SYMPOSIUM T
Polymer Nanocomposites
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*Invited paper
SESSION T1: INNOVATIONS IN POLYMER COMPOSITES

*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 an alternative to high-performance composites, and applications ranging from automobile 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.

*OPTIMIZATION OF A NAFION® PROTON-EXCHANGE MEMBRANE BY INFLTRATION OF AN H_2O_3-SIO_2-ZrO_2 GLASS.*
Francois Dieumeg, Lisa C. Klein, Rutgers University, Dept of Ceramic and Materials Engineering, New Brunswick, NJ.

Infiltration of a Nafion® membrane by a fast proton conducting silico-phosphate gel, belonging to the P_2O_5-SiO_2-ZrO_2 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 drying treatment show a conductivity of ~ 0.1 S/cm 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 severe than in the Nafion® sample. From the increase of the conductivity at 40%RH, the water content, \( \lambda = \frac{H_2O}{Nafion} \), is estimated to be \( \lambda = 6 \) in the composite membranes, compared to only \( \lambda = 3 \) in the Nafion® membrane. 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.

*POLYMER NANOCOMPOSITE FOAMS PREPARED BY MICROFABRICATION AND SUPERCRITICAL FLUID FOAMING TECHNOLOGY.*
L. James Lee, Changheun Zeng, Nianming Han, David L. Tomasko, Kurt W. Roelking, 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), which have attracted considerable environmental attention due to the ozone depletion 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 (CO_2) as a blowing agent is an attractive alternative for replacing ODS. Recently developed by microcellular foams researchers at MIT and Boeing, 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 cannot produce equivalent materials to the existing ODS containing foams because CO_2 is 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 superabsorbents, a microporous open cellular structure is required with pore sizes of 100-1000 microns and foam density less than 0.1. It is essential to produce CO_2 containing foams of equivalent performance to the wide range of existing foam products because CO_2 is an inexpensive, nonregulated, and unregulated gas. 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 non-nanocomposite foams, and on combining supercritical fluid 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 polyacrylamide and nucleation and foam growth mechanism can be tailored to generate a wide spectrum of foams. They include closed or open cellular structures; micro- (hundreds microns), micro- (<10 microns), or microcellular foams; and dual-mode cellular structures.

*POLYCOMPOZ® POLYURETHANE FOAMS VIA POSS BLENDS.*
Rocky McInnes, Steven Nett, Univ. of Southern California, Dept of Materials Science, Los Angeles, CA, Brent Viens, 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 silicate molecule has been used successfully to enhance performance of polymer systems using co-oligomerization and blend strategies. In our investigations, we use a commercial MDI Poly-urethane foam as a model matrix system in order to facilitate fabrication. For the microcellular, two minimum variations, C177/0H and B127/0H were chosen, and foam samples were synthesized. Structural characterization was accomplished by SEM, TGA, and DSC. The results from DSC and TGA were used in combination with XRF 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 Kimmich, Omni Tech International, midnight.

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 materials 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 T18 ORGANIC/INORGANIC NANOCOMPOSITES FROM FUNCTIONALIZED SILSESQUIOXANES. Jian Chen, Ryo Tamaki, Chad Brick, Seunggyoo Kim, Albert F. Yee and Richard M. Lane, Departments of Materials Science and Engineering, 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 Octasilsequioxanes [(RSiO1.5)n] as nanoscale blocks, organic and inorganic components can be easily incorporated into thermodynamically homogeneous one phase composites. The one phase nanocomposites 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 nanoscale reinforced nanocomposites. We present here our latest development of epoxy silsesquioxane nanocomposites and imide silsesquioxane nanocomposites.

11:00 AM T19 POLYMER NANOCOMPOSITES VIA REACTIVE MELT BLENDCING OF THERMOPLASTICS WITH MONOFUNCTIONAL POSS MONOMERS. Siian Zheng, Frank J. Heiber, Jun Xiao, Ren-Zhi Ju, 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 thermoplastics (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. bisphenol A polycarbonate or styrene-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 electron microscopy (SEM) will be described. Implications of our work for the development of other thermoplastic polymer nanocomposites will also be discussed.

