmorillonite, which has a surface dimension, about 200nm, smaller than the wavelength of visible light. The thermal properties of the polymer nanocomposites obtained by differential scanning calorimetry and thermogravimetric analysis as well as their morphological data obtained by small-angle x-ray scattering and transmission electron microscopy will be discussed in relation to the dispersion method and the rate of solvent removal.

11:30 AM T4.9

CRYSTALLISATION BEHAVIOUR OF POLYCAPROLACTONE/MONTMORILLONITE AND POLYETHYLENE-OXIDE/MONTMORILLONITE NANOCOMPOSITES. D.S. Homminga, N. Moussaif and G. Groeninckx, Catholic University of Leuven, Dept of Chemistry, Leuven, BELGIUM.

Polymer layered mineral nanocomposites are considered as a new class of advanced organic-inorganic materials. So far, most articles have focused on preparation (in-situ polymerisation/melt intercalation), morphological characterisation (WAXD/TEM) and mechanical and physical properties (tensile testing, flame retardancy and barrier properties). The influence on the crystallisation behaviour of the polymer in the nanocomposites has not been investigated thoroughly yet. An influence of silicate layers on crystallisation behaviour is expected for several reasons. Several groups describe the introduction of confinement effects on the polymer chains in nanocomposites. Also, the existence of a highly mobile phase close to the silicate layer surface is also under discussion. Finally, clay is known for its nucleating effect. Although the silicate layers are much smaller than conventional clay fillers, a nucleation effect could still take place. The larger surface area of the silicate layers compared to the conventional fillers could be beneficial. In this research the crystallisation behaviour of PCL/MMT and PEO/MMT nanocomposites has been studied with DSC (dynamic and isothermal), optical microscopy and SALLS. Of each polymer a series of 1,2,4 and 10 wt% clay nanocomposites has been prepared. TEM pictures show dispersed individual silicate layers, with an increasing amount of stacks at higher clay content. Of each polymer a microcomposite with 4 wt% unmodified clay has been made to compare with the nanocomposite. With both polymers a shift in onset and time of the crystallisation process is observed. The crystallisation kinetics is increased with increasing silicate content. At high silicate content, the crystallisation kinetics of the PCL nanocomposite is much higher than the PCL microcomposite. For PEO this is exactly the opposite.

11:45 AM T4.10

CHEMICAL AND PROCESSING ROUTES FOR POLY-PROPYLENE/LAYERED SILICATES NANOCOMPOSITES. Sylvain Boucard, Jannick Duchet, Patrick Prele, Daniel Rumeau, Jean-Francois Gerard, LMM/IMP, Villeurbanne, FRANCE.

Isotactic polypropylene / layered silicates are of a great interest both for automotive applications for which improved HDT is required and packaging industry as polypropylene is a poor oxygen barrier. The objectives of this work are to develop different routes for processing iPP/montmorillonite nanocomposites in such a way that exfoliation of the clay nanolayers is reached in the molten polymer. The strategies involved i/ the combination of MMT having different surface treatments, i.e. cationic exchange with various quaternary ammonium, and maleic anhydride grafted PP of various structures and ii/ the design of processing conditions using twin-screw extruder. The morphologies, i.e. the dispersion state intercalation vs. exfoliation of clay, studied by TEM and WAXS are discussed as a function of these parameters in addition to the rheological and mechanical properties.

SESSION T5: POLYMER NANOCOMPOSITES FOR ELECTRONIC AND MAGNETIC APPLICATIONS

Chairs: Frederick L. Beyer and Will Rodgers
Wednesday Afternoon, April 3, 2002
Franciscan I (Argent)

1:30 PM *T5.1

THE CHARACTERIZATION AND APPLICATION OF POLYMER NANOCOMPOSITES IN THE ELECTRONIC PACKAGING MATERIALS. Tsung-Yen Tsai, Sung-Jeng Jong, Union Chemical Lab., Industrial Technology Research Institute, Hsinchu, TAIWAN.

