SYMPOSIUM FF
Interfaces, Adhesion, and Processing in Polymer Systems

April 24 – 27, 2000

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*Invited paper
8:30 AM *FF1.1
PHASE SEPARATION AND INTER-DIFFUSION OF THIN POLYMER BLENDS FILMS. Charles C. Han, Materials Science and Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, MD.

One of the challenges in the science and technology of polymers today is in the area of surface/interface. This is especially true when multi-component polymers (polymer blends) are used. Not only does one have to consider the homopolymer interactions, but also the polymer surface interaction. Things may become more complicated, when the thickness of the film becomes comparable to the dimension of the thermal fluctuation length(s) or to the chain dimensions. In this talk, the thickness dependence of the phase separation mechanism of polystyrene/polybutadiene and deuterated polybutadiene/polyisoprene films will be presented. It will be shown that the phase separation of films on the surface can change from bulk-like behavior to surface driven layer structure and finally to lamellar phase separated structure as thickness decrease. With the combination of reflectivity, AFM, and optical microscopy techniques, the preferential surface enrichment by low surface energy component, the surface roughening after phase separation will also be discussed. The use of multi-layer Langmuir-Blodgett coated isopentecylcellulose cinnamate (IPCC) films as barrier membrane, inter-diffusion of polystyrenes with different molecular weights has also been studied. The selectivity of ultra thin IPCC membrane will be discussed.

9:00 AM *FF1.2
PATTERN FORMATION IN THIN POLYMER FILMS: A NEW MICROPHOTOGRAPHY. Jean-Loup Mission, Peter F. Green, Department of Chemical Engineering and Texas Materials Institute, The University of Texas at Austin, Austin, TX.

Researchers have shown thin, non-wetting, liquid homopolymer films dewet substrates, forming patterns that reflect fluctuations in the local film thickness. These patterns have been shown to be either discrete cylindrical holes throughout the surface of the film or bicontinuous “spinto-sphere” patterns. In this presentation we show the existence of a new morphology. We show that a random copolymer, styrene-4-arm isocyanite (SAN) of thickness h=12nm, dewets silicon substrates forming what we call an intermediate morphology. During the early stage of dewetting, discrete non-cylindrical, irregular, shaped holes appear spontaneously in the film. The number of holes, N, initially increase with time and the morphology of the late stage of growth, after 18 days, is characterized by a bicontinuous pattern, distinct from conventional spinodal dewetting patterns. The structural evolution of this intermediate morphology is discussed.

9:15 AM *FF1.3
WHAT DETERMINES THE ROUGHNESS OF SOLVENT CAST FILMS? Ken Strawhecker, Suma Kumar, Pennsylvania State University, University Park, PA; Aliamir Karim, NIST, Polymers Division, Gaithersburg, MD.

Solvent casting of polymers is routinely used in microelectronic packaging, and generally in casting applications to prepare films of controlled thickness and roughness. While roughness critically determines properties such as “gloss” [specular reflectivity of light], and surface friction, little is understood of the factors which control it. Here we show that, in the case of good solvents, rough films are created when rapidly evaporating solvents are employed, due to evaporation driven Marangoni instabilities, coupled to the fact that the films have insufficient time to level. Smooth films can always be created by minimizing the solvent evaporation rate. E. The critical role of solution leveling is emphasized by performing contact angle measurements for these solutions. While complete wetting is expected, the spreading time for solutions in volatile solvents is larger than the solvent evaporation time. Thus, these solutions do not spread completely, and yield large advancing contact angles. Our measurements stress the importance of leveling in controlling film roughness, and further show that contact angle experiments are a valuable tool to design operating conditions to obtain films of desired “gloss”.

10:15 AM *FF1.4
THE ROLE OF POLYMER SURFACE INTERACTIONS IN THE SELECTIVE ADSORPTION OF POLYMER THIN FILMS. Xueping Jiang, Sarah L. Clark and Paula T. Hammond, Massachusetts Institute of Technology, Dept. of Chemical Engineering, Cambridge, MA.

By controlling the relative amount of adsorption of polymer multilayer films on regions with a given chemical surface group, patterned monolayer films have been achieved. In this talk, the understanding of electrostatic, hydrophobic, and hydrogen bonding interactions involved in selective adsorption of polymers is explored. By comparing adsorption of polymers from aqueous solution onto different charged and uncharged surfactant monolayers, including acid, sulfonate, methyl and oligoethylene glycol functionalized surfaces, we can obtain a measure of the relative importance of these interactions with varying ionic strength and pH. Grating angle FTIR and AFM studies have been used to gain a better understanding of these interactions, particularly on acid and oligoethylene glycol functional surfaces. It is thought that the molecular architecture of the polymer backbone, as well as the degree of hydration of oligoethylene glycol groups on the surface, determine the preferred area of adsorption for polymers, whereas hydrogen bonding plays a greater role in the preferred adsorption site for polycarboxylic acids. These interactions may be tuned to create interesting composite film structures on patterned surfaces.

10:45 AM FF1.5
INSTABILITIES IN BLOCK COPOLYMER THIN FILMS ABOVE THE BULK ODT. Peter F. Green, and Rachelian Limeri, Department of Chemical Engineering and Texas Materials Institute, The University of Texas at Austin, Austin, TX.

We show that this symmetric poly(styrene-b-butyl methacrylate) (PS-b-PMMA) diblock copolymer films at temperatures higher than the bulk order-disorder transition temperature (ODT) of the copolymer dewet silicon substrates, forming topographical features that are characteristic on the initial film thickness h. Films of thickness h=15.5 nm dewet the substrate, forming bicontinuous spinodal-like patterns. When 3.5 nm < h < 7 nm, discrete holes are observed randomly throughout the surface of the film. For films of thickness in the range 15.5 < h < 35 nm, the copolymer exhibited nematic-like behavior whereby the top layer of thickness h-L dewets a dense "brush" of ordered copolymer of height L anchored to the silicon substrate. A bicontinuous spinodal pattern is observed for films of thickness in the range 15 nm < h < 35 nm. Discrete holes are observed for films where 15 nm < h < 35 nm. The structure of the top layer eventually evolves into droplets. For h > 35 nm the film is stable. The time dependent evolution of the structures in the metastable regime is discussed.

11:00 AM *FF1.6
ENVIRONMENTAL CONTROL PULSED FORCE MODE ATOMIC FORCE MICROSCOPY OF PATTERNED SELF-ASSEMBLED MONOLAYERS AND POLYMER BLENDS. Donna Sarno, University of Minnesota, Department of Chemistry, Greg D. Huisman, University of Minnesota, Characterization Facility; Wayne L. Gladfelter, University of Minnesota, Department of Chemistry, Minneapolis, MN.

Recent developments in atomic force microscopy (AFM) allow the mapping of topography, stiffness and adhesion via Pulsed Force Mode (PFM) operation. This study incorporates the PFM capability into an AFM, performing an array of force-distance curves at frequencies ranging from Hz to kHz speed, with data acquisition at MHz time-resolution. In addition, scanning frequencies are comparable to typical contact mode operation, and our software development has allowed efficient processing of large amounts of data. We are developing such PFM methodologies that incorporate environmental control, tip functionalization, and fluid media variation, such that specific tip-sample interactions in varying media can be studied. Most recently, we are applying these methodologies to study the effects of chemical functionality, fluid media, and the measured pulloff forces and energy dissipation during pulloff. The amplitude of the resulting freely oscillating cantilever after pulloff sheds light on the relative energy dissipated during that breaking away from the sample or fluid layer. Patterned self-assembled monolayers are prepared by microcontact printing on Au-coated Si substrates, and we apply this technique to elucidate the effects of chemical functionality. Polymer blends are then studied to distinguish the effects of differing mechanical properties.

11:15 AM *FF1.7
TACTICITY AND SURFACE CHEMISTRY EFFECTS ON THE GLASS TRANSITION TEMPERATURE OF THIN SUPPORTED PMMA FILMS. Yves Grebenc, Loic Hamon, Pascal Carriere, Yves Houll, Institut de Chimie des Surfaces et Interfaces, Mulhouse, FRANCE.

The understanding of the properties of polymers near the surface of an inorganic material is of practical importance in many applications such as coatings, adhesives or composites. Tg studies in confined geometry have highlighted a significant modification of the mobility of polymer in thin films as compared to the bulk. In this paper the Tg of thin layers of polymeric systems including stereoregular PMMA and blends has been studied by spectroscopic techniques.
ellipsometry. The influence of the surface treatment of the silicon wafer on the Tg of the thin film has also been addressed.

Stereochemical blockade of great interest for the understanding of the dynamic of confined polymers because of their well-known tacticity dependency of bulk Tg associated with a chiral chemical composition. From our ellipsometric experiments, it turns out that iPMMA increases its Tg above the bulk value for films thickness h < 60 nm whereas syndiotactic isomer exhibit a Tg depression for thin layers on silicon wafers covered by native oxide. The observed effects on the Tg of the thin layers are enhanced on highly hydrogenated SiOx/Si substrates and on silicon free SiH surfaces. Strong specific interactions of PMMA and SiOx/Si substrates are, therefore, required to modify significantly the Tg of the tactic PMMA in thin film geometry.

Stereo-specific adsorption of the isotactic PMMA sequences has been shown to occur on Si-OH terminated silicon. This segregation of the isotactic segments may lead to a particular interfacial organization of the polymer. This interfacial molecular resolution and hence density packing at the interface can be envisaged to explain the increase of the thin layer Tg for predominantly isotactic PMMA. s-PMMA chains are more loosely packed at the interface which is likely to increase the free volume for the isomer in the vicinity of the surface and then depressed the Tg.

11:30 AM FF1.8
STUDIES OF POLYSTYRENE INTERFACES BY VIBRATIONAL-LY RESONANT SUM-FREQUENCY GENERATION.
L.J. Richert, K.A. Briggsman, J.C. Steinhagen and W.E. Wallace, National Institute of Standards and Technology, Gaithersburg, MD.

Vibrational-resonant sum-frequency generation (VRSFG) is emerging as a powerful probe of the molecular structure of interfaces. VRSFG is a nonlinear vibrational spectroscopy in which an IR photon, resonant with the system of study, is mixed with a visible photon to produce a new photon at the sum frequency. It is uniquely interface specific as the mixing is symmetry forbidden in centro-symmetric media. Remarkably, there have been few studies in which the technique was applied to the characterization of polymer surfaces and interfaces. We report VRSFG studies of thin polystyrene films on Au and Si substrates. Surface contamination is routinely encountered, but reproducible spectra characteristic of the PS can be obtained from ethanol rinsed samples. Quantitative modeling of VRSFG spectra acquired for various film thicknesses allows identification of the signature from the buried and free interfaces. The orientational distribution of the phenyl rings at the free interface is found to vary dramatically between annealed, spin-coated films of low (4 k u) and moderate (300-800 k u) molecular mass. Quantitative analysis of the orientational distribution and comparison with existing XEAFS studies of ring alignment will be presented.

11:45 AM FF1.9
ULTRATHIN SOLID FILMS VIA TOPOLOGICAL PHOTO-POLYMERIZATION.
Jiehun Wu, IBM Almaden Research Center, San Jose, CA and Seagate Technology, RMO, Fremont, CA.

Molecular design and nanomaterials engineering of polymers in form of thin films has been of great challenge of ever decreasing size for miniaturization with molecular dimension, as protective coating, lubrication and functional components. The physics and chemistry underlying them has been the focus of research for many years. Two fundamental questions concerning thin films materials how to prepare them and how to make them adhere onto substrates. A respectable arsenal of techniques has been invented to produce desired thin films of which the thickness can be regulated up to atomic and molecular level. The adhesion between two components is still under intensive investigation. Cysteine esters are established high temperature, thermosetting polymers and have found a wide spectrum of applications in electronics and aerospace industries. Interested in potential range in ink drives, we have successfully prepared polycysteine thin films, starting from selected reactive monomers of cysteine esters. This work focuses on the polymerization mechanism and morphology of the monomer bisphenol A dicyanate (2% bis-dicyanamide) (BADC). The monomer is vapor deposited onto silicon wafers, the thickness of which can be controlled to a sub-molecular layer. The monomer film is then irradiated with ultraviolet light to convert the deposited monomer to form a solid, robust coating. The thin film adheres fast to the substrate surface and could not be removed or dissolved with methyl ethyl ketone or other solvents capable of dissolving the BADC monomer. The cured films is thermally stable and could tolerate temperatures level at least 100°C without showing adverse effects on thicknes, while the monomer film would quickly evaporate at this temperature. FTIR spectra show that 2950 cm⁻¹ double bond vibrational modes from the functional groups of CN triple bonds in the monomer remain, and new broad bands of peaks emerge in the range of 1800-900 cm⁻¹ in the resultant polymer film. XPS spectra witness a high shifting of bonding energies of the elements C, N, O. The data of NMR and TMD suggest that the photo polymerization of the monomer initiated by ultraviolet light follow a propagation mechanism. To form a new member ring, followed by an energetically stable, five-member ring, an end-capped product. Atomic force microscopy (AFM) is used to monitor the changes in topography of the surface with the addition of the polycysteine overlayer.

SESSION FF2: POLYMER-POLYMER AND POLYMER-WALL INTERFACES

Chair: Jacob Klein and Paula T. Hammond

Monday Afternoon, April 24, 2000
Metropolitan I (Argent)

1:30 PM FF2.1
SLIP AT MOBILE POLYMER-POLYMER INTERFACES.
Rui Zhao, Christopher Macosko, University of Minnesota, Minneapolis, MN.