11:15 AM T110 LAYERED ORGANIC/INORGANIC NANOCOMPOSITES BY CONTROLLED SELF-ASSEMBLY OF POLYHEXADRAL OLIGOMERIC SILSESQUIOXANE NANOPARTICLES. Lei Zheng, Sheng Hong, Amiya R. Tripathy, Samuel P. Giklo, Richard J. Ferris, E. Brynn 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/thyran-6 system. Preparations of nanocomposites of layered silicates and polymeric materials are often times complex and complicated. Integration of the interphase and the fillers, which results in complete dispersions or limited exfoliation. An exfoliated structure is necessary for significant property reinforcement. A novel approach to obtain nanocomposites containing inorganic nanomaterials is reported here. Polymeric oligomer silsesquioxane (POSS) nanoparticles are used to achieve the nanolayered structure through self-assembly. POSS is a class of well-defined molecules having an inorganic core comprised of SiO2 surrounded by eight tetrahedral substituents, i.e. cyclophosphazene. From this 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 microporosity 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 cyclohexene and POSS oligomer using a polymerization norbornene group. Interestingly, the nanostructure of the PB-POSS copolymer resembles that of the nanoscale shell with alternating inorganic crystalline layered and soft organic polymer 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 charaterizations of these materials will be presented. Their blending with homopolymers and POSS particles will also be addressed subsequently.

11:30 AM T111 HYBRID ORGANIC-INORGANIC POLYIMIDE NANOCOMPOSITES. Chia 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 the dielectric glass transition temperature, thermal stability, and processability 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 modified the thermodynamic properties of the polyimide 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 T112 ENHANCEMENT OF SCRATCH RESISTANCE OF NANO-PARTICLE FILLED GELATIN. Quan Chen, Linda Schäder, Richard Siegel, Rensselaer Nanotechnology Center, Rensselaer Polytechnic Institute, Troy, NY; Gök Irvin, John Mendel, Eastman Kodak Company, Rochester, NY.

Atomic force microscope and scratch testing were employed to investigate the scratch behavior of nanocrystallin filled deionized gelatin. The results showed that the addition of non-filled 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 transmission measurements of the polyimide composite show that the nano-filled composite had much higher transmitance than micro-filled composites. Both transmission and scanning electron microscope show excellent dispersion of the nano-particles in the gelatin matrix.
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 possible mechanism for improving the carbon nanotubes into a nanophase reinforcement in thermostable as well as thermostetting polymers. The resulting polymer nanocomposites exhibit a very low conducting permittivity threshold and substantially enhanced thermal, mechanical, and electrical properties. These results show 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 TENDUS: Gary G. Tilley, Iona C. Finney, Chongyang Kang, 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 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 0.1 Ohm cm. These conducting composites are valuable for applications such as radio frequency interference shielding, printed circuit boards, and electronic painting and static charges.

In order to make composites having excellent mechanical properties, good adhesion between fiber and matrix is essential. Carbon nanofiber-matrix adhesion was studied on surface treating the fibers using a variety of methods. Among as-grown fibers, those produced with longer gas phase residence times in the fiber growth reactor were less graphitic but adhered to a polyethylene matrix better than 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 carbonization was also found to increase adhesion to the matrix and increase composite tensile strength, while extended carbonization attacked the fibers sufficiently to decrease composite properties.

3:00 PM T2.4
MORPHOLOGICAL COUPLING DURING DEFORMATION OF CARBON NANOTUBE - POLYURETHANE NANO COMPOSITES: Richard A. Vein, Heather Bentley, Max Alexander, Air Force Research Laboratory, Wright-Patterson Air Force Base, William Click, Gary Price, Westlawn 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 of the resin to 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 extreme process-sensitivity complex hierarchical morphology of these systems. To begin to develop these relationships, this effort examines the coupling between mechanical deformation, reorientation 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 drawing indicates that the polymer deforms sufficiently small to reorient the nanotubes. These observations provide insight into the strain-dependent mechanical and electrical properties of these nanocomposites.