Epoxy/Clay nanocomposites have been prepared by exfoliating the modified clays, which are intercalated with the amine functional group, in an epoxy resin. Exfoliation of the clay within the cross-linked epoxy matrix was verified by using X-ray diffraction and transmission electron microscopy. The Epoxy/Clay nanocomposites are applied to prepare Epoxy copper-clad laminar, relatively higher thermal stability, lower coefficient of thermal expansion, and water absorption were observed when they compared with FR-4 laminar without clay existed.

2:00 PM T5.2

PARTICLE SIZE AND DENSITY CONTROL IN MAGNETIC POLYMER NANOCOMPOSITES. Angel Millan and Fernando Palacio, CSIC-Universidad de Zaragoza, Instituto de Ciencia de Materiales de Aragon, Zaragoza, SPAIN.

Polymers can be excellent matrix materials to control particle size and particle assembly in the production of nanocomposites. Magnetic nanocomposites formed by metal oxide nanoparticles and organic polymers can be produced from a polymer-metal ion complex material by a soft thermal treatment. The materials have been characterized by X-rays diffraction and magnetic measurements. A characterization by transmission electron microscopy is on the way. In this contribution the preparation and properties of iron oxide nanoparticles in polyvinyl pyridine composites is reported. With only slight variations in the preparation procedure it is possible to obtain: 1) different iron oxide phases, e.g., hematite (antiferromagnetic), goethite and akaganite (both canted antiferromagnets), and maghemite (ferrimagnetic); 2) nanocomposites with a different particle size, in a range from 2 nm to 20 nm; 3) nanocomposites with a similar particle size and a different particle density. The method is appropriate for establishing the variation of magnetic properties with the particle size, and the study of dipolar interactions between particles.

2:15 PM T5.3

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

We have investigated the magnetism of nanocomposites consisting of field-structured superparamagnetic nanoparticles in a solid or polymeric matrix. These nanocomposites are of two types: magnetic nanoparticles structured into chains by aligning the dipoles with a uniaxial field ("positive" dipole interactions); and magnetic nanoparticles structured into sheets by applying an audio frequency rotating field ("negative" dipole interactions). Particles in these configurations have dipolar interactions that tend to add, creating extremely large local fields not found in random particle composites. These strong collective interactions cause large enhancements in the magnetic susceptibility along the chains and in the plane of the sheets, and a susceptibility reduction along the orthogonal axes. Below the blocking temperature these composites exhibit ferromagnetism, and both the magnetic remanence and the

susceptibility at the coercive field are strongly anisotropic. The observed magnetism is shown to be in good agreement with Brownian dipole dynamics simulations of these anisotropic composites.

2:30 PM T5.4

AN INVESTIGATION OF THE INFLUENCE OF BLOCK RATIO ON THE MAGNETIC PROPERTIES AND HYPERFINE STRUCTURE OF CoFe_2O_4 SELF-ASSEMBLED NANOPARTICLES WITHIN BLOCK COPOLYMER TEMPLATES. Sufi R. Ahmed, Ramamoorthy Ramesh, Dept of Materials & Nuclear Engineering, University of Maryland, College Park, MD; Peter Kofinas, Dept of Chemical Engineering, University of Maryland, College Park, MD; S.B. Ogale, Dept of Physics, University of Maryland, College Park, MD; Georgia C. Papaefthymiou, Department of Physics, Villanova University, PA.

