

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 one has to consider the polymer-polymer interaction, 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 lengths 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 wave directed layer structure and finally to lateral 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. With the use of multi-layer Langmuir-Blodgett coated isopentylcellulose 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 MORPHOLOGY. Jean-Loup Masson, Peter F. Green, Department of Chemical Engineering and Texas Materials Institute, The University of Texas at Austin, Austin, TX.

Researchers have shown that 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 "spinodal-like" patterns. In this presentation we show the existence of a new morphology. We show that a random copolymer, styrene-ran-acrylonitrile (SAN) of thickness $h=12\text{nm}$, 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, Sanat Kumar, Pennsylvania State University, University Park, PA; Alamgir Karim, NIST, Polymers Division, Gaithersburg, MD.

Solvent casting of polymers is routinely used in microelectronic packaging, and generically in coating applications to prepare films of controlled thickness and roughness. While roughness critically determines properties such as "gloss" [the 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 POLYION-SURFACE INTERACTIONS IN THE SELECTIVE ADSORPTION OF POLYION 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 polyion multilayer films on regions with a given chemical surface group, patterned layer-by-layer films have been achieved. In this talk, the underlying electrostatic, hydrophobic, and hydrogen bonding interactions involved in selective adsorption of polyions is explored. By comparing adsorption of polyions from aqueous solution onto different charged and uncharged surface groups, 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. Grazing angle FTIR and AFM studies have been used to obtain a better understanding of these interactions, particularly on acid and oligoethylene glycol functional surfaces. It is thought that the molecular architecture of the polyion backbone, as well as the degree of hydration of oligoethylene glycol groups on the surface, determine the preferred area of adsorption for polyamines, whereas hydrogen bonding plays a greater role in the preferred adsorption site for polyacids. 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 Ratchana Limary, Department of Chemical Engineering and Texas Materials Institute, The University of Texas at Austin, Austin, TX.

We show that thin symmetric poly(styrene-*b*-methyl 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 depend on the initial film thickness h . Films of thickness $h < 3.5\text{ nm}$ dewet the substrate, forming bicontinuous spinodal-like patterns. When $3.5\text{ nm} < h < L = 7\text{ nm}$, discrete holes are observed randomly throughout the surface of the film. For films of thickness in the range $L < h < 5L = 35\text{ nm}$, the copolymer exhibited autophobic 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 $L < h < 19\text{ nm}$. Discrete holes are observed for films where $19\text{ nm} < h < 5L$. The structure of the top layer eventually evolves into droplets. For $h > 5L\text{ nm}$ the film is stable. The time dependent evolution of the structures in the autophobic 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 Staarup, University of Minnesota, Department of Chemistry; Greg D. Haugstad, 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 of 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 on chemically and mechanically heterogeneous surfaces. With these developments, we have investigated the effects of relative humidity from 1%-95% RH, tip chemical functionality, and fluid media on the measured pull-off forces and energy dissipation during pull-off. The amplitude of the resulting freely oscillating cantilever after pull-off 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 are studied 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 Grohens, Loic Hamon, Pascal Carriere, Yves Holl, 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

ellipsometry. The influence of the surface treatment of the silicon wafer on the T_g of the thin film has also been addressed. Stereoregular PMMA are of great interest for the understanding of the dynamic of confined polymers because of their well-known tacticity dependent bulk T_g associated with a identical chemical composition. From our ellipsometric experiments, it turns out that i-PMMA increases its T_g above the bulk value for films thickness h < 60 nm whereas syndiotactic isomer exhibit a T_g depression for thin layers on silicon wafers covered by native oxide. The observed effects on the T_g of the thin layers are enhanced on highly hydroxylated SiO_x/Si surfaces and decreased on silica free Si-H surfaces. Strong specific interactions of PMMA and SiO_x/Si substrates are, therefore, required to modify significantly the T_g of the tactic PMMA in thin film geometry.

Stereospecific adsorption of the isotactic PMMA sequences has been shown to occur on Si-OH terminated silica. This segregation of the isotactic segments may lead to a particular interfacial organization of the chains. Strong intermolecular association and hence denser packing at the interface can be envisaged to explain the increase of the thin layer T_g for predominantly isotactic PMMA. s-PMMA chains are more loosely packed at the interface which is likely to increase the free volume for that isomer in the vicinity of the surface and then depressed the T_g.