3:15 PM T2.5

Amorphous hydrogenated carbon (α-C:H) with embedded metallic clusters has attracted significant attention in the past year 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 carbon (α-C:H/Au) due to the apparent lack of reactivity between gold and carbon. Further, this results in the absence of chemical shifts of the C and Au core levels in the X-ray photoemission 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 gold and reactive ion source laser-induced deposition of carbon. The data suggest that the carbon nanotubes are uniformly dispersed in the polymer matrix and maintain a large aspect ratio of length to width.

3:30 PM T2.6
PRESSURE TUNING OF TRANSPORT PROPERTIES FOR C-NANOTUBES: F. Chen, K.L. Stakes, Weile 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 polyethylene and polystyrene. Temperature dependence of thermopower (S) and resistance (ρ) for these samples was measured under hydrostatic pressure up to 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 application of single-wall 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, NCRI c/o NASA-Goddard 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 flow rate, flame gas flow rate and 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 C2H2 is understood as reflecting mepanoparticle restructuring, interactions between condensates and reactant pyrolysis products. Fe is found to exhibit preferential reactivity towards CO for SWNT synthesis with this reactivity being strongly dependent upon catalyst particle size within our flame conditions. H2 appears to moderate the dissociative adsorption through electronic interactions with condensates, 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 Nickel nitrate solution are entrained in the reactive fuel mixture through particles sufficiently small to catalyze single-wall nanotubes (SWNTs) are produced, only nanofibers are produced. Using different reactive gas mixtures consisting of CO or C2H2 or their combination, Ni nanoparticles exhibited a high preferential reactivity towards C2H2 to form nanofibers. These results are interpreted as a result of CO enhancing the dissociative adsorption of C2H2 to facilitate an electronic charge donation mediated by the Ni nanoparticle and physically protecting active sites against blockage by amorphous carbon.
T3.1 THE CORE-SHELL APPROACH TO FORMATION OF ORDERED NANOPOROUS MATERIALS WITH MPEG-6-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 of the molecular level based on MPEG-6-PDLLA block copolymer templates. This approach provides for rapid self-assembly and structural recognition at room temperature. Selected MPEG-6-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 silicas 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 a variety of liquid and solid state 13C and 29Si 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 hydrophilic cores and hydrophobic shells of the block copolymer templates. In this process, the silica precursor becomes bound to hydrophilic regions of the ordered copolymer after hydration at the aqueous solution interface. The core-shell mechanism for a nanoporous structure evolution is based upon the size-controlling micellar packing arrangements that are dictated by the copolymer.

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

Our goal is to develop structure-property-processing relationships in nanocomposites prepared using functional silsesquioxanes [RSiO1.5]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, methacryl, etc.) appended to inorganic cubes and polymerized them to give organic/inorganic nanocomposites. Results from both bulk and nanoindentation tests are present at the 1-2 nm scale and discontinuous. Their properties are found to be governed by the nanoarchitecture of the organic tetrahedra as will be discussed here.

References:

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

Characterization of viscoelastic nature of polymeric layered silicate nanocomposites is crucial to gain a fundamental understanding of the processibility and structure-property relations to deliver them to new value in polymer academia as well 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 were prepared with different type of clays, i.e., non-pole (OC20A and OC25A) and pole (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 (\(\omega = 10^{-10} \text{rad/s}\)) and application of time-temperature superposition principle, master curves on the linear viscoelastic data of storage G' and loss modulus G'' were constructed. At low \(\omega = \omega_0\) (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, \(\alpha\), were estimated from the obtained curves, where \(\omega = \omega_0\) if the activation energy \(E_a\) was obtained at the corresponding temperatures. With further treatment of viscoelastic data by the empirical Haarhoff-Negami (HN) fitting function, the single average relaxation time, \(\tau_{HN}\), were determined. The \(E_a\) and \(\tau_{HN}\) were shown to provide a unique means to evaluate the activation energy on the basis of the molecular mobility. For the hybrids with silicate loading in excess of 7 wt%, \(E_a\) and \(\tau_{HN}\) increased remarkably compared to those of the hybrids with 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, \(\tau_{HN}\), can provide another method to evaluate the structural change in the nanocomposites of various silicone loading.