We have synthesized CoFe_2O_4 doped diblock copolymers with varying block ratio and investigated the effect of metal doping on the hyperfine structure and magnetic properties of the self-assembled nanoparticles. The overall goal of this research is to explore techniques for the development of novel binary magnetic oxide nanoparticles uniformly distributed within a polymer matrix and control their magnetic properties. Diblock copolymers of norbornene (NOR) and norbornene dicarboxylic acid (NORCOOH) were synthesized by ring opening metathesis polymerization (ROMP). The self-assembly of the mixed metal oxide magnetic nanoparticles took place within the spherical microphase separated morphology of the block copolymer which served as the templating medium. The self-assembly of the magnetic oxide within the diblock copolymer matrix was achieved at room temperature by introducing FeCl_3 and CoCl_2 precursors into the second polymer block (NORCOOH) and by subsequent processing of the copolymer by wet chemical methods to substitute the chlorine atoms with oxygen. The formation of CoFe_2O_4 was verified using x-ray diffraction. The polymers synthesized with a block ratio of $[\text{NOR}]:[\text{NORCOOH}] = 400:50, 400:150$ and $400:200$ are superparamagnetic at room temperature and ferromagnetic below 77°K . The superparamagnetic blocking temperature T_B increases with increasing size of the NORCOOH block and becomes equal to 300°K for the polymer synthesized with a block ratio of $[\text{NOR}]:[\text{NORCOOH}] = 400:250$. Mössbauer spectroscopy was used to study the hyperfine structure of the nanoconfined metal oxide and verify the formation of the mixed metal oxide nanoparticles, which exhibit an inverse spinel structure at room temperature. This study provided a better understanding of the nucleation, growth and distribution of metal oxide nanoparticles within block copolymers and indicated ways to control the magnetic properties of polymeric based nanocomposite materials.

3:15 PM T5.5

SYNTHESIS AND CHARACTERIZATION OF GAN-CARBON COMPOSITE NANOTUBES. Wei-Qiang Han, Alex Zettl, Department of Physics, University of California, Berkeley, CA, and Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, CA.

GaN and related alloys InGaN and AlGaN are a prominent topic of current research since their wide direct band gaps encompass a broad range of energies (2.0-6.2 eV). One-dimensional structures such as nanowires and nanotubes have great potential for testing and understanding the roles of dimensionality and size on their physical properties. Here we report for synthesizing large quantities of GaN-carbon composite nanotubes a method using a chemical vapor deposition. The reaction is achieved by a combination of carbon nanotube-confined reaction and chemical vapor deposition. The morphology and microstructure of the composite carbon nanotubes have been studied in detail. Inside the composite nanotubes GaN appears as a rod-like filling with diameters 5-50 nanometers and length of up to 30 micrometer. The outer graphitic shells of the composite carbon nanotubes have 1 to 10 carbon layers. The composite carbon nanotubes can be straight or with saw-like edges. The growth mechanism will also be discussed.

3:30 PM T5.6

SYNTHESIS AND CHARACTERIZATION OF ELECTROSTATIC SELF-ASSEMBLY $\text{CdSe}/\text{POLYMER}$ NANOCOMPOSITE FILMS. Liangmin Zhang, Fajian Zhang, Kristie Cooper, and R.O. Claus, Virginia Polytechnic Institute and State University, Bradley Department of Electrical and Computer Engineering, Blacksburg, VA.

Using a novel electrostatic self-assembly (ESA) method to incorporate CdSe quantum dot into polymer we have successfully synthesized an ultrathin film. This method allows the molecular-level thickness control and layer-by-layer formation of multilayer thin and thick films using alternative anionic and cationic molecular solution dipping. From ellipsometric measurements, we obtained that the thickness of per bilayer is around 3.7 nm. UV-vis absorption spectra versus

number of bilayers have also performed using an Hitachi 2001 spectrometer. The size of CdSe quantum dot has been measured using transmission electron microscopy before CdSe quantum dots are incorporated and confirmed using atomic force microscopy after the formation of the film, respectively. Both measurements indicate that the diameter of CdSe quantum dots is 2-3 nm. X-ray photoelectron spectroscopy indicates that the concentration of CdSe quantum dots in the film is 2.14%.

3:45 PM T5.7

STRUCTURE AND PROPERTIES OF SILVER-DENDRIMER COMPOSITE NANOPARTICLES. M. Francesca Ottaviani, Institute of Chemical Sciences, Univ of Urbino, ITALY; Regina Valluzzi, Tufts Biotechnology Center, Dept of Chemical Technology, Medford, MA; Millicent Firestone, Argonne National Laboratories, Argonne, IL; Lajos Balogh, Center for Biologic Nanotechnology, Univ of Michigan, Ann Arbor, MI.