Using layer multiplication dies in coextrusion, two or more polymers can be alternatively combined into hundreds or even thousands of continuous layers[1]. One of the unique features in the layer multiplication process is the layer thickness ranging from a few nanometers to micrometers over an area that is large enough to simulate the complex morphology developed in melt blends and the lack of control, the data obtained cannot be used to justify the existence of interfacial slip. With the coextruded multilayers, we were able to test the interfacial slip. PP/PS with closely matched viscosity from shear rate 0.10 to 500 s⁻¹ were used in this study. The steady shear and dynamic shear viscosity of the blends was first measured in a capillary rheometer or a rotational shear rheometer using parallel plates geometry. While the steady shear viscosity of the blends was lower than that of both homopolymers, the dynamic shear viscosity of the blends was the same as that of the homopolymers within the instrumental error. The pressure drop of the coextruded multilayer melts through a slit die was measured. The data showed that the pressure drop of multilayer melts was lower than that of both homopolymers and decreased with an increase in the number of layers, which indicates interfacial slip. The steady shear viscosity of the multilayer sample was also measured in a rotational shear rheometer using parallel plates geometry. The viscosity of the multilayers was shown to be lower than both of the components when the stress was higher than a critical value, which also confirmed interfacial slip. However the dynamic viscosity measurement didn’t show any interfacial slip, and the linear viscoelasticity of the melt blends and multilayers can be well described by the Palierne model. This is not predicted in de Gennes and Fredrickson’s theory of interfacial slip. The experiment also showed that diblock copolymer was able to suppress interfacial slip. More work needs to be done to produce the mechanism of block copolymer suppressing interfacial slip.

References:

2:00 PM FF2.2
REACTION KINETICS OF END-FUNCTIONALIZED CHAINS AT A POLYSTYRENE/POLY(METHYL METHACRYLATE) INTERFACEx.
Jonathan S. Schaefer, Timothy P. Lodge and Christopher W. Macosko, Department of Chemistry and Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN.

Polymer blending often relies on reactive compatibilization to create stable mixtures of two otherwise immiscible polymers. In reactive compatibilization, a fraction of polymer chains in each phase is functionalized. During blending, these functionalized chains react at the polymer/polymer interface to form block or graft copolymers that stabilize the mixture. Several factors may affect the rate of reaction during compatibilization: external convection during mixing that creates interfacial area, diffusion of the reactive polymer chains through the bulk to the interface, and the chemical reaction that
occurs between different functional groups. Forward recall spectrometry (FRES) has been used to monitor the extent of reaction between model functional polymer/micelle interface in the absence of external convection. Bilayer samples comprising a high molecular weight polyethylene layer containing terminal quinonic 4,4-diphenyl-2,2'-biquinone (PMMMA) layer were annealed for various periods. Significant reaction with the PMMA-anch. ind, was observed by an interfacial wax, was observed with three molecular weights of dPS-NH2. The measured growth of the interfacial wax with time for all three molecular weights of dPS-NH2 is well described by recent theories of diffusion-controlled interfacial reaction. Furthermore, a novel bilayer sample geometry suggested that the reactive dPS chains can diffuse through the PS matrix and sample the PS/PMMMA interface several times before a significant amount of reaction occurs. The results of this study are consistent with other experimental systems where in situ copolymer formation is limited by reaction rate, rather than the diffusion of reactive chains through the bulk.

2:15 PM **FP2.3**

NMR STUDIES OF DYNAMICS OF PERFLUOROCYCLOTETRACYCLIC PERFLUOROPOLYETHER THIN FILMS ON AMORPHOUS CARBON SUBSTRATES: CONFINED FLUIDS AND INFORMATION STORAGE. Charles G. Ward, Guangzuo Chao, Mark Sherrwood, Bing Yin, LMB Almaden Research Center, Science and Technology Function, San Jose, CA, Chris Klag, Yoonjoon Kim, Stanford University, Dept. of Chemical Engineering, Stanford University, Stanford, CA.

The 19F and 13C NMR spectra and relaxation studies have been used to study the dynamics of microcrystallites in perfluoropolyethers (PFPEs) on amorphous carbon/hydrogen films. These systems are important in magnetic disk drives because the PFPE serves as a lubricant on the disk carbon overcoat in the head disk interface. The microcrystalline order, as monitored by the 19F NMR spectra, is controlled, and the measurements extend into the sub-monolayer region, where the PFPE is a confined fluid. 19F spin lattice (T1) relaxation as a function of temperature and surface coverage shows little change between liquid and surface confined phases, indicating that the backbone motion undergoes little change between these phases. This is a very unusual result given the large thermodynamic changes measured for such changes. Spin-spin relaxation (T2), however, changes significantly between the bulk and surface samples. Spectral editing of the carbon NMR in the carbon/hydrogen amorphous overcoat allows identification of the carbon/hydrogen moieties in the system. NMR findings are compared with detailed surface energy measurements in identical systems of confined PFPE fluids.

2:30 PM **FP2.4**

TIME-RESOLVED OBSERVATIONS OF FAILURE OF POLYMER-Glass INTERFACES IN HUMID ENVIRONMENTS. Tom Dickinson, Stuart Irwin and Steve Longfold, Washington State University, Dept. of Physics, Pullman, WA.

Adhesive interfaces play a critical role in microelectronic packaging, as well as in aerospace, automotive, and civil structures. The acceleration of bonded adhesion bonds due to moisture of considerable interest. By study of very small bonded areas (between 5 and 100 square microns) one greatly enhances the influence of environmental attack, allowing for accelerated testing. To measure failure kinetics, we require video microscopy of failure along ethylene vinyl acetate/zoledrite glass interfaces vs. relative humidity (RH) with simultaneously acquired measurements of applied force. The interface is viewed through the glass substrate with an optical microscope. With increasing applied stress and relative humidity, the time required to produce an observable defect and the total time (1-200s) to failure decrease in a monotonous fashion. With increasing stress, the size of the crack at the onset of unstable critical crack growth also decreases. Visible crack growth prior to unstable failure is apparently rate limited by the diffusion of water to the crack tip. The time required to produce a visible defect can be accounted for on the basis of a chemically reacted failure, where the crack velocity depends directly on the change in surface energy due to water sorption (not transport limited). A quantitative model for the dependence of failure on stress and humidity is presented. We also present data acquired using an Atomic Force Microscope to detect strong mechanical interlocking between particles at the crack tip, again showing strong dependence on RH, on time scales of ms.

This work is supported by the NSF Surface Engineering and Tribology Program under Grant CMS-98-00230.

3:15 PM **FP2.5**

MUSHROOMS AND BRUSHES IN THIN FILMS OF DIBLOCK COPOLYMER/HOMOPOLYMER MIXTURES. Costas Tsonis and J. D. Androulidakis, University of Patras, GREECE; S. H. Anastassiadis and H. Retsos, Foundation for Research and Technology-Hellas and University of Crete, Crete, GREECE; G. Smith, Los Alamos National Laboratory, Los Alamos, NM; G. Hadjipavlou-Lambert, University of Patras, GREECE; J. de Boer, University of Utrecht, NETHERLANDS; A. Terzis and D. N. Theodorou, University of Patras, Department of Chemical Engineering and FORTH, Institute of Chemical Engineering and High-Temperature Processes, Rio Patras, GREECE.

The interfacial segregation of block copolymers to substrate/polymer interface from their mixtures with the homopolymers is investigated in the context of selective adhesion. The adsorbed chain configuration was probed as a function of the ratio of block lengths. The segment density profiles of PV2P-P3 diblocks adsorbed at the substrate interface as a function of the adsorbing block are evaluated with the damping block being kept constant. The composition profiles and conformational characteristics of all chain species present in the interfacial region are also investigated using a liquid field self-consistent field (LSCF) model. The work of Scheutjens and Fleer. Inputs to the model are the relative amounts, molecular weights, conformational stiffness and bulk densities of all polymer species, as well as interaction parameters extracted from experimental binary interfacial widths. Both experimental and theory reveal evidence for a broad transition from a "mushroom" to a "wet brush" configuration of the dangling chains by changing the ratio of the block lengths.

3:45 PM **FP2.6**

STABILIZING COLLOIDS IN A POLYMER MELT BY END-GRAFTED CHAINS: A PROBLEM AND A SOLUTION. Leszek Brezawa and Ludwik Lebowitz, University of Texas, Austin, 167, CNRS/Isle-Atochem CAL, Levallois-Perret, FRANCE.

An important method of stabilizing colloidal mixtures against attractive van der Waals forces is to increase the surface coverage of the interface by adsorbing polymer chains with a layer of end-grafted polymer chains. This method works well when the colloid is immersed in a regular solvent. However, when the surrounding medium is a polymer melt, subtle entropic effects might lead to desorption and flocculation. In this presentation we discuss this problem and suggest a mechanism for stabilizing the colloidal suspension. The model consists of spherical particles covered with end-grafted polymers (brushes) immersed in a polymer melt. It is shown that the structure of the brush has a crucial effect on the inter-particle interactions. The density profiles and the interactions between the particles are calculated by solving numerically the self consistent field (SCF) equations of the system within the Derjaguin approximation. Scaling arguments are used to describe the structure of a single brush in contact with a polymer melt. The effect of van der Waals interactions is studied by taking into account the contact at the two particle-brush interfaces as well as that of the brush-melt interfaces.

4:00 PM **FP2.7**

ON THE INTERFACE BETWEEN HARD CHAIN FLUIDS AND A HARD PLANAR WALL. Frank van Swol, Sandia National Laboratories, Catalysis and Porous Materials Dept. and The University of New Mexico, Department of Chemical and Nuclear Engineering, Albuquerque, NM.

We present the first data for the interfacial properties of the simplest possible polymer fluid substrate interface, namely that of a hard chain fluid against a planar hard wall. We use molecular dynamics simulation to calculate the surface free energy and the adsorption isotherms for hard chains of 8, 20, 100, 400 and 1000 beads. The results are compared to those of the hard sphere fluid. We find that chain fluids differ markedly from the simple spheres in that both the adsorption and the surface free energy change sign and display an extremum as a function of density. The surface free energy exhibits a Boyle density where at a nonzero density the surface free energy is equal to that of an ideal gas. The data that we present here are the first of its kind for polymer fluids should prove particularly useful in further developing approximate density functional and integral equation approaches to polymer interfaces. In order to facilitate the future comparisons between exact simulation data for the hard chain systems and theoretical predictions, we suggest that comparisons are made for surface tensions as functions of the pressure as derived from the contact values. We observe over most of the pressure range is linear with pressure. Finally, for very low density chain fluids (i.e. below the semidilute regime) we analyze the scaling behavior of the adsorption profile in terms of a profile of universal shape, following recent suggestions based on the scaling behavior of thread like polymers.

4:15 PM **FP2.8**

SCALING THEORY FOR END-FUNCTIONALIZED POLYMERS CONFINED BETWEEN TWO SURFACES. Dmitri V. Kumachev and Anna C. Balazs, Department of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania.

Using scaling theory, we investigate the equilibrium behavior of melt
of functionalized chains, non-functionalized polymers and two infinite, planar surfaces, which model clay sheets. The functionalized chains contain end-groups and are highly attractive to the surfaces. We calculate the free energy of polymers confined between the two sheets as a function of the surface separation for a wide set of parameters: the end-group adsorption energy, length of the functionalized and non-functionalized chains, volume fraction of end-functionalized chains in the bulk, and the interaction energy between the different chains. For chains between the surfaces, we also analyze the distribution of the different chain conformations; namely, we determine the distribution of tangles, tails and free chains within this gap. Finally, we isolate conditions for the formation of ‘exfoliated’, ‘intercalated’ and immiscible polymer/clay mixtures.

4:30 PM FF2.9
ELASTICITY MEASUREMENTS OF SWOLLEN CROSSLINKED MICROSPHERES ATTACHED TO WALLS USING OPTICAL MICROSCOPY
Duncan Cameron, Colin McAllister and Omar Owel, Tribikram Manna Research Center, Boca Raton, FL, USA, Institute of Natural Science, University of Bremen, Bremen, IN, USA.

The elastic properties of crosslinked swollen polycholublyne polymers were determined in various solvents vi optical microscopy. Model polymer compounds were prepared as uniform microspheres using the suspension polymerization technique. By this technique, a toluene solution of butyl rubber and sulfur monochloride as the crosslinking agent was suspended in an aqueous phase and crosslinked therein to give polymers in the form of beads of uniform sizes. Typically, a polymer sphere was attached to a glass surface. A stainless steel cantilever beam was pressed on the sphere through which forces transmitted to the sphere and the corresponding displacements were determined. Changes in deflection of the beam and distortion of the sphere were measured simultaneously under the microscope, as the swollen sphere was squeezed incrementally between the walls. The elasticity was then determined in a function of the observed deformation of the sphere, versus deflection of the cantilever beam. The forces transmitted through the beam were measurable within an accuracy of ± 10⁻⁸ Newtons. Differences in the elastic behavior of microspheres attached to rigid walls and large swollen elastic bodies were investigated by using the molecular theories of rubber elasticity.

4:45 PM FF2.10
NEUTRON REFLECTIVITY MEASUREMENTS OF POLYMER INTERDIFFUSION IN THE POLYMER/SOLID INTERFACE
Eric K. Liu, Shaulin K. S. Sajna, National Institute of Standards and Technology, Gaithersburg, MD, 1 Dept Materials Science and Engineering, Univ of Delaware, Newark, DE.

Polymers chain mobility near a solid surface is measured using neutron reflectometry by monitoring the rate of interdiffusion between bilayers of deuterated poly(methylmethacrylate) (d-PMMA) and hydrogenated PMMA supported on polished silicon wafers. Neutron reflectometry is a powerful technique to do non-destructive measurement of interfacial structures because of its high resolution and the opportunity to selectively label organic molecules with deuterium. Interdiffusion of segments over distances < 15 nm is measured at varying distances from the substrate surface. From a series of samples, an estimate of the effective distance an attractive solid substrate perturbs polymer diffusion from bulk values is determined and correlated with chain conformations calculated using self-consistent field theory. The effect of varying polymeric surface interaction energies is determined by using self-assembled monolayers to modify the native oxide silicon surface. The effect of different molecular weights between the surface layer and the matrix polymer is also explored.