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

The mechanical behavior of clay loaded polycarbonate nanocomposites 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 ALKYNYLSE LANE TERMINATED AMIDE ACID OLIGOMERS AND CARBON NANOTUBES. Joseph G. Smith Jr. and John W. Cornell, 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 importing electrical conductivity while maintaining optical transparency is 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 currently ongoing 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 improving sufficient electrical conductivity to low color polymers for ESD sensitive potential space applications, SWNTs were combined with controlled molecular weight amide acid oligomers terminated with alkynylsilanes groups. The terminal alkynylsilane groups can presumably react with functionalities focused on the ends of oxidized SWNTs such as carbonyl 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 alkynylsilane groups. Thin films were cast from the hybrid into the use of 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 Yamashita, McMaster Univ., Dept of Materials Science and Engineering, Hamilton, ON, CANADA; Eiichi Yashira, 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; Yasuhiko Takebe, 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 though 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 fully-furfuryl alcohol, condensate, Hinfuran 302, commercially available from Hindco Chemical Co., Ltd. After curing and post-curing process, the furan (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 of 1773 K for 1800 s 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 a mortar. The surface of graphite layer was approximately 10% 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 specimens heat-treated at higher temperatures exhibited a cage structure. In the case of the 3273K treatment, about 10 graphite 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 Krimidinova, Galina Kozub, Institute of Problems of Chemical Physics, Chernogolovka, RUSSIA; Igor Chusov, Anatolii Pronomnikev, Institute of Synthetic Polymeric Materials, Moscow, RUSSIA; Aleksandr Gussev, Russian Federal Nuclear Centre, Sarov, RUSSIA.

The present work was aimed at the synthesis of composite materials based on conductive polymeric nanotubes. We synthesized SWNTs and studied their electrochemical properties in the 21-150°C range. SWNTs used in the present study were prepared by the pyrolytic technique using a Cr/Ni mixed catalyst. The tube content after purification is about 90% by metal. 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 polyaniline-nanotubes composites is about 3 vol% and the composites with filler concentration higher than 6 vol% have conductivity of 10⁻⁰⁷ - 10⁻⁰⁹ S/cm. For composites containing 12 vol% of nanotubes, conductivity is almost unchanged in the 20-110°C temperature range. The value of S(T/°C) (20°C) 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 NANO COMPOSITES. Heather Bentley, Max D. Alexander, Jennifer Stucky, Air Force Research Laboratory, Wright-Patterson Air Force Base, OH; Chris Shuan 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 thermosetting or thermoplastic polymer using a solution method. The electrical, mechanical, and thermal properties of the resulting polymer nanocomposites are characterized as a function of carbon nanotubes concentration. The thermophysical 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-PMMAl-MATRIX COMPOSITES POLYMERICIZED WITH GAMMA RADIATION. Victor H. Polkite, OCHEN, Santiago, CHILE; Maria Elena Alonso, Mauro E. Pileux, Universidad de Chile, IDHEC, Santiago, CHILE.

Filled polymer composites prepared with low concentrations of a metallic powder and PMMA were polymerized with gamma radiation. Gamma polymerization was induced by means of an appropriate dose of gamma radiation. The minimum dose for complete polymerization was 10 kGy for 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 381 Ω·m for Ag. The results 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 (350 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 COARSE GRAINED MOLECULAR DYNAMICS SIMULATION OF NANOSCALE RIGID RODS IN A POLYMER MELT. Anshul Sinha, University of Virginia, Dept of Materials Science and Engineering, Charlottesville, VA; R.A. Van 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 interfacing 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 types 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 chains. Both polymers and rigid rods are represented by a bead-spring model where chains of spheres are connected by the inhomogeneous FENE potential. From the calculated results, 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. Murali, K. Kuri Institute of Chemistry, University of Sind, Jamshoro, Sindh, PAKISTAN.