Preparation of noble metal nanoclusters is very important in the development of optical materials, polymer conductors, catalyst carriers and other applications. Silver-dendrimer nanocomposites, in addition to their interesting optical properties, have a great promise to be used as nanoscopic antimicrobial devices. To achieve optimal performance it is fundamental to control the properties of silver nanocomposite particles through composition, size, structure and polydispersity. In this study internal structural characteristics of silver-dendrimer complexes and nanocomposite particles are reported both in solution and in the solid state. Poly(amidoamine) PAMAM dendrimers of various generations and termini were used as organic templates to form complexes and nanocomposites of silver under controlled conditions. In addition to chemical analysis methods, EPR, SAXS and high resolution energy filtered TEM were also utilized. Copper(II) ions were used as a probe for electron paramagnetic resonance (EPR) technique. In the presence of silver ions the interior of the dendrimer repulsed copper ions, which were then confined to sites not occupied by silver ions. Transformation of Ag(I) into Ag(0) by gamma-irradiation completely modified the Cu(II) interactions with the dendrimer in the direction of favoring the internalization of copper(II) ions in the polymeric network. In nanocomposites, Ag(0) atoms primarily occupy the smaller outer cavities of the dendrimer interior forcing a portion of copper ions into the larger cavities. The initially homogeneously dispersed silver atoms undergo a slow migration then form secondary structures within the polymeric host of the nanocomposites.

4:00 PM T5.8

FABRICATION AND PROPERTIES OF TRANSPARENT CONDUCTING POLYMERIC NANOCOMPOSITE COATINGS. Jiakuan Sun, William W. Gerberich, Lorraine F. Francis, Univ of Minnesota, Dept of Chemical Engineering and Materials Science, Minneapolis, MN.

Transparent conducting coatings have been fabricated by casting an aqueous suspension of nanosized antimony-doped tin oxide (ATO) particles ($\sim 20\text{nm}$) and poly (vinyl acetate-acrylic) copolymer latex particles ($60\sim 600\text{nm}$) onto a substrate and drying at room temperature. During drying polymer particles coalesce to form a dense microstructure with ATO particles segregated to the interstices and boundaries between the latex. Electrical conductivity data show a percolation phenomenon with a threshold at 10vol.% ATO for coatings that are $18\sim 20\ \mu\text{m}$ thick. The critical conductivity exponent obtained by fitting the experimental dc conductivity data with the classical percolation scaling law is 2.88, indicating a tunneling-dominated percolation. Coatings are also transparent. For example, coatings with 20vol.% ATO have a relatively high dc conductivity of $\sim 0.2\ \text{S/cm}$ and a high optical transparency (from 65% to 85% in visible light range). The optical transmission loss appears to be due to the slight absorption of ATO near the blue light wavelength and the light scattering by ATO particles. These coatings also have the advantages of low temperature processing and flexibility.

SESSION T6: FUNDAMENTALS OF POLYMER NANOCOMPOSITES

Chairs: Gary W. Beall and Donald R. Paul
Thursday Morning, April 4, 2002
Franciscan I (Argent)

8:00 AM *T6.1

MICRO/NANOSCALE MODELLING OF MECHANICAL AND BARRIER PROPERTIES OF POLYMER NANOCOMPOSITES. Nuo Sheng, Alberto Gallino, Mary C. Boyce, David M. Parks; Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA.