SESSION FF3: POLYMER INTERFACE AND ITS EFFECT ON PROCESSING
Chairs: Christopher W. Macosko and Jeffrey T. Koberstein
Tuesday Morning, April 25, 2000
Metropolitan I (Argent)

8:30 AM *FF3.1
NEUTRON REFLECTION FROM GRAFTED POLYMER BRUSHES UNDER SHEAR, Sajlin S. Sajina, Robert Ilovsky, Paul Butler, NIST Center for Neutron Research, Gaithersburg, MD, I.J. Peters, Exxon Research and Engineering, Annandale, NJ.

We report recent results of neutron reflectivity studies of chemically end grafted polyethylene brushes subjected to very high shear solvent flow. These brushes were studied with both toluene and cyclohexane as solvents. We have subjected the brushes to shear rates as high as 130,000/s, which is nearly 15 times higher than the shear rates reported previously. However, even at these very high shear rates we do not observe any brush thinning or thickening. In fact, the neutron reflectivity data for profiles at 0/60% solids are highly attractive to the surfaces. We calculate the free energy of polymers confined between the two sheets as a function of the surface separation for a wide set of parameters: the end-group adsorption energy, length of the functionalized and non-functionalized chains, volume fraction of end-functionalized chains in the bulk, and the interaction energy between the different chains. For chains between the surfaces, we also analyze the distribution of the different chain conformations; namely, we determine the distribution of tangles, tails and free chains within this gap. Finally, we isolate conditions for the formation of ‘exfoliated’, ‘intercalated’ and immiscible polymer/clay mixtures.

9:00 AM *FF3.2
SLIP AND FRICTION OF POLYMER MELTS ON MODIFIED SOLID SURFACES
Hubert Hervet, V. Koutsa, T. Charpentier, L. Legé, Laboratoire de Physique de la Matière Condensée, Collège de France, Paris, FRANCE.

Slip and friction of polymer melts flowing on solid surfaces covered with irreversibly adsorbed polymer chains have been studied. The material under study is a mixture of a random copolymer melt of styrene-butadiene (SBR, molecular weight from 5.9k to 15.3k, Mw/Mn = 1.2) with 5% by weight of the same polymer labeled with a fluorescent probe (NBD). Such a labeling enables to determine the surface and bulk velocities of the melt. The stress applied on the solid surface is simultaneously measured. In all force - displacement curves there is a transient behavior due to different friction mechanisms depending on the applied shear rate: 1) at low shear a linear friction regime with low slip; 2) at intermediate shear rate a stick-slip regime appears, reminiscent of the intermediate regime observed in polydimethylsiloxane (PDMS) [1, 3] at higher shear rates there is a transition to a low friction regime with high slip. Such a behavior is typical of a strong coupling between the surface chains and the bulk ones through entanglements: when the shear rate increases the surface chains deform under the friction and finally disentangle from the bulk to induce high slip. Results on the variation of the onset of the stick-slip and the high slip regimes depend on the adsorbed chains and the molecular weight of the bulk and surface chains will be presented. Differences in repetition times could explain the changes observed between PDMS and SBR in the intermediate regime.


9:15 AM *FF3.3
EFFECT OF BORON NITRIDE IN THE PROCESSING OF METALLOlene POLYOLEFINs
Sara G. Hozier, Dept. of Chemical Engineering, The University of British Columbia, Vancouver, BC, CANADA.

The influence of a new processing additive (a composition of fine particles of Boron Nitride) on the rheology and processing behavior of polyolefins in extrusion is studied. It is shown that the use of a small amount of Boron Nitrate, typically 0.1-1.0 ppm, not only eliminates surface melt fracture but also postpones the onset of gross melt fracture to significantly higher shear rate values depending on resin and boron nitrate type, temperature, and the additive content. To identify a possible mechanism for this unique effect on the processability of the resin, rheological measurements by means of parallel-plate, sliding plate and extensional rheometers were carried out. A visualization technique was also used to visualize the development of flow patterns at the entrance of a transparent die made out of fused quartz, with and without the presence of the Boron Nitrate.

10:15 AM *FF3.4
ADHESION, SHEAR AND INTERFACIAL SLIP OF POLYMERS ON SOLID SURFACES
Jacob Klar, Eugene-K kmochleva, Rafael Tidnner, Dept. of Materials and Interfaces, Weizmann Institute of Science, Rehovot, ISRAEL. * present address: Dept. of Chemistry, Toronto University, CANADA.

Polymers adhered to surfaces that experience a shear field may either stretch, slide along, or detach from the surface (or a combination of these), situation which can occur in many flow processes. Using a surface force balance, we have examined the way in which solvated polyethylene chains end-attatched to a solid substrate respond to progressively increasing shear forces applied by compressing and sliding past them a similar polymer-coated surface. Our results suggest that beyond a certain shear stress the chain detaches from and slide along the surfaces. For long chains we find plug-like flow to occur between the sliding surfaces, while for short chains, this detachment and compression lead to expulsion of chains between the gap, illustrating qualitatively why the chains are held under stress. Our results may be understood in terms of a simple model where the shear stress overcomes the adhesion energy of the chain ends to the surface.

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10:45 AM FFS3.5
SHEAR AND ELUBRICATION OF ADSORBED POLYMERS IN A GOOD SOLVENT. Uri Raviv, Rafael Tadmor, Jacob Klein, The Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot, ISRAEL.

Direct measurements of the shear and normal forces between two atomically smooth mic surfaces immersed in dilute solution of polyethylene oxide (PEO) in toluene have been carried out as a function of surface separation. Toluene is a good solvent for PEO and two different PEO weights were used, 11.5k. Polymeric adsorption of the PEO force-distance law was indicated with repulsion beginning at a distance of ~2±1Rg (where Rg is the unperturbed gyration radius) with stronger attraction at shorter distances. In this study, uniform back and forth shear motion was applied in a series of separations. Shear response commenced at a distance of ~(2±0.4)Rg and increased monotonically at shorter distances. In the lower molecular weight case, normal force measurements taken after shear showed no forces up to separation of 5nm, below which stronger attraction was indicated. This suggests that sliding of the two surfaces past each other ripped PEO 37k off the mic surfaces. Using analysis based on the implications of the scaling theory of adsorption we have estimated that about 10% of the polymers are still left on the surface and the attraction between the surfaces is due to bridging effect, which is known to take place at low surface coverage. In the higher molecular weight, shear forces increased monotonically for 1.5k< D<2.4Rg. At short separations the shear forces increased very little with increasing the normal load. Normal forces taken after shear were similar to those before shear. This suggests that even though the shear tangential force was able to detach the polymers off the surfaces, they reattached to the surface because the longer chains are heavily entangled and did not diffuse out of the gap. As the polymers remained within the gap they behaved as a good lubricant.

11:00 AM FFS3.6
MOLECULAR-DRAIN-STRAIN COUPLING IN BRANCHED POLYMER MILKS. Richard Blackburn, Tom McLeish and Oliver Harlen, Department of Applied Mathematics and Interdisciplinary Research Centre in Polymer Science and Technology, University of Leeds, Leeds, UNITED KINGDOM.

The “pom-pom” model of McLeish and Larson (J. Rheol. 42 (1): 81-110, 1998) provides a simple molecular theory for the nonlinear rheology of long chain branched polymer melts. The Edwards-de Gennes tube concept is used to derive a constitutive equation for a simple branched molecule composed of two star polymers linked by a single backbone chain. A feature of this model is that the backbone section of tube can stretch up to maximum length given by the maximum entropic drag-force from the arms, after which the star arms are withdrawn into the backbone tube. This produces a sharp transition in the extensional viscosity at this maximum stretch. This unphysical feature results from an over-simplification of the behaviour near the branch points. In this paper we introduce a simple treatment of the coupling between related and unrelated polymer segments at branch-points. This allows for localised displacements of branch-point within a quadratic potential before maximum extension is reached. This characteristic length is equal to the length of the tube outside the tube and so reduces the drag on the star arms. This smoothes out the sharp transitions in extensional viscosity in the original “pom-pom” model at the cost of introducing an extra unknown parameter. This modification improves the prediction of the nonlinear rheology of H-polymers whose molecular structure is known. Alternatively, for polymers of unknown structure such as commercial Low Density Polyethylene, the model parameters may be fitted from linear viscoelastic and uniaxial extension data, to provide predictions for the behaviour in transient nonlinear shear and planar extension. By including local branch-point displacement we find improved agreement with the data for Low-Density Polyethylene.

11:15 AM FFS3.7
SHEAR-INDUCED DROPLET COALESCE IN IMMISCIBLE POLYMER BLENDS AND THE EFFECT OF INTERPHASIC MODIFICATION. S. D. Hafso, A. M. Jameson, I. Minor-Zuckower, B.E. Burkhardt, G.V. Pratt, Case Western Reserve Univ, Cleveland, OH.

Experimental data on the rate of shear-induced coalescence in binary and emulsified immiscible polymer blends is interpreted in the context of current analytical models. Coalescence consists of three steps: first droplet collision, then drainage of the matrix film between the droplets, and finally coalescence. Analysis of the experimental data indicates that coalescence efficiency yields an independent measure for the probability of each step. Coalescence theory [1] has been verified. For sufficiently weak capillary number, the probability of film drainage is unity, and coalescence is limited by the efficiency of the other two processes. Block copolymer additives that adsorb to the interface may influence the efficiency of each step, leading to an increase in coalescence efficiency. The effect of poly(ethylene oxide)-b-propylene oxide-ethylene oxide copolymers on the coalescence efficiency in blends of poly(propylene oxide) and poly(ethylene oxide) was investigated. The solubility and the degree of interfacial adsorption of the copolymer were adjusted by means of temperature and its molecular weight. In each case, the copolymer was sufficiently soluble that the equilibrium amount of adsorbed species was established rapidly and only weak interfacial tension gradients could be measured. Therefore, under these circumstances, the capillary number was directly related to the coalescence efficiency and reduced only slightly, and the primary effect of the block copolymer was to inhibit drainage. Modifications of Milner's coalescence-efficiency theory [2] account for copolymer solubility, and of Chesters' theory [1] to incorporate the presence of copolymer have been developed and tested.


The authors gratefully acknowledge the financial support of the Goodyear Tire and Rubber Co., GE plastics, and NSF grant CTS-9215162.

11:50 AM FFS3.8
SCALING HIERARCHY OF POLYMER BRUSHES. Jürgen Büthe, Markus Biesalski, Martin Schimmel, University of Freiburg, Institute for Microsystems Technology (IMTEK), Freiburg, GERMANY; Diethelm Johnsmann, Max-Planck-Institute for Polymer Research, Mainz, GERMANY.

Both from a theoretical and from an experimental point of view much attention has been directed towards systems where macroscopic-cuits are terminated attached to a solid substrate. Several such systems were developed in the past, mainly to investigate the properties of the polymers are reactive with appropriate surface sites (grafting to technique). To avoid some problems associated with this technique, we investigated the polymer systems directly on the surfaces of the substrates by using self-assembled monolayers of inhibitors and polymerization in situ (grafting from). Following this grafting from approach polymer monolayers having a precisely controlled film thickness over the range between 1.5 and 1500 Å could be synthesized. By adjusting the chemical composition of the attached polymer, surfaces with tailor-made properties can be prepared. The swelling of neutral and charged polymer brushes in contact with solvent is studied by Total Internal Reflection Ellipsometry. The scaling behavior of neutral and polyelectrolyte brushes attached to solid surface will be described.

SESSION FF4/DD4: JOINT SESSION:
POLYELECTROLYTES AND PROTEINS AT SURFACES
Chair: Alagnet Kairaa
Tuesday, April 25, 2000
Metropolitan I (Argent)

1:30 PM FF4.1/DD4.1

Adhesion, proliferation, differentiation and migration of cells in their native environment are critically dependent on their interaction with the surrounding extracellular matrix (ECM). Therefore, in order to promote biointeraction, cells must "believe" they are "at home". In the future, a better understanding of cellular processes between the ECM ligand proteins and the cell membrane receptors will give us tools to engineer the developing of cell cultures (potentially human tissue) to give desirable properties. For the development of bioactive polymer surfaces, it is important to be able to control and retain the conformation of immobilized ligand groups, since this has an effect on the surface-cell interaction. Surfaces prepared by coupling of ligands directly to the surface can exhibit reduced biological activity owing to steric hindrance or conformational changes. A spacer group between the matrix and the ligand may facilitate effective binding and shield the ligand from the surface to circumvent these problems as will be presented here.

2:00 PM FF4.2/DD4.2
BIOLUBRICATION: THE SHEAR OF ADSORBED POLYELECTROLYTES AND OF POLYMER BRUSHES. Jacob Klein, Xueyan Zhang, Manfred Wilhelm, Weizmann Institute of Science, Rehovot, ISRAEL.

The lubrication of mammalian joints takes place at the interface between articular cartilage layers as they rub past each other. To study and understand this effect at a microscopic level, we have used a...
surface force balance with unique sensitivity in measuring both normal and frictional forces to examine the friction between compressed layers of neutral polymers and charged polymer brushes. Our results reveal that entropic factors play a crucial role in reducing the frictional forces and may thus underlie the extremely efficient lubrication known to be active in biological joints. For the case of neutral random walks, chains, configurational entropy resulting from excluded volume effects leads to large osmotic repulsion between the compressed surfaces, and enables large loads to be borne with a very fluid interfacial layer as they slide past each other. For the case of charged random walks, an additional potential barrier is formed by the electrostatic interactions, leading in this case to the formation of a closed-loop conformation. We have employed the self-assembly and cell recognition properties of peptide fragments (thus far derived from extracellular matrix fragments) that we have ligated synthetically by attaching a phospholipid-lipase, double-chain, hydrotropic tail. Lipidation confers interesting amphiphilic and self-assembling properties on the molecules and enables the stable deposition of layers of peptide amphiphiles on surfaces. Specifically, we have been using peptide amphiphiles to functionalize surfaces with peptide fragments derived from collagen and fibronectin. Deposition of these molecules by Langmuir-Blodgett methods gives a very high degree of control over the density and orientation of the surface molecules. This in turn enables us to explore the effects on cell response of peptide density and molecular architecture variations with a great degree of precision. The principal results so far, which seem to have some generalization for different kinds of peptides, are that there is an optimum peptide density for each kind of peptide fragment, and that the architecture of peptide presentation is a very sensitive control of bioactivity. Examples will be given of these effects.