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

T3.12 ASSESSING EXFOLIATION IN ORGANOCLAY-POLYMER NANOCOMPOSITES. Michael P. Balagh, Deborah F. Eddel, Chemical and Environmental Science Laboratory, General Motors Research and Development Center, Warren, MI; Paola D. Fausto, 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 through 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 polymer nanocomposite materials. Data from organoclay-reinforced nylon, polyethylene and thermoplastic urethane will be presented.

SESSION T4: POLYMER-LAYERED SILICATE NANOCOMPOSITES

Chairs: Richard A. Van and Ann C. Balins
Wednesday Morning, April 3, 2002
Francesco 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 academic as well as in industry. The hybrid structure of incorporating layered silicates in filled polymers possess a unique combination of properties. In nature an abundant amount of mineral can be found that fulfill the requirements of stiff layered platelets with a thickness of about one and a diameter of a few hundred nanometers. The clay mineral montmorillonite is an example of 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 behavior, interaction of polymers between the clay layers and exfoliation of the clay layers polymer 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 usually not enough to be 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 were the advantage is minor it makes no sense to push these materials forwards. 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 effort on these areas more specific in the future. (1) A. Okada et al. Polym. Prep., 28, 147 (1987).

8:30 AM T4.4
MECHANICAL BEHAVIOR OF INTERCALATED POLYMER LAYERED SILICATE NANOCOMPOSITES. Alex J. Bialek, 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 investigated. Poly(butylmethacrylate) (PC) nanocomposites consisting of organically modified montmorillonite in a melt-processed matrix exhibited 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 under tensile loading, while those with 2.5 wt% or less of nanoclay display a slight decrease in the elongation at 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 flow in stress 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. Forrester, 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 nanoclay 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 non-optimization 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
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, Arnav 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 interplay between the polymer matrix, organoclay modifier, and layered silicate clay mineral affect morphological and physical behavior. However, recent years have seen a growth in the effort given to understanding a theoretical basis for the morphological behavior of these systems. In this ongoing work, the predictions of the BALAS mean-field model for these systems are systematically probed. A series of model surfactants based on poly styrene have been synthesized, and exchanged with the naturally occurring interlayer cations in montmorillonite clay. The model surfactant is then mixed with poly styrene homopolymer, formed into a pellet with contact pressure, and then annealed at both 105°C and 165°C for varying lengths of time. Previously, we have shown that at high levels of exchange (apparent 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 and surfactant concentration on the morphological behavior of this model system will be presented.

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

InMx 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 levels lower than those of the matrix 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 with low cost. One of the difficulties is that the nano-dispersed silicate clay does not agglomerate, one must control both the solid content and electrolyte balance. The nano-dispersed clay in InMts formulations is locally ordered. This mesoscopic structure of the silicate clays is not found in any other coating 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 coatings with thicknesses that are 1/30th microns thick, and applications resulting from this will be discussed.

InMts technology can also lead to thinner, more effective protection against chemical warfare agents.

11:14 AM T4.10 CHEMICAL AND PROCESSING ROUTES FOR POLY-PROPYLENE/LAYERED SILICATES NANOCOMPOSITES. Sylvain Boucard, Jannick Duclet, Patrick Pele, Daniel Rumetz, Jean-Francois Gerard, LIMM/IPV, Villeurbanne, FRANCE.

Isotactic polypropylene / layered silicates are of great interest both for automotive applications for which improved HDI is required and packaging industry in polypropylene is a poor oxygen barrier. The objective of this work is to develop different routes for processing IPP/layered silicate nanocomposites in such clays with good barrier properties. Firstly, 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 coatings with thicknesses that are 1/30th microns thick, and applications resulting from this will be discussed.

InMts technology can also lead to thinner, more effective protection against chemical warfare agents.