Polymer nano-clay composites have been observed to exhibit dramatic

enhancements in mechanical and transport properties with relatively low filler loadings (1-4 percent volume fraction). Furthermore, the property enhancements extend to relatively high temperatures and, indeed, act to substantially increase transition temperatures such as the heat distortion temperature over that of the parent homopolymer (an increase of 80C has been observed for clay-filled nylon. These property enhancements have been speculated to be linked to the nanometer lengthscale of the local polymer morphology surrounding the particles acting to percolate throughout the matrix. Here, we explore the connections between the underlying material structure and both mechanical and barrier properties through a series of micro/nanoscale modelling of the nano-clay particle filled polymer. We first explore the potential contribution of composite level effects on the observed macroscopic stiffness and permeability of clay-filled thermoplastics. Prediction of the macroscopic anisotropic modulus and permeability as a function of particle volume fraction, particle aspect ratio and particle dispersion (regular vs random) are presented. The corresponding local nanoscale field quantities (strain and stress fields for the mechanical study; partial pressure and flux fields for the permeability study) are also presented. The impact of local polymer morphology on the behavior is discussed.

8:30 AM T6.2

ANALYSIS OF DEFORMATION MECHANISMS DURING A NANOTUBE PULL-OUT FROM A POLYMER MATRIX. S.J. Frankland and V. M. Harik, ICASE, NASA Langley Research Center, Hampton, VA.

Analysis of the load-transfer mechanisms between a carbon nanotube (NT) and polymer matrix is conducted for a NT pull-out via molecular dynamics (MD) simulations, scaling analysis and rheological modeling. The MD-predicted variations in polymer viscosity and velocity profiles are analyzed to determine the deformation mechanisms of molecular clusters as the NT pull-out progresses. Different stages of NT pull-out are parametrized and then characterized by the parameter-group relations derived by the scaling analysis of the problem and its scaling constants. As a result, a connection between the NT/polymer flow properties and a rheological model is established.

8:45 AM T6.3

LOAD TRANSFER AND WORK HARDENING PROCESS OF CNT-POLYMER COMPOSITE. Chenyu Wei, NASA Ames Research center, CA and Dept of Mechanical Engineering, Stanford University, CA; Deepak Srivastava, NASA Ames Research Center, Moffett Field, CA; Kyeongjae Cho, Dept of Mechanical Engineering, Stanford University, CA.

We use classical MD simulation to study the mechanical properties of carbon nanotube-polyethylene composites, interacting through van der Waals (VDW) potentials. Young's modulus is found to be enhanced by about 30% compared with polymer matrix. The load transfer is found to be within 1% tensile strain in the presence of VDW potentials. High strength of CNT ($Y = 1$ TPa) is found to contribute to the enforcement of stiffness of polymer. Simulations on loading sequences show that Young's moduli of CNT-polymer composites to be increased with mechanical stretching processes due to work hardening process.

9:00 AM *T6.4

FORMING SPATIALLY ORDERED COMPOSITES FROM MIXTURES OF NANOPARTICLES AND BLOCK COPOLYMERS. Russell Thompson, Jae Yoon Lee, Anna C. Balazs, University of Pittsburgh, Chemical Engineering Department, Pittsburgh, PA; David Jasnou, University of Pittsburgh, Physics Department, Pittsburgh, PA.

The interactions between mesophase-forming copolymers and nanoscopic particles can lead to highly organized hybrid materials. The morphology of such composites depends not only on the characteristics of the copolymers, but also on the features of the nanoparticles. To explore this vast parameter space and predict the mesophases of the hybrids, we developed a mean field theory for mixtures of soft, flexible chains and hard spheres. We apply this theory to a blend of AB diblock copolymers and a mixture of spherical nanoparticles. The particle mixtures contain both A and B spheres or spheres that display a dispersity in size. The introduction of particle mixtures leads to novel effects in the distribution of the solids and the overall morphology of the system. We rationalize our findings through a scaling theory in the strong segregation limit. Our results indicate that particle mixtures can be exploited to modify the mesophases of the diblock copolymers and thereby create nanocomposites with new structures.

10:00 AM *T6.5

COARSE-GRAINED SIMULATIONS OF THE FORMATION OF POLYMER NANOCOMPOSITES. B.L. Farmer, R.A. Vaia, Materials

and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson AFB, OH; Anuchai Sinsawat, University of Virginia, Charlottesville, VA.