3:15 PM FF4.5/DD4.5

BIOFUNCTIONALIZATION OF SURFACES WITH PEPTIDE AMPHIPHILES. Matthias M. Eggeling, College of Engineering, University of California, Santa Barbara, CA.

Peptides carry enormous capacity and versatility for participating in specific ligand-receptor interactions. As small parts of proteins, they offer the possibility of delivering a selected activity in constructing a biofunctionalized surface or interface, absent other, undesired activities present in the full protein molecule (e.g., immunogenicity). We have been exploring the self-assembly and cell recognition properties of peptide fragments (thus far derived from extracellular matrix fragments) that we have ligated synthetically by attaching a phospholipid-lipase, double-chain, hydrotropic tail. Lipidation confers interesting amphiphilic and self-assembling properties on the molecules and enables the stable deposition of layers of peptide amphiphiles on surfaces. Specifically, we have been using peptide amphiphiles to functionalize surfaces with peptide fragments derived from collagen and fibronectin. Deposition of these molecules by Langmuir-Blodgett methods gives a very high degree of control over the density and orientation of the surface molecules. This in turn enables us to explore the effects on cell response of peptide density and molecular architecture variations with a great degree of precision. The principal results so far, which seem to have some generalization for different kinds of peptides, are that there is an optimum peptide density for each kind of peptide fragment, and that the architecture of peptide presentation is a very sensitive control of bioactivity. Examples will be given of these effects.

3:45 PM FF4.6/DD4.6

POLYELECTROLYTE BRUSHES: SIMULATION AND SCALING THEORY. Christian Seidel, Felix S. Casjens, Roland R. Netz, Max-Planck-Institut für Colloide und Interfacen, Gölz, GERMANY.

Polypeptide brushes are important with respect to fundamental as well as applied research. However, both in experiment and in theoretical work, polyelectrolytes are a challenging subject with many unresolved problems. In this situation, computer simulations are a powerful tool to validate theoretical models, and to predict new phenomena and regimes which are not easily observable experimentally. We use stochastic molecular dynamics to study end-grafted polyelectrolytes for varying chain lengths, anchoring densities, degrees of ionization, concentration sizes and Bjerrum lengths. The model includes counterions explicitly, and the full Coulomb interaction is treated using a direct summation technique proposed by Echemendia and modified by Speth. At Bjerrum lengths slightly below the Manning condensation limit we obtain new collapsed phases for strongly charged chains. The brush height scales linearly with grafting density, a behavior which is known for uncharged brushes in poor solvent. This is in disagreement with the accepted scaling law for the osmotic regime, which states that the brush height becomes independent of grafting density. We believe that this is caused by strong counterion condensation effects. The new brush phases can be understood by an extended scaling model which includes Coulomb correlation between charged monomers and counterions. For partially charged brushes a boundary layer exists between the scaling regimes given by theory. Reducing the counterion size we find the osmotic regime in agreement with our scaling theory. The phase diagram, Varying the Bjerrum length we obtain a non-monotonic behavior of the brush thickness with a maximum followed by a coupling where already a considerable part of counterions has left the brush.

4:00 PM FF4.7/DD4.7

ADSORPTION OF HYDROPHOBIC POLYELECTROLYTES (PSE) ONTO NEUTRAL SURFACES. O. Tóthdoly, R. Ober, C. Williams, Collège de France, Paris, FRANCE.

We are interested in the adsorption of strongly charged polyelectrolytes (Polyethylene sulfonate with a ratio of between 20 and 90 %) on neutral and hydrophobic interfaces. The case of solution/air interface is investigated by Langmuir trough measurements, ellipsometry and X-ray reflectivity. The low adsorption rate, common for most polyelectrolytes, is also observed here and is explained by an electrostatic barrier effect. A maximum of adsorption with the ratio of saturation is observed. We revealed coexistence of a barrier that prevents complete desorption. The existence of these energetic barriers leads to strong hysteretic phenomena and the state of an adsorbed layer in contact with a solution strongly depends on its history. Concurrently, adsorbed layers at the solid/liquid interface are studied by a new technique of high-energy X-ray reflectivity across water adsorbed layers are always very thin (≤20 Å) confirming the fact that the layers are monomolecular.
Anomalous adsorption of polyelectrolytes onto charge-regulated self-assembled monolayers (SAMs) has been observed in recent experiments (M. Mayes and M. Mayes, submitted). In these studies, the charge density of the surfaces was changed through variations in the pH. The thickness of the adsorbed layer was observed to change abruptly from 25Å to 5Å over a narrow pH range. We extend the investigation to include the adsorption of charged biopolymers (e.g., polylysine). Further, to determine the influence of the spatial distribution of surface charge on the adsorption process, charge-modulated SAMs were prepared using the micro-contact printing technique (J. Thomas, Advanced Materials, 11, 1031 (1999)) and polyelectrolyte adsorption on those modulated surfaces was investigated.

4:30 PM FF4.9/DF4.9 ENDOTHELIAL CELL GROWTH AND PROTEIN ADSORPTION ONTO HETEROGENEOUS SELF-ASSEMBLED INTERFACES. B.J. Furgiuele, Bastille Pacific Northwest National Laboratory, Richland, WA; C. Tisdell, B. Rosner, University of Washington, Seattle, WA; D.L. Albala, Pennsylvania State University, University Park, PA.

Biological interactions onto interfaces such as endothelial cell adhesion and growth are of great importance to medical technologies including artificial implants and tissue engineering. The success of a biomaterial depends largely on how well surfaces promote or inhibit protein and cell interactions. It is believed that proteins adsorb onto surfaces and then mediate interactions with cells via specific interactions between protein domains and integrin cell membrane receptors. The role of the surface in controlling responses, however, is not well understood. The effects of surface chemistry features such as functional group density and surface structure have not been well studied largely due to lack of availability of well controlled and characterized surfaces. We report studies of endothelial cell adhesion and growth and protein adsorption onto tailored chemically heterogeneous self-assembled interfaces composed of thick gold containing mixtures of COOH-CH3 and COOH-CH2 functional groups. Surface composition and site arrangement was studied using x-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectroscopy (TOF-SIMS). We found that endothelial cell growth was maximized onto mixed functionality surfaces compared to single component surfaces. There were differences in cell growth between the two mixture types which we attribute to higher degrees of phase segregation in the COOH-CH3 compared to COOH-CH2 mixtures. The adsorption and stability of albumin (Alb), vitronectin (Vn) and fibronectin (Fn) varied with mixed SAM surface composition. Cell growth was maximal on the highest surface fraction of adhesive proteins and the lowest Vn adsorbability (i.e. decreased Vn binding strength). These results suggest that the mixed surfaces control the composition and binding strength of adsorbed proteins via a phase-separated layer which affects cell receptor interactions and mitogenic activity.

4:45 PM FF4.10/DD4.10 PROTEIN INTERACTIONS WITH PDMS DURING INTERFEcial PDMS RESTRUCTURING AND DEFORMATION. Feng Li and Maria Santore, Lehigh University, Department of Chemical Engineering, Bethlehem, PA.

We report the influence of surface properties on the adsorption kinetics of immunoglobulin onto modified PDMS (polydimethyl siloxane) surfaces. It was found that the hydrophobic surface of native PDMS has a high affinity for immunoglobulin, which adsorbs in abundance at the transport-limited rate. Corona treatment of PDMS yields a relatively hydrophobic surface with minimal affinity for immunoglobulin. In the ~100 hours following surface treatment, the hydrophobic nature of the surface recovers (as evidenced by contact angle evolution). The affinity, rate of adsorption, and ultimate coverage of immunoglobulin also increase, but not at the rate of the contact angle evolution. Stretching the surface after corona treatment accelerates this effect and increases the extent of recovery. The recovery is attributed to oligomeric PDMS fragments that diffuse to the surface after its chemical treatment.

SESSION FF5: POSTER SESSION.
INTERFACES, ADSORPTION, AND PROCESSING IN POLYMER.
separated films. We report on the study of mapping phase dynamics of polymer blend films using near-field scanning optical microscopy (NSOM). NSOM was used to identify the presence of a sharp fiber-optic probe with the sample of interest to image surfaces with a resolution beyond the diffraction limit of conventional optics. We investigated the phase dynamics of a thin film blend of polystyrene (poly(styrene)) and poly(3-octylthiophene) (poly(3-OT)). Simultaneous topography, transmission, and fluorescence NSOM images taken on these samples at different annealing stages revealed many previously unobserved details of phase separation. For example, our results showed that poly(3-octylthiophene) in the film sample even below the glass transition temperature (Tg) of bulk polystyrene when these molecules are cast with polystyrene which has a lower Tg and acts as a plasticizer. Samples annealed at temperatures above or below the Tg of poly(3-octylthiophene) showed that poly(3-octylthiophene) covers the polystyrene in these films. Artifacts that appear in near-field data on samples with large or varying film thickness or topography were also identified and shown clearly being pursued towards a correct quantitative evaluation of these films

**F5.4**
POLYMERIZATION KINETICS OF NORBORNENE ON GOLD NANOPARTICLES. Qinghong Fu, Dale L. Huber, Thomas A.P. Seely, Institute of Materials Science, University of Connecticut, Storrs, CT.

Polymerization of norbornene was initiated by a ruthenium alkylidene (Grubbs catalyst) on modified gold nanoparticle surfaces. 1HNMR was used to determine the polymerization kinetics of norbornene on modified gold nanoparticles as well as in solution. 5-Norbornene-2-carboxyl chloride was synthesized in order to modify the gold nanoparticles that were previously prepared with hydrogel end groups to introduce norbornene on the surfaces. Bis(tricyclohexylphosphine) benzylidene ruthenium(IV) chloride, was then used to react with the surface-bound norbornene molecules. The concentration of the monomer left during the polymerization was calculated according to the changes in the areas between the peaks on norbornene double bonds and the peaks on double bonds in polymer backbone. It was found that polymerization of norbornene at the same monomer to catalyst ratio by the homogeneous catalyst was completed in less than 10 minutes. However, the polymerization on modified gold exhibited first order polymerization kinetics.

**F5.5**
THERMOMECHANICAL RELIABILITY MODELING OF POLYMER/METAL INTERFACES IN MICROELECTRONIC APPLICATIONS. Sung-Yong Kong, Department of Materials Science and Engineering, Stanford University, Department of Materials Science and Engineering, Stanford, CA; Aml Kirtikar, Intel Corporation, Assembly Technology, Chandler, AZ.

Adhesion and progressive (time or loading cycle dependent) debonding may significantly affect the performance and reliability of microelectronic packaging structures. In particular, temperature and moisture stress responses are expected to play a major role in the long-term reliability of these packages. Models that incorporate these effects are currently being developed, they can lead to premature failure and reduced lifetimes. These models are driven by residual stresses remaining from processing, thermal cycling during use, and mechanical or vibrational loading. In this study, the effect of environment on the long-term reliability of the devices was investigated on interfacial adhesion and subcircular debonding of a representative polymer/metal interface under both monotonic and cyclic fatigue loading conditions. While the steady-state interfacial fracture energy is expected to be insensitive to moisture conditions, increasing humidity decreased the initiation value for debonding, even at low partial pressures of water vapor. Fatigue debond extension threshold values and the entire subcritical debond curves were extremely sensitive to temperature, and proportional to the relative humidity of the water in the test environment. Debonding was modeled using chemical reaction rate theory and rheological process at the debond tip. Activation energies were determined for the different stages of the debonding and growth, and a model was presented to account for the effects of loading, humidity and temperature on subcritical debond-growth rate behavior.

**F5.6**
STUDY ON POLYSTYRENE CAPSULED EXPLODED GRAPHITE/SBS COMPOSITES. Peng Xiao, Kecheng Gong, Polymer Structure & Modification Res. Lab, South China University of Technology, Guangzhou, PR CHINA.

Inorganic particulate-filled polymer systems a significant problem is caused by the nonuniformity of dispersion of the discrete phase in the polymer matrix, giving rise to fluctuations in the composite properties. Generally surface modification of the filler by a suitable coupling agent partly reduces this problem by enhancing surface interaction between the two phases. Here a surface modification method of fiber's encapsulation by polymerizing monomer in the presence of filler is put forwarded. Surface modification of exploded graphite is carried out by encapsulating exploded graphite by styrene polymerization. Then we introduce the encapsulated exploded graphite into styrene/butadiene/styrene triblock copolymer (SBS) by melt mixing. Result shows encapsulation of alternate dispersions in the composite. The composite has a relative low threshold value of electrical conduction than that of unmodified exploded graphite filled SBS system. And also high mechanical strength, high thermal conductivity and low density compositions are obtained.

**F5.7**
NOVEL SILICON ORGANIC COMPOUNDS TO ENHANCE INTERFACIAL ADEHSSION AND PROCESSABILITY OF POLYMERS. W.-F. Wang, Kecheng Gong, Polymer Structure & Modification Res. Lab, South China University of Technology, Guangzhou, PR CHINA.

Traditionally, silicon-containing fillers must be surface modified with oxidative coupling agent or with organosilicon reagents to reduce the interfacial adhesion process to promote polymers-filler interaction via covalent chemical linkage. However, organosilanes are expensive and significantly increase the cost of products. Here, we present a novel, inexpensive type of silicon organic compounds containing hydrophilic and functionally hydrophilic groups through a new surface-activation process. These silicon organic compounds are some viscous transparent liquid and stable to air for months. They can be used not only to replace expensive silane coupling agent and silicon oil, but also to improve the processability of polymer. After addition of the silicon organic compounds, an inter-phase region between fillers and polymer developed acting as binders, coupling agents, lubricants, and additive. A small amount of the silicon organic compounds is used to modify precipitated silica on filling silicone rubber, the results show that the properties of rubber can compared with the rubber filled with organosilane-modified silica.