SESSION T5: POLYMER NANOCOMPOSITES FOR ELECTRONIC AND MAGNETIC APPLICATIONS

Chairs: Frederick L. Beger and Will Rodgers
Wednesday Afternoon, April 3, 2002
Francisco I (Argentina)

1:30 PM T5.1 THE CHARACTERIZATION AND APPLICATION OF POLYMER NANOCOMPOSITES IN THE ELECTRONIC PACKAGING MATERIALS. Sung-Jung Jung, Samsung Electronics Co., Ltd., Industrial Technology Research Institute, Hilsung, TAIWAN.

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

2:00 PM T5.2 PARTICLE SIZE AND DENSITY CONTROL IN MAGNETIC POLYMER NANOCOMPOSITES. Angel Milian and Fernando Palacios, CSIC-Universidad de Zaragoza, Instituto de Ciencia de Materiales de Aragun, 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-ray diffraction and magnetic measurements. A change in magnetic orientation by transmission electron microscopy is on the way. In this contribution we present the preparation and properties of iron oxide nanocomposites in polyvinyl pyrrolidone composites is reported. With only slight variations in the preparation procedure it is possible to obtain: (i) iron oxide, (ii) iron oxide ferrite, (iii) iron oxide ferrite, and (iv) iron oxide ferrite,

2:15 PM T5.3 FIELD-STRUCTURED SUPERPARAMAGNETIC NANOPARTICLE COMPOSITES. James E. Martin, Eugene Venturini, Sandia National Laboratories, Albuquerque, NM.

We have investigated the magnetic properties 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 an uniaxial field (“positive” dipole interactions); and magnetic nanoparticles structured into sheets by applying an radio 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 among the chains 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 CoFe2O4 SELF-ASSEMBLED NANOPARTICLES WITHIN BLOCK COPOLYMER TEMPLATES. Sufi R. Ahmed, Nanomaterials Research Group, Department 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; George C. Papanikolaou, Department of Physics, Villanova University, PA.

We have synthesized CoFe2O4 doped dikylv carboxylates by varying block ratio and mixed metal doping on 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. Dikylv carboxylates of boron and boron doped ferromagnetic (NOR) and boron doped ferrimagnetic (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 block copolymer matrix was achieved at room temperature by introducing FeCl3 and CoCl2 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 CoFe2O4 was verified using X-ray diffraction. The particles synthesized with a block ratio of [NOR][NORCOOH] = 0.40:5.0:0.1:15 and 0.40:20:0 are superparamagnetic at room temperature and ferromagnetic below 77 K. The superparamagnetic blocking temperature T_B increases with increasing size of the block and becomes equal to 300K for the polymer synthesized with a block ratio of [NOR][NORCOOH] = 0.40:25.0. 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 polymer-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 room temperature operation. 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 graphic shells of the composite carbon nanotubes have 1 to 10 carbon layers. The composite carbon nanotubes can be strung together with nanowires as edges. The growth mechanism will also be discussed.

3:30 PM T5.6 SYNTHESIS AND CHARACTERIZATION OF ELECTROSTATIC SELF-ASSEMBLY CdSe/POLYMER COMPOSITE FILMS. Lingmin Zhang, Fajian Zhang, Kristie Cooper, and R.O. Chiao, Viginia Polytechnology Institute and State University, Bradley Department of Electrical and Computer Engineering, Blacksburg, VA.

Using a novel electrospray self-assembly (ESA) method to incorporate CdSe quantum dot into polymer we have successfully synthesized an ultrathin film. This method allows the molecule-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 5.3 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 Valentini, Tufts Biotechnology Center, Dept. of Chemistry, Medford, MA; Millicent Firestone, Argonne National Laboratories, Argonne, IL; Linea Biologo, 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(methoxyamine) 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(I) ions were used as a probe for electron paramagnetic resonance (EPR). In the presence of silver ions the interior of the dendrimer regulated 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(I) interactions with the dendrimer in the direction of favoring the interaction of copper(I) ions in the polymer network. In nanocomposites, Ag(0) atoms primarily occupy the smaller outer cavities of the dendrimer interior forming 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. Jin-Kun 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 nanoscale metal-organic-doped tin oxide (MOS) particles (~20nm) and poly (vinyl acetate-acrylic) polymer latex particles (60-600nm) onto a substrate and drying at room temperature. During drying polymer particles coalesce to form a dense micrometre thick dielectric material that is continuous, adherent and boundaries between the latex. Electrical conductivity data show a percolation phenomenon with a threshold at 0.10% ATO for coatings that are 18-20 µm 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. Cortis are also transparent. For example, coatings with 20% ATO have a relatively high dc conductivity of ~0.2 S/mm and a high optical transparency (from 60% to 80%) 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