Nanosopic dispersions of inorganic nanoparticles in a polymer have been shown to enhance many aspects of the material's performance. Critical to advancing nanocomposite technology are understanding and controlling the thermodynamic and kinetic factors which determine the nano- and mesoscale morphology of the constituents (inorganic, polymer, and additives). Coarse grain molecular dynamics simulations have been used to examine the behavior of three general types of systems. The same bead-spring model was used to represent the low molar mass fluids, the polymer chains, and the inorganic phase (either rod-like or layered) nanostructure. The first system examined layered silicates in binary (low molar mass) fluid mixtures, a model relevant to the morphology development and phase behavior for in situ polymerized nanocomposites (e.g. silicates in a two-component epoxy system). It is found that partitioning of the fluid components is governed both by the relative strengths and individual magnitudes of the interactions between the fluids and the silicate sheets. Results suggest that the mixing sequence used for two-part reactive materials could substantially influence the structure and properties of the resulting nanocomposite. The second system examined the initial stages of polymer melt intercalation into layered silicates, relevant to Nylon-silicate nanocomposites, among many others. The influence of the sheet stiffness, sheet dimensions, and the relative energies of polymer-sheet and sheet-sheet interactions on intercalation behavior were studied. The behavior for polymer chains above and below the entanglement length and the influence of pre-existing galleries between sheets have been considered. The third system studied the initial dispersion of a rod-like rigid phase in a polymer melt, relevant to carbon nanotubes composites. The influence of rod stiffness and the relative energies of polymer-rod and rod-rod interactions on the mixing behavior were studied.

10:30 AM T6.6

FILLER SIZE EFFECT ON THE STRUCTURE OF THE INTERFACE WITH THE POLYMER MATRIX IN POLYMER BASED NANOCOMPOSITES - ENTROPIC AND ENERGETIC EFFECTS. Catalin Picu, Murat Ozmusul, Rensselaer Polytechnic Institute, Department of Mechanical, Aerospace and Nuclear Engineering, Troy, NY.

The atomic and molecular scale structure of polymer chains in the close neighborhood of the surface of a spherical nanoparticle is studied by lattice Monte Carlo simulations. The structure of the interface (thickness of the affected polymer volume, the degree of chain segment orientation and density variation) depends on both entropic and energetic interactions. Here the focus is on understanding the role of energetic interactions in conjunction with the curvature of the interface in setting the polymer structure. An attractive wall potential leads to an increased density at the particle surface, while strong cohesive interaction within the bulk polymer lead to the opposite effect. In the dense system limit, the bond and segment orientation is not highly affected by the details of the energetic interactions. These results are similar to those previously obtained for the flat surface. Increasing the curvature of the wall weights down these effects. However, interesting results are obtained when the particle diameter becomes of the order of the chain end-to-end distance. In this case chains tend to wrap around the filler and this leads to a dramatic reduction in chain and bead mobility. Finally, the effect of filler density (the high confinement limit) is investigated.

10:45 AM T6.7

MORPHOLOGY AND PROPERTIES OF NANOSTRUCTURED POLYMER MATERIALS: COMBINING MESODYN AND PALMYRA SIMULATIONS. Gerhard Goldbeck-Wood, Simon McGrother, Accelrys, Cambridge, UNITED KINGDOM; Albert H. Widmann-Schupak, MatSim GmbH, Zürich, SWITZERLAND.

We have combined two commercially available software packages (Cerius2 MesoDyn from Accelrys and Palmyra from MatSim) to obtain structures and ensuing properties of nanostructured polymer materials. MesoDyn is based on a dynamic density functional theory for polymer systems, and yields nanoscale morphologies from coarse grained descriptions of the polymers. Palmyra is a finite element code for composites, which predicts a wide range of properties from knowledge of the pure component behaviour. In our work, we have interfaced both codes, which allows morphology and properties of nanostructured polymers to be simulated from their basic molecular description. The design of novel polymer membranes for gas separation is used as an illustration of the significance and potential of the method.