**F5.8**
ADHESION MICROMECHANICS OF SOFT POLYMERIC ADHESIVES ON SILICONE RELEASE COATINGS. Géraldine Josse, Costantino Creton, Laboratoire PCSI, ESPCI, Paris, FRANCE.

We investigated the adhesion mechanisms of model acrylic pressure-sensitive-adhesives (PSA) on silicone release coatings. We used a custom designed probe test setup, allowing the video observation of the mechanisms of deformation in situ, while a flat-ended cylindrical probe was removed from the adhesive film. The adhesive was an emulsion copolymer based on n-Butyl acrylate and 2-ethylhexyl acrylate and acrylic acid. A layer approximately 100 m thick was deposited by doctor-blading on a microscope glass slide. The release coatings were crosslinked elastomers of pol(ydimethyl silicone) and were deposited by spin-coating (thickness of about 1 μm) on the previously polished steel probe. The adhesion energy of the acrylic adhesive on a surface coated with a PDMS elastomer was very low. However, when a rigid and relatively poly bulky resin was incorporated into the network, the adhesion energy was increased significantly, while the surface tension of the silicone was hardly modified. We investigated the role of the resin in the bonding mechanisms and the coupling existing between the rheological properties of the adhesive and the bulk deformation mechanisms occurring in the adhesive layer, and the surface properties of the silicone layer. We observed in particular that the presence of the polar resin in the elastomer favored the nucleation of multiple crack and interfacial splitting, which also favored the propagation of finger instabilities. Also the growth rate of these multiple interfacial cracks for a given value of applied average strain was much lower for the resin-rich elastomers favoring therefore the formation of fibrils, which increased the adhesion energy.

**F5.9**
THE EFFECTS OF GRADED ELASTIC AND YIELD PROPERTIES ON ADHESION IN AN UNDERFILL-SILICON DIOXIDE SYSTEM. Don Maibeneg, Reinhold Dasakal, Stanford University, Department of Materials Science and Engineering, Stanford, CA.

Adhesion of polymers is greatly affected by the amount of plastic deformation in the polymer. In this study, the well-known effect of underfill settling, where hard silica beads tend to accumulate toward the bottom of the underfill layer, is utilized to provide graded elastic and plastic properties in the polymer layer. Samples were fabricated with an underfill layer sandwiched between two silicon substrates. Significant settling of the underfill beads was achieved with standard curing conditions. Samples were cut into double-cantilever beam fracture specimens to accurately quantify critical adhesion energy. Comparisons were made between the interface to which the beads had settled and the interface away from the settled region. Cross-section SEM micrographs were analyzed to determine the volume fraction of the silica beads as a function of position in the
Adhesion strength of polyimide/Cr interfaces was measured using T-peel test on polyimide/Cr/Cu structure fabricated on RF-plasma treated BPDA-PDA polyimide, and correlation between adhesion strength and angle was investigated. Adhesion strength of BPDA-PDA/Cr interface decreased with increasing the Cu/Cr film thickness to a critical value, and then increased with further increasing the metal film thickness. When the thickness of Cu/Cr metal film was below a critical value, plastic bending of metal film occurred during T-peel test. However, plastic bending of polyimide has been observed with metal films thicker than a critical thickness. A critical thickness of metal film, where transition from metal bending to polyimide bending occurred, became thinner with decreasing the yield strength of metal film and increasing thickness of polyimide. Without depending on the plastic bending of metal film or polyimide, adhesion strength increased with increasing the peeling angle during T-peel test.

**F5.11**  "NMR INVESTIGATION OF THIN FILM ZDL BACKBONE DYNAMICS ON CARBON SURFACES". Xuejin Kim, Christopher A. Khug, Department of Chemical Engineering, Stanford University, Stanford, CA; Charles G. Wade, Materials Analysis and Characterization, Almaden Research Center, IBM, Sun Jose, CA.

Perfluoropolyether lubricants are used to decrease dynamic as well as static friction during head-disk contacts in today’s hard disk drives. Increasing growth in storage densities places great demands on the performance of this fabrication. Conversions of 19F NMR spin-lattice relaxation time, $T_1$, and spin-spin relaxation time, $T_2$, for monodisperse Zhd [H(OH)OCF$_2$OC(O)OH] and [H(OH)OCF$_2$OCF$_2$OC(F)OH] film on carbon surfaces were made to obtain information about the backbone mobility of the surface bound polymer. The spin-lattice relaxation time decreases and the line width increases with decreasing Zhd coverage, while the spin-spin relaxation time constant as the coverage of Zhd is varied. Further variable temperature relaxation studies show that the fast, local motions of the polymer are not affected while the slower, longer-range motions are greatly restricted when the polymer is adsorbed on the surface. These results correspond to the fast, local conformation of the polymer described by other studies using surface energy and TPD measurements and ab initio calculations.
fact that the particle pertains or not to a cluster, and to the cluster size). This indicates that, under our test conditions, the rupture of contact can not be expressed or was expressed in terms of kinetic work of adhesion. Viscoelastic and plastic dissipations occur in a zone whose dimensions are governed both by velocity and by sample size. Compared to the other adhesion tests, the nanoscope one highlights that the adhesion force of latex at very low concentration depends not only on molecular characteristics of the latex but also on cooperative effects of the nearby particles.

**FF5.16**
**DETERMINATION OF SUB-MICRON ORIENTATIONAL ORDER**
**PARAMETERS IN THERMOTROPIC LIPID CRYSTAL**
**POLYMER BLENDS**
Jennifer E. Taylor, Matthew Libera, Stevens Institute of Technology, Dept of Chemical, Biological, and Materials Engineering, Hoboken, NJ.

A novel electron-optical approach has been developed to evaluate structure-processing relationships in lipid crystal poly(cholesteric) (LCP) fibers at sub-micron length scales. This method is based on both digital control and data acquisition from a 200keV Transmission Electron Microscope (TEM). Spatially resolved diffraction data can be used to quantitatively define molecular orientation with a spatial resolution that is more than ten times better than X-ray techniques. Furthermore, the degree of orientation from each focal plane of the electron beam can be correlated with real-space image data. This paper describes the application of spatially resolved orientation mapping to re-drawn and annealed HBA/HNA fibers. The average orientation order parameter increases as expected, when drawn fibers are annealed. Director maps constructed at a spatial-resolution of ~100nm show that domains in local order can depart by as much as ~20% from the average. No obvious skin-core effect is detected in these fibers (~15 microns in diameter) though skin-core structure is clearly present in larger dimension markings where gradients in shear flows are more pronounced. Some local regions (~100nm) in the annealed fibers appear to have crystal-like order.

**FF5.17**
**AMINE-QUINONE POLYIMIDES AS COATINGS THAT PROTECT IRON AGAINST CORROSION.** M.J. Han, Haimin Bie, Gary W. Warren and David E. Niles.

Amine-quinone diamine monomers were prepared by reaction of benzoxazine with either 4,4’-methylene diamine or 4-Acetoxynaphthylene. The monomers were used to prepare a series of amine-quinone polyimides by condensation with a tetracarboxylic acid dianhydride, either 3,3’/4,4’-dianhydride terephthalic acid, 4,4’- [hexafluoroisopropylidenedi]phthalic anhydride, to give the polyimide amide, followed by thermal imidization. The polyimides had thermal decomposition temperatures in excess of 500°C. An amine-quinone polyimide amide was coated onto iron squares, and then thermally imidized. For comparison, a conventional polyimide coating was prepared that contained 4,4’-methylene dianhydride and 3,3’/4,4’-dianhydridoterephthalic acid. The coatings were exposed to sodium chloride electrolyte and electrochemical impedance spectroscopy was used to characterize the changes that occurred. After three days exposure a second time constant appeared in the low frequency region of the phase angle curve for the conventional polyimide. The second time constant was due to an electrochemical double layer and was indicative of electrolyte diffusing through the coating and breaking the adhesive bond between the polymer and the metal. The iron showed evidence of corrosion. After more than 24 days exposure, the coating containing the amine-quinone polyimide did not show a second time constant. Clearly the adhesive bond between the amine-quinone polyimide and the iron surface was stronger and better able to resist attack by moisture.

**SESSION FF6/EE6: JOINT SESSION**
**NANOSTRUCTURES FROM THIN FILMS TO BULK**
Chair: Peter F. Green and Sanat K. Kumar
Wednesday Morning, April 26, 2000
Metropolitan I (Angle)

**8:30 AM • FF6.1/EE6.1**
**STRUCTURE, DYNAMICS, AND PROPERTIES OF POLYVINYLCYCLOXANE BASED PENTABLOCK COPOLYMERS.** Frank S. Bates, Martin Vigild, Kim Chaffin, Chin Chiu, University of Minnesota, Minneapolis, MN; Glenn Fredrickson, UC Santa Barbara, Santa Barbara, CA; Stephen Hahn, Dow Chemical Company, Midland, MI.

Polyyvinylcyclohexane (V), which is produced by catalytically hydrogenating polyisoprene, is characterized by a glass transition temperature of 147°C, a high modulus, and excellent optical properties. However, owing to a large entanglement molecular weight (Mw=40,000 g/mol) this material is extremely brittle thus restricting the range of engineering applications. In order to improve the mechanical properties we have prepared VEV triloblock and VEVV pentablock copolymers where E refers to semicrystalline hydrogenated polybutadiene. The phase behavior (morphology and order-disorder transitions), rheological, and nonlinear viscoelastic temperature dependencies of the copolymers have been characterized revealing several dramatic effects associated with the change in architecture from triloblock to pentablock including heretofore unreported shear-induced microstructure alignment and improvements in toughness. These findings will be discussed in the context of current theory and experiment regarding the thermodynamics and dynamics of block copolymers.

**9:00 AM • FF6.2/EE6.2**
**DOMAIN MORPHOLOGY IN LIQUID-CRYSTAL POLYMER BLENDS.** Amelia M. Lopez, Andrew J. Liu, UCLA, Department of Chemistry and Biochemistry, Los Angeles, CA; Sharon C. Glotzer, Stephen A. Langier, NIST, Gaithersburg, MD.

Small molecule liquid crystals and polymers demix into two coexisting phases, one rich in polymer and isotropic, and the other rich in liquid crystal and orientationally ordered. The domain morphology of liquid crystal/polymer blends therefore depends on the interplay of two kinetic processes, the kinetics of phase separation and the kinetics of phase ordering. We show that the interplay can lead to morphologies not observed in isotropic binary blends and to slower domain.

**9:30 AM • FF6.3/EE6.3**
**ENTROPICALLY DRIVEN PHASE SEPARATION OF HEAVILY BRANCHED LINEAR POLYMERS.** Baoan Chen, Frank S. Bates, Timothy P. Lodge, Univ of Minnesota, Dept of Chemical Engineering and Materials Science, Minneapolis, MN.

Small Angle Neutron Scattering (SANS) has been used to examine the melt phase behavior of heavily branched random copolymer poly(ethylene/ethylenylsiloxane) blended separately with two linear random copolymer poly(ethylene/ethylene). Molecular architecture is the only difference between the two components of the blends. The molecular weights of the two linear random copolymer poly(ethylene/ ethylenylsiloxane) are 57 kg/mol and 201 kg/mol, respectively. The heavily branched polymer has a molecular weight of 750 kg/mol. Unlike many previous studies that concentrate on the branched species, this heavily branched polymer consists of 54 long branches on average, where each of them has molecular weight of 13 kg/mol. Three different volume compositions of 25/75, 50/50, and 75/25 have been investigated for both types of blends. SANS results indicate that all blends containing the low molecular weight linear polymer (57 kg/mol) form single phase mixture while all blends containing the high molecular weight linear polymer (201 kg/mol) phase separate.

**9:45 AM • FF6.4/EE6.4**
**PHASE SEPARATION IN POLYMERIC FLUIDS SUBJECTED TO A TEMPERATURE GRADIENT.** Ming Li, Shengqiang Xu, Eugenia Kamacheva, University of Toronto, Department of Chemistry, Toronto, ON, CANADA.

We studied phase separation in thin horizontal layers of binary and ternary off-critical polymeric fluids subjected to a vertical temperature gradient. Under particular conditions surface-tension- or buoyancy-driven convection occurs in the liquid layer that is imposed on phase separation in the system. Convection produces hexagonal and roll patterns with a high degree of order and symmetry on the length scales substantially smaller than in single-component systems. We demonstrate that convection patterns can be trapped in a solid state by using UV-induced polymerization of the reactive oligomers.

**10:15 AM • FF6.5/EE6.5**

A series of oligomeric and polymeric materials comprising mildly amphiphilic monomers have been investigated by OM, TEM and rheological analysis in order to observe the process by which they order and to determine the structure and properties of their self-assembled structures. Polyelectrolytes with pendant hydrophobic groups were used. The phenyl groups were bisubstituted in the 3 and 4 positions, or trisubstituted in the 3,4, and 5 positions, with allyl tails of various length. Narrow molecular-weight polydispersity samples were obtained with the average degree of polymerization for different samples ranging from 4 to 1000. Low and high molecular weight materials that form the columnar hexagonal phase were compared, and oscillatory shear rheology indicates only in the high molecular weight material that significant fluctuations of order remain up to 20°C above the
10:30 A.M. FF6.6/EE6.6
THE MORPHOLOGY OF BLENDS OF LINEAR AND SHORT-CHAIN BRANCHED POLYETHYLENES IN THE SOLID STATE BY SMALL ANGLE X-RAY SCATTERING, DIFFERENTIAL SCANNING CALORIMETRY AND TRANSMISSION ELECTRON MICROSCOPY. G.D. Wignall, J. S. Lin, Oak Ridge National Laboratory, Solid State Division, Oak Ridge, Tenn.; R. C. Adams, University of Florida, and Florida State University, Department of Chemical Engineering, Tallahassee, Fla.; J. D. Landa, DuPont Central Research and Development, Wilmington, Del.; L. Mandelkern, Florida State University, Institute of Molecular Biophysics, Tallahassee, Fla.; M. H. Kim, Oak Ridge National Laboratory, Chemical and Analytical Sciences Division Oak Ridge, TN; G. M. Brown, Exxon Chemical Company, Baytown Polymers Center, Baytown, TX.