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

8:00 AM T6.1 MICRO/NANOSCALE MODELLING OF MECHANICAL AND BARRIER PROPERTIES OF POLYMER NANOCOMPOSITES. Nuo Sheng, Alberta Galindo, Mayo Croyer, 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% volume fraction). Furthermore, the properties enhanced to relatively high temperatures by indeed, act to substantially increase transition temperatures such as the glass transition temperature over that of parent homopolymer (an increase of 80°C has been observed for clay-filled nylon). These trends highlight the importance of understanding the behavior of micrometer- and submicrometer-scale aspects of the matrix-particle interactions and the effect on the overall transport properties of the nanocomposite system. The focus of this study is therefore on the nanoscale morphology and transport properties of the nanocomposite system. The focus of this study is therefore on the nanoscale morphology and transport properties of the nanocomposite system.

8:30 AM T6.2
ANALYSIS OF DEFORMATION MECHANISMS DURING A NANO TUBE PULL-OUT FROM A POLYMER MATRIX
S.J. Frankland and V.M. Hark, 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 pulled out from the matrix using 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 the polymer matrix as the NT pull-out progresses. Different stages of NT pull-out are parameterized 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
Chengyu Wei, NASA Ames Research Center, CA and Dept of Mechanical Engineering, Stanford University, CA; Deepak Srivastava, NASA Ames Research Center, Moffett Field, CA; Kyongsik 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. A proper choice of parameters can contribute to the enforcement of stiffness of polymer. Simulations on loading sequences show that Young's modulus of CNT-polymer composites can be increased with mechanical stretching processes due to work hardening process.

9:00 AM *T6.4
FORMING SPATIALLY ORDERED COMPOSITES FROM AXIAL DEVICE WITH THE POLYMER MATRIX IN POLYMER-BASED NANO COMPOSITES - ENTROPIC AND ENERGETIC EFFECTS
Carole Pierre, Murat Ozcan, Remscher Polytechnical 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 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 detail of the energetic interactions. These results are similar to those previously obtained for the flat surface. Increasing the curvature of the nanoscale interface is investigated. 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 local mobility. Finally, the effect of filler density (the high confinement limit) is investigated.

10:45 AM T6.7
MOLECULAR AND PROPERTIES OF NONSTRUCTURED POLYMER MATERIALS: COMBINING MEASYDYN AND PALMYRA SIMULATIONS
Gerhard Goldbeck-Wood, Simon McGrotcher, Accelrys, Cambridge, UNITED KINGDOM; Albert H. Wixmann-Schöpf, Macsim GmbH, Zürich, SWITZERLAND.

We have combined two commercially available software packages (Ceria2 MesDyn from Accelrys and Palmyra from MacSim) to obtain structures and ensuing properties of non-structured polymer materials. MesDyn 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 the complete family 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 nanocomposites is based on the use of advanced separations used as an illustration of the significance and potential of the method.

11:00 AM T6.8
KINETIC THEORY FOR FLOWS OF POLYMER-ORGANICALLY
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 case 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 Vain, Air Force Research Laboratory, Materials and Manufacturing Directorate, AFRL/MLRP, 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 (<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 aluminochlorine 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 continuous 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-Gilson, 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 viscous 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 mesoscopic clays have generated significant interests both in shear induced structural changes and in network dynamics. The shear orientation of these polymers-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. These relaxation times will be correlated with the relaxation times obtained from flow birefringence and SANS.

11:45 AM T6.11

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 5862 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.