11:00 AM T6.8

KINETIC THEORY FOR FLOWS OF POLYMER-ORGANICALLY

MODIFIED CLAY NANOCOMPOSITES. Qi Wang, Department of Mathematics, Florida State University, Tallahassee, FL.

A kinetic theory for flows of polymer-organically modified clay nanocomposites will be presented. The theory accounts for the long range clay-clay interaction, polymer-organically modified clay interaction, and clay-clay interaction mediated through polymers. A special care is given to the treatment of incompressibility which results in a modified translational flux for both clays and flexible polymers. The theory is shown to produce a positive entropy and thereby satisfy the second law of thermodynamics. A few applications of the theory will be presented as well.

11:15 AM T6.9

FLOW ALIGNMENT OF ORGANICALLY MODIFIED MONTOMORILLONITE SUSPENSIONS. Hilmar Koerner, Weidong Liu, Univ of Dayton Research Institute, Dayton, OH; Richard Vaia, Air Force Research Laboratory, Materials and Manufacturing Directorate, AFRL/MLBP, OH.

Critical to forwarding polymer nanocomposite technology is the development of a detailed understanding of the spatial distribution of the various constituents (inorganic, polymeric and additives), the associated influence on thermodynamic and kinetic (rheological) aspects of the system and techniques to control nano (1-100nm) and meso (100-1000nm) scale morphology. The goal of this work is to investigate the complex kinematics associated with unique parallel and perpendicular flow alignment of organically modified aluminosilicate layers in nanocomposite processing. Morphological alignment associated with pressure flow through a slit (Poiseuille flow) was monitored using two-dimensional, in situ Small Angle X-ray Scattering (SAXS) at Brookhaven National Light Source (X27C). Basal reflection from within the layer stack and featureless small angle scattering reveal development and relaxation of orientation on various length scales. Results from step and continues flows show unusual behavior in the orientation of the layered silicate, depending on flow speed and concentration. Similarities with block-copolymer and liquid crystal kinematics, such as tumbling, are discussed.

11:30 AM T6.10

POLYMER CLAY NANOCOMPOSITES. S. Lin-Gibson, C.C. Han, Polymers, NIST, Gaithersburg, MD; G. Schmidt, Dept of Chemistry, Louisiana State University, Baton Rouge, LA.

Poly(ethylene oxide) and Laponite, a synthetic hectorite clay, form highly viscoelastic solutions in water. These solutions can be described as physical crosslinked networks where clay platelets undergo equilibrium adsorption/desorption with polymer chains. Complex fluids such as these containing anisotropic clays have generated significant interests both in shear induced structural changes and in network dynamics. The shear orientation of these polymer-clay solutions are investigated by means of rheology, flow birefringence and small angle neutron scattering (SANS). The dynamic interactions are best characterized by stress relaxation and scattering experiments. Several relaxation times are observed for temperature dependent stress relaxation experiments. Those relaxation times will be correlated with the relaxation times obtained from flow birefringence and SANS.

11:45 AM T6.11

ULTRASONIC CHARACTERIZATION OF ELASTOMERS AND ELASTOMERIC COMPOSITES. J.H. Dick, T.A. Craychee, C.J. O'Brien, J. Du, B.R. Tittmann, The Pennsylvania State University, Dept. of Engineering Science and Mechanics, University Park, PA.

Understanding the elastic properties of the various types of rubber is important for many commercial and academic applications. A sample set consisting of generic elastomeric compounds was studied using non-destructive non-contact ultrasonic techniques. The longitudinal sound wave velocities in the sample and wave amplitude attenuation in the sample were measured. These non-contact measurements were taken with the Second Wave Inc. Non-Contact Analyzer 1000 (NCA1000). These results were corroborated via a contact method, using a Panametrics 5852 pulser/receiver. The transducers were commercially available contact and non-contact transducers. The coupling media for the contact method were gel and honey. The results suggest that the differences in attenuation are driven by polymer type and also to a lesser extent the loading level of carbon black fillers. Here the technical approach to the experiments, results, and an outline for future work are presented.