Differential scanning calorimetry (DSC), transmission electron microscopy (TEM), small-angle neutron and X-ray scattering (SANS and SAXS) have been used to investigate the solid state morphology of blends of linear (high density) and model short-chain branched (linear low density) polyethylenes (HDPE/LDPE). SANS indicates that the mixtures are homogenous in the melt for all compositions when the ethylene branch content in the copolymer is low (i.e., < 4 branch/lb., or 10 branch/mol, for a typical molecular weight of 100,000). However, due to the structural and melting point differences between HDPE and LDPE, the components phase segregate in the solid state and form a lamellar morphology with a periodicity typically in the range of 10-100 nm. The degree of separation is controlled by the crystallization kinetics and DSC, TEM, SANS and SAXS experiments have been used to investigate the solid state morphology as a function of component composition, the thermal history and the rate of cooling. It is shown that the combination of scattering microscopy and calorimetric techniques can provide detailed insight into the morphology on nm-length scales and give the compositions of the various populations of the lamellar crystals and the amorphous regions that these lamellae form.

*Managed by Lockheed Martin Energy Research Corporation under contract DE-AC05-84OR2140 for the U.S. Department of Energy.

10:45 A.M. FF6.7/EE6.7
CRYSTALLOGRAPHY, CURVATURE AND COORDINATION OF BICONTINUOUS BLOCK COPOLYMER NANOSTRUCTURES. H. Jinmai, Kyoto Inst. of Technology, Dept. of Polymer Science & Engineering, Kyoto, Japan; R. J. Sponzak, North Carolina State Univ., Dept. of Chemical Engineering and Materials Science & Engineering, Raleigh, NC; Y. Nishikawa, T. Hashimoto, Kyoto Univ., Dept. of Polymer Science & Engineering, Kyoto, Japan; S. D. Smith, Procter & Gamble Co., Corporate Research Division, Cincinnati, OH.

Within relatively narrow composition windows, block copolymers and their blends with a homopolymer, a second copolymer or a solvent have been found to microphase-order into bicontinuous nanostructures such as clusters, rods or ribbons (micronewton in tricomponent blends) morphologies. In-depth investigation of these morphologies by transmission electron microscopy and small-angle scattering is non-trivial due to the complexity of such nanostructures. In this work, we provide a detailed analysis of the gyroid morphology in terms of its crystallographic signature (compared to that of the double-diamond), its interface curvature (compared to a constant-thickness model) and its coordination distribution (including structural variation due to a grain-boundary) as discerned from transmission electron microtomography reconstructions. Results obtained from the gyroid indicate that the nanostructure is nearly cubic and possesses 3D symmetries. Three-fold coordination is, for the most part, observed and the distance distribution between junctions is determined. These results are quantitatively compared to those derived for the sponge, as well as those for polymer blends undergoing spinodal decomposition. The хорошо-averaged mean curvature for these systems is found to be sensitive to composition, whereas the хорошо-averaged Gaussian curvature is not. Structural characteristics exhibiting evidence of universality are identified, and experimental results are compared to those for a consistent set of model copolymers in the intermediate segregation regime when possible.

11:00 A.M. *FF6.8/EE6.8
SURFACE SEGREGATION IN MISCELLANEOUS BINARY POLYMER BLENDS. Christopher Ferrery, Polymer Program, University of Connecticut, Storrs, CT; David Pan, Xerox Corporation, Rochester, NY; Jeffrey T. Koberstein, Department of Chemical Engineering and Applied Chemistry, Columbia University, New York, NY.

The composition at the air-polymer interface of a multi-component polymer generally differs from that of the bulk material. In an immiscible polymer blend, this phenomenon is referred to as blending and depends on surface energy differences and other co-aggregation considerations. In miscible systems, the phenomenon is called surface segregation, and the resultant surface composition is dependent on a balance between the exchange chemical potential required to separate a monomer vapor to a molecular level from the surface and the resultant decrease in interfacial free energy. In this paper, we examine surface segregation for miscible blends of poly(styrene) and poly(vinyl methyl ether), a system with a lower critical solution temperature (LCST). Surface compositions were determined by analysis of surface tension data on polymer melt blends. Surface composition depth profiles were determined by angle dependent x-ray photoelectron spectroscopy. Data are presented for blends containing either a linear or polymerized poly(styrene). Permeation microscopy clusters the bulk interaction parameter and allows investigation of its effect on the surface segregation of the blend. We model the data using the Schmidt-Binder approach to square gradient theory. For the required equation of state, we employ both the incompressible Flory-Huggins theory and the Sanchez-Lucombe-Bhushan extension of compressible lattice fluid theory. The latter approach provides a more appropriate description of the bulk phase behavior for LCST blends.

11:30 A.M. FF6.9/EE6.9
SOLID-STATE BLENDING AND COMPATIBILIZATION OF POLYMER BLENDS BY CRYOGENIC MECHANICAL ALLOYING. Andrew P. Smith, Richard Scheber, Cail Aldred, North Carolina State University, Department of Materials Science and Engineering and *Physics, Raleigh, NC.

Cryogenic mechanical alloying has been employed to blend poly (methyl methacrylate) (PMMA) with up to 25 wt% polystyrene (PS) and poly (ethylene-alt-propylene) (PEP). High-energy ball milling in the solid state is considered here as a highly non-equilibrium process which may cause the phase separation that often plagues polymer mixing in the melt or in solution. Mechanical milling of the individual polymers reveals that their molecular and bulk properties depend sensitively on milling time, post-milling, and, for PMMA temperature. While molecular weight reductions are observed for PMMA and PEP, PI undergoes crosslinking due to the formation of free radicals during milling. In addition, the molecular weight decay for PMMA is more pronounced at higher temperatures, in contrast with the expectation of increased brittleness with decreasing temperature. Characterization of the as-milled blends by scanning transmission x-ray microscopy and transmission electron microscopy has demonstrated a nanoscale mixing within the blends, with the degree of mixing increasing with increasing milling time. Phase domains as small as 10 nm are observed after alloying for 10 hrs. Post-milling of the blends above the Tg of PMMA (which is dependent on milling time) induces morphological evolution, which varies for blends with PI and PEP. In blends containing PMMA thermodynamic compatibility is expected to drive phase separation within the system so that the intimal mixing gained as a result of milling is largely lost. Conversely, PI crosslinking inhibits molecular mobility so that the milling induced phase separation for PMMA and PI is, for the most part, retained even after annealing for long periods at high temperatures. These results indicate that cryogenic mechanical alloying consists of producing intimate blends of immiscible polymers that can, depending on interchain reaction, retain their nanoscale morphology.

11:45 A.M. FF6.10/EE6.10
STRUCTURE EVOLUTION DURING POLYMER DEWETTING AND DEMIXING: MANFRED SCM T.3, Peter Mueller-Buschbaum 3, Jochen Gutmann 3, 1Institut für Polymere, Dresden e.V., Dresden, Germany; Garching, Germany

Polymer thin films on a solid substrate can be unstable and then show the tendency depending on film thickness and temperature to dewet the substrate. In a polymer blend of incompatible components the dewetting is in competition with surface and interfacial segregation effects, and lateral phase separation will generally occur. These phenomena can be used to generate nanostructures, where regularly spaced droplet films of different morphologies and materials are investigated by scattering techniques as well as by direct imaging techniques, which are shown to be complementary. By Fourier transform of scanning force microscopy image a power density pattern is obtained, which gives a prominent length scale to be recognized. Scattering techniques on the other hand also provide information from the interface of the sample, where phase separation may have taken place. A wide range of structured surfaces and different roughnesses at the surface of the thin films can be formed.
SESSION FF7/D7. JOINT SESSION: MECHANICAL ASPECTS OF SOFT BIOMATERIALS INTERFACES
Chairs: Samuel I. Stupp and Kenneth R. Shull
Wednesday Afternoon, April 26, 2000
Metropolitan I (Argent)

1:30 PM **FF7.1/D7.1
BIOADHESIVE POLYMER FORMULATIONS THAT PROLONG DRUG DELIVERY ACROSS MUCOCAL SURFACES. Allan Hoffman, Chad Brown, Masashi Nakamura, Gochun Chen, and Yoshi Hayashi, Dept of Bioengineering, University of Washington, Seattle, WA; Wayne Gunzburg, Dean Pettit, Lotte Kreigard and James Mansour, Immunex Corp, Seattle, WA; Michael Roberts and Milton Harris, Sherwood Polymers, Huntsville, AL.

Bioresynthetic polymers are often added to drug formulations in order to prolong the residence time on mucosal surfaces such as the eye, the nose or the intestines. This does not necessarily lead to prolonged drug release from such formulations, since the drug may still be released too rapidly for the formulation swells and dissociates.

We have designed a family of polymeric formulations that combine bioadhesive polymers with additives or conjugates that cause gelation of the formulation. These formulations should be in the form of viscous gels at body temperatures, and should also be bioadhesive, leading to extended retention on oral surfaces, as well as to retarded diffusion of drug and prolonged duration of drug release. The synthesis, properties, drug loading and in vitro delivery profiles of several of these hybrid carrier systems will be described and discussed.

2:00 PM FF7.2/D7.2
THE INTERFACIAL INFLUENCE OF INTERFACE MECHANICAL BEHAVIOUR UPON DEFORMATION AND FRACTURE OF COMPOSITE POLYMER GELS. M. P. Plackett, V. N. Normand, S.J. Pomfret, D. Ferdinando and W.J. Frith, Unilever Research, Colworth Laboratory, Sharnbrook, Bedfordshire, UNITED KINGDOM.

The large deformation mechanical behaviour of mixed biopolymer gel composites, which are potential structural additives for foods, has been examined in both tension and compression. Composite gels were fabricated by addition of protein from mixed biopolymer solutions into a gelatin base, followed by gelatin, which results in discrete included particles that are co-set within a 'continuous' matrix phase. This structure can also be inverted by reversing the volume fractions of the respective phases. Two systems were investigated, gelatin/multidextrin, and gelatin/apoase.

The mechanical response of these materials was primarily determined by the individual constituent behaviour and the interfacial fracture resistance. For the gelatin/multidextrin system, interfacial debonding was observed, which resulted in a pseudo-yielding' response. A simple elastomer model was used to indirectly calculate an approximate interfacial fracture energy of ~0.25 J m^{-2} for this system. There was good agreement between this value and that obtained directly by peel testing, where a gelatin layer was cast directly onto multidextrin and subsequently peeled off. Conversely, debonding was not observed for the phase-separated gelatin/apoase system. Hence, it was possible to conduct peel tests with a gelatin layer cast onto apoase. The fracture energy obtained in this case was approximately 30 times greater than that for the gelatin/multidextrin system. This dramatic increase in interfacial fracture energy for this system, relative to gelatin/multidextrin, is believed to result in the lack of observed interfacial debonding noted for the actual composite structure.

2:15 PM FF7.3/D7.3
INTERFACIAL ADHESION OF BIOPOLYMER GELS MEASURED USING THE PEEL TEST. S.J. Pomfret, K.P. Plackett, V. Normand, W.J. Frith, Unilever Research Colworth, Bedford, UNITED KINGDOM.

The adhesion between layers of biopolymer gel has been measured using the 90 degree peel test. Gel bilayers, including gelatin, apoase, multidextrin and kappa-carragenan, were prepared in several ways. Some contract between two pre-gelled layers, while others are cast on top of one another, and phase separation between layers. The force required to separate these layers was measured and the results allow the interfacial interpolymer work to be compared with the function of gel preparation method used, and layer contact time. The expression that describes the force required to peel two layers apart includes terms to account for alternative methods of energy dissipation, such as peel arm extension, that occur in addition to interfacial fracture. Preliminary work has been made to evaluate these terms and hence allow determination of the interfacial fracture energy of the systems involved. The value of approximately 0.23 J m^{-2} for the interfacial fracture energy of a multidextrin/gelatin interface, formed by casting gelatin on multidextrin, is in good agreement with values indirectly observed from particle/matrix debonding experiments performed on composite systems.

3:30 PM FF7.4/D7.4
PH-DEPENDENT SWELLING BEHAVIOR OF HYDROPHILIC GELS WITH POLYSACCHARIDE, XICIE TIAN, Jian Xiao, Naof Lu, Xiaoning, Yang and Xing Fu, South China University of Technology, College of Food Engineering & Biotechnology, Guangzhou, PR CHINA.

It was known that charged polymeric networks have been recognized as useful matrices for delivering drugs because of their volume change in response to pH variation. However, most of the synthetic polymers have so far studied have poor bio-compatibility and probably have side effects when they are applied to human body as a biomaterial. On the other hand, polysaccharide, which is natural polymer, has good bio-intermiscibility. Therefore, the gel with polyanhydridic can be expected as a novel material like to biopolymer gel. In this study, the graft of polysaccharide and xylonitrile starch-PAN gel were prepared and also, the swelling behaviors of the gel with polyanhydridic in an aqueous with different pH values were discussed. The response of the graft gels was investigated by the pH-dependence of weight swelling ratio.

In a lower pH regionG=4, the swelling ratio of the graft gel glucose group in starch AN, 1; 6; molar ratio was almost constant. In a pH range above pH=4.0, the swelling ratio increased strikingly with pH up to pH=6.0, and showed a maximum at pH=7.0. Swelling and deswelling of the graft gel could be reversibly repeated many times by switching the pH values of 4.0 and 7.0. Also, experimental data indicated that the deswelling and swelling behavior was sharp and quick in the stage and then, became slow in the late stage. This is due to different mechanisms during the overall process of both deswelling or swelling. Also, the discussion of the aggregation structure-PH responsive property relationships of the graft gel with polysaccharide will be presented.

3:15 PM FF7.5/D7.5
ADHESION OF INJECTABLE SEMI-INTERPENETRATING POLYMER NETWORKS: Elizabeth A. Sile, Kevin E. Northwestern University, Departments of Biological Material and Biomedical Engineering, Chicago, IL; Elizabeth Fabbroni, Kenneth R. Shull, Northwestern University, Department of Materials Science and Engineering, Evanston, IL.

Neither polymer scaffolds nor tissue-engineered cartilage adheres to the native tissue lining cartilage defects which decreases the likelihood that integration will occur. Previously, we developed injectable poly[4-(N-isopropylacrylamido-co-acrylamide] [P[NIPAAm-co-AAC] hydrogels that supported bovine articular chondrocyte viability and promoted the formation of cartilage-like tissue in vitro. The goal of our current work was to develop injectable semi-interpenetrating networks (semi-IPNs) comprised of P[NIPAAm-co-AAC] hydrogels and linear peptide-functionalized P[AAC] chains containing sequences that adhere to the extracellular matrix of native cartilage. The primary objective of this study was to determine the effects of synthesis conditions on the material properties of the semi-IPN. The solvent, the molar ratio of AAC:NIPA Am in the hydrogel, and the molecular weight of the P[AAC] chains were varied, and the injectability, the volume change when heated to 37°C, and the lower critical solution concentration (LCST) of the semi-IPNs were determined. P[NIPA Am-co-AAC] hydrogels served as control. The semi-IPNs demonstrated significantly smaller volume changes, as compared to P[NIPA Am-co-AAC] hydrogels, due to the P[AAC] chains. However, the P[AAC] chains did not significantly affect the LCST. The molecular weight of the chains affected the injectability of the semi-IPNs, as matrices with higher molecular weight chains were more difficult to inject. Finally, the solvent and the molar ratio of AAC:NIPA Am significantly affected the LCST and volume change of the semi-IPNs. To assess adhesive properties of the matrices, nanowire adhesion assays were performed on (1 × 10^6) monolayers of a semi-IPN using a coated hemispherical glass indenter. We observed a time-dependent increase in adhesion energy/disk modulus as a function of displacement, consistent with data reported previously for a model system. This work describes a methodology to study the effects of semi-IPN formulation and peptide sequence on adhesion to cartilage tissue. These semi-IPNs may be useful in cartilage regeneration applications.

3:30 PM FF7.6/D7.6
ADHESION OF PRESSURE SENSITIVE ADHESIVES WITH APPLICATIONS IN TRANSDERMAL DRUG DELIVERY. Marc B. Task and Reinhold H. Draxler, Dept of Materials Science and Engineering, Stanford Univ, Stanford, CA.
The growing use of transdermal devices for drug delivery, as well as the development of increasingly complex and novel patch designs, necessitates an understanding of the adhesion occurring between the device and the soft dermal layer. Pressure sensitive adhesives (PSAs) are used as the adhesive in this system due to their desirable properties of good peel, good bond strength, long-term adhesion, clean removability, and skin and drug compatibility. In addition, their high viscoelastic properties are necessary prerequisites for attachment to soft tissue. However, the adhesion of PSAs is not well understood, and the lack of knowledge or quantification is scientifically utilized in a mechanics approach to quantify the adhesion properties of representative PSAs. Adhesion of PSAs is accomplished by cavitation in the PSA and the formation of an expansive cohesive zone. The presence of such large-scale bridging provides significant energy dissipation and increased resistance to deformation. The strain energy release rate (G) during delaminating of a cantilever-beam sample, containing cavities as thin a layer of PSA as possible, was determined by the analysis of the data from these experiments using the compliance method. The indentation depths achievable are on the order of hundreds of nanometers for soft materials. This test method allows probing of the mechanical properties of the treated surface layer in energy-tREATED or mechanically altered polymers. Polystyrene was chosen as the material for this study because of its clinical and industrial importance. Further, polysiloxane can be produced with controlled morphology and molecular properties. This control provides a means for assessing the importance of these variables on both the surface properties and response to plasma treatment.

4:30 PM FFF7/10/DD7.10
STRENGTH AND TOUGHNESS OF AN ORGANICALLY REINFORCED CARBONATED APATITE BONE MINERAL SUBSTITUTE
Victoria C. Jeng, Reinholf H. Drexler, Stanford University, Dept. of Materials Science and Engineering, Stanford, CA.

Carbonated apatite materials resembling the mineral phase of bone have received considerable attention for biomedical applications. When formed at physiological temperature, they present significant potential for rapid bone repair, fracture fixation, and augmentation of load bearing hardware. To date, the strength and resistance to fracture of such apatites has been extremely low. This study investigates strategies to enhance the mechanical properties of a carbonated apatite bone cement, utilizing the addition of soft biological organic phases such as albumin, fetal bovine serum, collagen, and gelatin. The distribution of phases and the interface between the added phase and the apatite are characterized. The addition of soft organic phases is shown to have a marked impact on strength, reliability, and toughness of the bone mineral substitute.

SESSION FFF8: POLYMER COMPOSITES AND ADHESION

8:30 AM FFF8.1
INVESTIGATION OF PRESSURE SENSITIVE ADHESIVE STRUCTURE THROUGH LATEX BLENDING
Christophe Verge, Christian Laurichesse, Karine Loyer, CERDATO, Elf Atochem, Senningen, FRANCE, Ludwik Leibler, UMR167, CNRS Elf Atochem, Levallois, FRANCE.

Waterborne pressure sensitive adhesives (PSA) are widely used to bond together different materials. Typical examples are adhesive tapes, labels or stamps. The PSAs are often pressure-sensitive due to a fast spreading and drying polymer layer. It is important to ensure that the resulting film is not only sticky but also presents a significant creep and static shear resistance. Fine tuning of viscoelastic properties of the polymer is crucial. An attractive way to
enhance the creep resistance without adversely affecting film stickiness & to introduce in the latex, monomers able to develop specific interfacial reactions and thus yielding to a physically cross-linked network. Here we show how the introduction of ureido acrylic monomers in the latex changes the adhesive and cohesive properties of latex films. We use specific rheological measurements on thin films to comprehend the influence of viscoelastic properties of temporarily cross-linked polymers on adhesion strength and shear resistance of adhesive bonds. We show the importance of interfacial phenomena taking place at more microscopic scales namely at the latex surfaces. These effects can be exploited at large scale by the film formation process itself: the chains initially in the latex particles must interdiffuse, at least partially, to create a film with significant cohesion. In order to reach new insights on the mechanisms involved, we have studied blends of model hemexes having the same particle size and the same glass transition temperature set far below room temperature to allow chain diffusion. The blends investigated are constituted of an ureidoemulsion latex and a latex bearing controlled amounts of an ureido acrylic monomer. We find that even for low concentrations of latter hemexes the static shear resistance increases meaning that significant chain interdiffusion is possible even for polymers able to form physical cross-links.

9:00 A.M. FFS.2
ADHESION OF TRIBLOCK COPOLYMER-BASED THERMO-REVERSIBLE GELS AND PRESSURE SENSITIVE ADHESIVES. Kenneth R. Shull, Alfred J. Croasby, Cynthia M. Flammang, Northwestern University, Department of Materials Science and Engineering, Evanston, IL.

Triblock copolymers with poly(methyl methacrylate) (PMMA) end blocks and a poly(n-butyl acrylate) (PnBA) midblock have been synthesized as model thermoreversible gels and pressure sensitive adhesives. Three different monomers are dissolved in a variety of solvents at temperatures above 60 degrees C to form freely flowing liquids. At lower temperatures the PMMA endblocks associate so that the solutions form ideally elastic solids. In our case the solvent is 2-ethylhexanol, polymer volume fractions vary from 0.15 to 1.3 and the elastic moduli are close to 10,000 Pa. We have conducted three types of experiments to elucidate the origins of adhesion and bulk mechanical properties of these materials: 1) Weakly adhering gels: the adhesive properties of the gels are dominated by the PMMA endblocks. Very little adhesion hysteresis is observed in this case, although we do observe hysteresis associated with the fractional response of the gels. 2) Strongly adhering gels: by heating the gels in contact with a PMMA substrate, it is possible to bond the gels to a surface. Development of adhesion as the PMMA blocks penetrate into the PMMA substrate can be probed in this case. The cohesive strengths of the gels are found to be substantially greater than their elastic moduli, so that these materials can be reversibly extended to very high strains. These properties have enabled us to probe the origins of elastic shape instabilities that play a very important role in the behavior of thin adhesive layers. 3) Dried gels model pressure sensitive adhesives. Improving the solvent at low temperatures, the underlying structure of the gel is preserved, giving a thin elastic layer with excellent performance as a pressure sensitive adhesive.

9:15 A.M. FFS.3
SIMULATION OF INTERFACIAL FRACTURE IN HIGHLY CROSSLINKED ADHESIVES. Mark J. Stevens, Sandia National Laboratories, Albuquerque, NM.

The fracture of highly-crosslinked networks is investigated by molecular dynamics simulations. The sequence of molecular structural deformations that lead to failure are determined, and the connectivity is found to strongly control the stress-strain response and failure modes. A set of model, ordered networks are constructed to manipulate the deformation sequence to alter the fracture behavior. Compared to random, dynamically formed networks, these ordered networks can be made to have either much larger or smaller failure stresses and strains. By varying the number of bonds to the surface, the failure mode can be controlled to be either adhesive or cohesive. The ideal strength for an interface can be determined from the fracture of functionalized self-assembled monolayers (SAMs). Unlike the random networks, the failure stress of an ordered network is close to the ideal stress equal to breaking all bonds to the substrate. The strength for a SAM (e.g., octadecanethiol) is much lower than this ideal value for two main reasons. The number of interfacial bonds for an adhesive is much less than for two SAMs. Thus, the ideal interfacial fracture stress of the network is in fact much smaller than for the SAMs. However, all the linear SAMs have no chain bending, so the ideal stress is the same as for the interface. In this case, the strength of the SAM is much smaller than the ideal value. In the case of the interfacial strength of the SAMs, the strength is significantly reduced by the presence of a SAM on the substrate. However, the substrate has no effect on the strength of the SAM. The ideal stress for the interface is then the same as for the interface. Thus, the ideal stress for the SAMs is significantly reduced. In contrast, in the case of the interfacial stress of the network, the strength is significantly reduced by the presence of a SAM on the substrate.
interfacially entangled chains. Initial crack propagation results have confirmed our expectations in the compression-molded samples, demonstrating the importance of interfacial elements. It is also important to consider common industrial processing methods. Specifically, contact time, interface roughness, and molecular orientation are altered significantly when compression-molded samples are replaced with multi-layer coextruded samples. However, initial crack propagation test on multi-layer coextruded samples demonstrate similar trends in interface strength as compared with the compression-molded samples. This suggests that the importance of selecting polymeric components with appropriately tailored properties cannot be overlooked.

11:00 AM *FFS.7 THE EFFECT OF SURFACE CONTAMINATION ON ADHESIVE FORCES AS MEASURED BY CONTACT MECHANICS.
John A. Emerson, Gregory V. Miller, Christopher R. Screven, Sandia National Laboratories, Alburquerque, NM; Raymond A. Pearson, Lehigh University, Bethlehem, PA.

The contact adhesive forces between two surfaces, one being a soft hemisphere and the other being a hard plate, can readily be determined by applying an external compressive load to make the two surfaces and subsequently applying a tensile load to peel the surfaces apart. The contact region is assumed to be the superposition of elastic Hertzian pressure and of the attractive surface forces that act only over the contact area. What are the effects of the degree of surface contamination on adhesive forces? Clean aluminum surfaces of varying roughness were coated with hexadecane as a controlled contaminant. Values of the mechanical work of adhesion (Wa) were derived through the contact mechanics, via the KKR model, using a model silicone network for the elastomeric contact sphere. Variations in the thickness of the hexadecane were determined by ellipsometry. As the film thickness of hexadecane increases, Wa decreases. We have found that the Wa plane is the film thickness. However, for small amounts of contamination, there is no decrease in Wa. This work supported by U.S. DOE Contract DE-AC04-94AL85000.

11:15 AM *FFS.8 THE ROLE OF FIBER/MATRIX INTERFACE AS A STRESS TRANSFER MEDIUM IN POLYMERIC COMPOSITES.
Costas Galatios, Institute of Chemical Engineering and High Temperature Chemical Processes, Foundation of Research and Technology-Hellas, Patras, GREECE.

It is now well established that the tensile strength of a fiber reinforced material is determined by the strength distribution of the embedded fibers and the local stress redistribution caused by fiber fracture. The stress build-up in the broken fiber as well as the magnitude and stress redistribution in the intact fibers are governed by the material properties and, most importantly, by the strength and toughness of the fiber/matrix interface. Practically, long and short fiber composites are designed to provide toughening mechanisms by increasing the interface toughness in such a way as to balance the beneficial reduction of stress concentration with the resulting detrimental increase of the transfer length. The complexities of the mechanical behavior of composite materials are related to the fracture mechanics concept with the statistical aspects of both fiber and interfacial strength make the modeling of the strength of fiber composites a very difficult endeavor. In this paper, the link between interfacial characteristics such as fiber-matrix treatment, fiber size, as well as fiber type/modulus upon the fracture characteristics of high carbon fiber/epoxy resin composites were investigated. Three different coupon geometries were employed: namely single fiber model composites, 2D micro-composite tapes and full composite tensile coupons and beams. In all cases, the point-bypoint stress in the fiber was measured with the technique of remote Raman microscopy (ReRaM). The composite specimens were loaded incrementally in tension and the stress transfer profiles corresponding from fibers breaks, were closely monitored. The stress or strain along individual fibers as different levels of applied load has been monitored in an attempt to measure the transfer lengths in all three geometries and the stress concentration factors/affected lengths (PAL) in the case of full composites. The corresponding shear stress distributions were obtained through the stress transfer profiles with the use of a simple balance-of-forces equation. The redistribution of stress in fibers adjacent to a fiber break in the 2D and full composite geometries were determined as a function of distance from the fiber break.

11:45 AM *FFS.9 MEASURING INTERFACE STRENGTH IN SINGLE FIBER COMPOSITES: THE EFFECT OF STRESS CONCENTRATIONS.
Gale Holmes and Richard Peterson, National Institute of Standards and Technology, Gaithersburg, MD.

Fiber-matrix interface strength is known to be a critical factor in controlling the long-term performance of structural composites. This parameter is often measured by the single-fiber fragmentation test (SFPT). In the SFPT, a single fiber is aligned along the axis of a dog bone in an instrument having an extension failure that is typically 3 to 5 times higher than the fiber. The matrix is strained until the resulting fiber fragments are too short for a sufficient load to be transmitted into them to cause additional failure. The point load caused by the increase of the applied strain is determined by incorporating the average of the measured fragment lengths into a-micro-mechanics model. Recent observations in this laboratory have shown that the current models do not accurately account for the nonlinear behavior exhibited by the matrix during fiber fragmentation. As a result, a nonlinear viscoelastic model was developed (Holmes et al. 1999). Theoretically, this new model indicates that the interface strength is dependent on the testing rate. Experimentally, it has been shown that the final fragment length distribution in some systems is dependent on the testing rate (Holmes et al. 1999). However, data analysis using the new model indicates that the strength of the composite is promoted by the presence of high stress concentrations at the end of the fiber fragments. From the model, these stress concentrations were found to exist at very low strain values. Experimentally, the fragment distributions obtained from specimens tested by different testing rates were found to be significantly different at strain values well below the saturation strain. These results are consistent with the research of Johnkham and Galakas (1991) and finite element calculations performed by Correia (1990) and the composite failure is predicted by the presence of high stress concentrations and minimize failure of the fiber-matrix interface.

SESSION FF9: POLYMER SURFACES AND SURFACE MODIFICATION
Chair: Gregory S. Ferguson and Costantino Creton
Thursday, April 27, 2000
Metropolitan I (Argent)

1:30 PM *FF9.1 STRUCTURE AND RHEOLOGY OF INTERCALATED POLYMER COMPOSITES: POLYSTYRENE-PIVOLYESTER/POLYIMIDE COMPOSITES. Bhanwar Kishan-Singh, Jinhua Ren, University of Houston, Department of Chemical Engineering, Houston, TX.

The structure and viscoelastic properties of a series of polystyrene-polyisoprene block copolymers (PS-PI) based nanocomposites with varying amounts of dimethyl dioctadecyl ammonium modified montmorillonite (2C18M) are studied. The layered structure of the nanocomposites, with a typical height of 2.5-4.1 nm and independent of stress concentrations can promote failure of the fiber-matrix interface on the molecular level. Our results support this conclusion. In addition, our research results suggest that altering the SFPT testing rates can alter the magnitude of these stress concentrations and minimize failure of the fiber-matrix interface.

2:00 PM *FF9.2 MODELING SURFACE AND INTERFACE PROPERTIES OF LINEAR AMORPHOUS POLYMERS. Sylvain Goudem, Jocelyne Gay, Jean-Francois Gerard, Laboratoire Matériaux Macromoléculaires, INSIA Lyon, Villeurbanne, FRANCE, Rene Flichon, LMPB, Université C. Bernard, Villeurbanne, FRANCE, Jean-Louis Buret, Dept. Physique des Matériaux, Université C. Bernard, Villeurbanne, FRANCE.

Much attention has been recently focused on the observation and characterization of polymer surfaces at a molecular level. Experimental data concerning surface-Tg and mobility, chain orientations, or end-group segregation are now well-documented for reference polymers such as PS and PMMA. The interface properties, i.e. interfacial tension and interfacial thickness of incompatible blends of these polymers are also well-known experimentally. The aim of this work is to compare such experimental data with the results obtained by two different methods which are based on the calculation of intermolecular interactions between PS and PMMA (Mannino et al., 1997): first approach relies on EVT (Pressure-Volume-Temperature) experiments. Specific volume vs. temperature...
and pressure measurements done a dilatometric apparatus are fitted with various theoretical equations of state (based on Flory-Groth-Vrij or Prigogine models) to extract the cohesive energy density of CED, as well as surface tension. The surface properties of polymer blend, i.e., surface tension, interfacial tension, and interface width, were investigated. In a second approach, molecular dynamics simulations have been carried out at the atomistic level on amorphous polymer cells using the software package MSA Cirus2 & Insight II with accurate force-field designed especially for polymers. Both bulk and surface simulations were simulated. The simulation of thin films allows to observe thin film evolutions and the increase of surface mobility. The comparison between bulk and surface simulations leads to the surface tension of polymers.

2:15 PM *FP0.3 ELECTROGRAPHING OF SURFACE PROPERTIES WITH POLYMER BRUSHES. Marek Strzejch 1,*, Sergiy Minke 2,*, Alexander Szlekeny 2,3,4,5,6. 1Institut für Polymere Freie Universität Berlin, Berlin, Germany, 2Max-Planck-Institut für Polymerforschung, Mainz, Germany, 3Institut für Physik, Universität Mainz, Mainz, Germany, 4Lehrstuhl für Physik, Universität Mainz, Mainz, Germany, 5Institut für Physik, Universität Mainz, Mainz, Germany, 6Institut für Physik, Universität Mainz, Mainz, Germany.

By the grafting of a polymer layer to a solid substrate the surface properties may be changed. Using mixed layers of chemically distinctly different materials quite interesting surface properties are obtained and a reversible switching between different surface states becomes possible. An example are grafted layers of polystyrene and poly(2-vinylpyridine), where a switching between a hydrophilic and hydrophobic behaviour is possible. This is achieved by a structural rearrangement of the brush-like surface layer, where either one or the other component is the outermost layer. The surface change is caused by photoelectron spectroscopy, scanning force microscopy, contact angle measurements and optical techniques. Potential applications of reversibly switchable and environmentally adjustable surface layers in the area of materials science and biocompatibility are discussed.

3:15 PM **FP0.4 SURFACE MODIFICATION OF CONDUCTING POLYMERS ONTO ITO SURFACES. Simon Eggert, Christine Herming, Robert Jerome, Center for Education and Research on Nanomolecules, University of Liege, Liege, Belgium, Viktor Gensk, Roberto Lazzaroni, Service des Matériaux Nanosystèmes, University of Mons-Hainaut, Mons, Belgium.

Polythiophene derivatives are frequently used as emitting layers in LEDs. In such devices, one of the electrodes must be transparent, which explains that plates of glass or transparent polymer are coated by a thin layer of ITO and used as substrates. The improvement of the interfacial adhesion of the conducting polymer to these substrates remains however a challenge. A possible strategy for tackling the problem could be found in the extension of the electrochemical technique of polymer grafting onto metals (Re, Ni) to ITO glasses (1-2). The cathodic electrographic of the acrylate of thiophene will be discussed followed by the aromatic polymerization of thiophene. The electroactivity of the organic film will be analyzed and the dependence of the film thickness on the electrochemistry conditions, as well. A series of properties of the electrografted film will be compared to polythiophene films prepared by traditional electrochemical polymerization, including electron microscopy, adhesion, and ultraluminescence properties.


3:45 PM *FP0.5 SURFACE MODIFICATION OF POLY(ALKYL/ARYL-PHOSPHAZENE) THIN FILMS. John V. St. John, Patti Wiseman-Nelson, Southern Methodist University, Dallas, Texas.

Poly(aryl/alkylphosphazenes) are a unique class of inorganic polymers. The alternating -[PR2=N]- backbone provides for stable bulk properties of the materials while allowing extensive surface modification of the alkyl/aryl groups. The use of substitution reactions have allowed for attachment of organofunctional groups that include alcohols, carboxylic acids, ketones, diols, esters, and a variety of substituted siloxanes. This research demonstrates studies of surface modification of poly(arylphosphazene) thin films with the goal of enhancing the surface chemical functionality while maintaining bulk properties of the films. Functionalized groups such as alcohols, thiols, and carboxylic acids can be used to enhance the interfacial properties of poly(arylphosphazene) thin films for specific substrates. In direct contrast, the surface properties of these films can be tailored to prevent interaction with surfaces. The use of photocrosslinking substrates allows the potential for patterned polymer surfaces which have regions containing different chemical functionalities. This yields the possibility for new materials which can be used to assemble ordered arrays of nanostructures which have specificity for different chemical.

4:00 PM *FP0.6 RADIATION ENHANCED POROSITY AND ROUGHNESS OF BIOMATERIALS. A.L. Evelyn, D. Ha, R.L. Zimmerman, Center for Innovation of Materials, Arizona State University, Normal, A., M. G. Rodrigues, University of Sao Paulo, IFM-FCLIP, Ribeirão Preto/SP, BRAZIL, D.B. Polder, D.K. Hensley, Oak Ridge National Laboratory/SMAC, Oak Ridge, TN.

Glasy polymeric carbon (GPC), made from cured phenolic resins, is a sufficiently chemically inert and biocompatible that is suitable for medical applications, such as heart valves and other therapeutic devices. We have used energetic ion bombardment of partially and fully cured precursor phenolic resins to enhance biological cell/tissue growth on, and to increase tissue adhesion to, polymeric devices made from GPC. GPC samples were bombarded with energetic ions ranging from 1 keV to 10 MeV. The surface roughness and topographic changes were observed using optical microscopy and atomic force microscopy. The increased porosity was measured by introducing lithium from a molten LiCl salt into the GPC and using (p, a) nuclear reaction analysis (NRA) to measure the concentration of Li retention in the modified GPC. The NRA measurements of increased pore availability were correlated with the observations of increased surface roughness.

4:15 PM **FP0.7 SURFACE INITIATED POLYMERIZATION FROM GaAs. Hongxing Gao, Thomas A. Seely, Institute of Materials Science, University of Connecticut, Storrs, CT.

Polymer layers attached to GaAs wafers were prepared by polymerization from a surface-terminated organometallic catalyst. As an example, thiol modified terminal alkynes were bonded to the surface of a GaAs wafer through the thiol group. The terminal hydroxyl groups were shown to be capable of reacting with titanium tetrachloride. The resultant titanium (IV) alkoxide species was able to catalyze the polymerization of hexyl isocyanate to form a polymer layer on the GaAs surface. This presence of the poly(hexylisocyanate) product was confirmed using grazing incidence infrared spectroscopy. The terminal hydroxyl group could also be reacted with norbornene carbonyl chloride to give surface bound norbornyl species. After addition of a ruthenium alkylidene complex (Grubbs catalyst), the polymerization of norbornene could be catalyzed by the tethered Ru catalyst to form a poly(norbornene) layer on the surface. Attached polymer layers were characterized by IR, XPS and ellipsometry analysis.

4:30 PM **FP0.8 SURFACE-ATTACHED POLYMER NETWORKS. Oswald Puder, Kristin Müller, Jürgen Ihle, University of Freiburg, Institute for Microsystem Technology (IMTEK), Freiburg, Germany.

The fabrication of surfaces with thin films of polymer networks is of great interest in various fields ranging from the protection of surfaces against corrosion to various biotechnological concepts, e.g. to improve the biocompatibility of implant surfaces. In all cases a firm long-term adhesion of the network structure to the solid support is mandatory, otherwise the network would be detached from the surface. Clearly the best way to achieve this goal is to covalently attach the network to the substrate. Hence, we were interested in developing synthetic pathways for that purpose. To address several issues connected to this general goal, we established three strategies to form such surface-attached polymer networks either by simultaneous network formation and surface attachment or in subsequent steps. In our contribution we present synthetic details and results of the characterization of the networks with regard to their thickness, strength of adhesion and swelling behavior.

4:45 PM **FP0.9 MICROCELLULAR POLYMERIC FOAMS PRODUCED IN SUPERCRITICAL CARBON DIOXIDE. Saraswas Sircar, Yoon Gyu, Joseph R. Royer, Joseph DeSimone, Richard J. Sperling and Sand A. Khan, Department of Chemical Engineering, North Carolina State University, Raleigh, NC.

Fumed microcellular plastics have received considerable attention in recent years for a myriad of reasons. The goal of replacing solid polymers by microcellular polymers without compromising application-specific functionality is driven by a combination of material savings and waste management. The worldwide banning of chlorofluorocarbons (CFCs) has forced the foam industry to explore novel, environmentally benign blowing agents such as supercritical carbon dioxide (scCO2). In addition, scCO2 possesses interesting properties, such as liquid-like densities, which account for its high solvent power, and gas-like viscosity, yielding high rates of diffusion. It has been previously demonstrated that many commodity
thermoplastics can be readily foamed by scCO2. Most studies reported on microcellular plastics produced in this fashion involve batch foaming. More recently, a continuous extrusion process has been proposed to avoid the lengthy time periods required to saturate the polymer with the blowing agent. These two foaming processes have substantially different tunable operating parameters, in which case a comparative study is necessary to identify and possibly combine the advantages of both processes. We have constructed experimental systems for batch and continuous extrusion processes in scCO2 with superior process control relative to many comparable systems that are currently employed for microcellular foam generation. Foaming experiments have thus far been conducted using polystyrene and poly(methyl methacrylate) homopolymers as model materials. The morphologies and mechanical properties of microcellular foams prepared by both processes have been analyzed in terms of cell size distribution, foam density and impact strength. These results are quantitatively compared for foams produced at different operating conditions in batch and continuous mode.