11:30 AM **FF1.8**

STUDIES OF POLYSTYRENE INTERFACES BY VIBRATIONALLY-RESONANT SUM-FREQUENCY GENERATION. L.J. Richter, K.A. Briggman, J.C. Stephenson and W.E. Wallace, National Institute of Standards and Technology, Gaithersburg, MD.

Vibrationally-resonant sum-frequency generation (VR-SFG) is emerging as a powerful probe of the molecular structure of interfaces. VR-SFG 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 centrosymmetric media. Remarkably, there have been few studies in which the technique was applied to the characterization of polymer surfaces and interfaces. We report VR-SFG 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 VR-SFG spectra acquired for various film thicknesses allows identification of the signals 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 (900 k u) molecular mass. Quantitative analysis of the orientational distribution and comparison with existing NEXAFS studies of ring alignment will be presented.

11:45 AM **FF1.9**

ULTRATHIN SOLID FILMS VIA TOPOLOGICAL PHOTO-POLYMERIZATION. Junhua 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 shall meet some aspects of the challenge of ever-decreasing size for microminaturization 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. There are 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 to atomic and molecular level. The adhesion between two components is still under intensive investigation. Cyanate esters are established high temperature, thermosetting polymers and have found a wide spectrum of applications in electronics and aerospace industries. Interested in potential usage in disk drives, we have successfully prepared polycyanate thin films, starting from selected reactive monomers of cyanate esters. This work focuses on the polymerization mechanism and morphology of the monomer bisphenole A dicyanate (2,2'-bis(4-cyanatophenyl)isopropylidene) (BADC). The monomer is vapor deposited onto silicon wafers, the thickness of which can be controlled to a submolecular layer. The monomer film is then irradiated with ultraviolet light to convert the deposited monomer to form a solid, robust overlayer. The cured film adheres fast to the substrate surface and could not be removed or dissolved by rinsing with methyl ethyl ketone or other solvents capable of dissolving the BADC monomer. The cured films is thermally stable and could tolerate at least 220°C for 10 minutes without showing any decrease in thickness, while the monomer film would quickly evaporate at this temperature. FTIR spectra show that ~2250 cm⁻¹ doublet vibrational modes from the functional groups of CN triple bonds in the monomer disappear after UV curing 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 SIMS suggest that the photopolymerization of the monomer initiated by ultraviolet light follows a process differing from the cyclotrimerizing of three monomer molecules as major steps in the catalyzed thermal polymerization of the monomer at high temperature. In the photopolymerization process, the monomer molecules cyclodimerize to form a transition four member ring, followed by a ring expansion to produce a energetically stable, five-member ring, an oxadiazole product. Atomic force microscopy (AFM) is used to monitor the changes in topography of the wafer surfaces with the addition of the polycyanate ester overlayer.

SESSION FF2: POLYMER-POLYMER AND POLYMER-WALL INTERFACES

Chairs: Jacob Klein and Paula T. Hammond
Monday Afternoon, April 24, 2000
Metropolitan I (Argent)

1:30 PM ***FF2.1**

SLIP AT MOLTEN 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 large amount of well-defined interfacial area generated in such a way that the effect of rheology and interfacial properties is eliminated up to the point of layer breakup. This provides a model system to study interfacial phenomena in immiscible blending. A number of researchers have reported an anomalous lowering of viscosity in immiscible polymer blends[2]. Interfacial slip due to lack of entanglements has been proposed to explain these observations[3,4]. Because of 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 0.01 to 500 1/s 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. 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 understand the mechanism of block copolymer suppressing interfacial slip.

References:

1. W.J. Schrenk and T. Alfrey, in Polymer Blends, edited by D.R. Paul and S. Newman, 2,129, 1978.
2. L.A. Utracki and M.R. Kamal, Polymer Engineering and Science, 22, 96, 1982.
3. P.G. de Gennes, Physics of Polymer Surfaces and Interfaces, Butterworth-Heinemann, Massachusetts, 55, 1992.
4. J.L. Goveas, and G.H. Fredrickson, European Physical Journal B, 1998.

2:00 PM **FF2.2**

REACTION KINETICS OF END-FUNCTIONALIZED CHAINS AT A POLYSTYRENE/POLY(METHYL METHACRYLATE) INTERFACE. Jonathan S. Schulze, 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 recoil spectrometry (FRES) has been used to monitor the extent of reaction between model end-functional polymers at a PS/PMMA interface in the absence of external convection. Bilayer samples comprising a high molecular weight polystyrene layer containing amino-terminal deuterated polystyrene (dPS-NH₂) on an anhydride-terminal poly(methyl methacrylate) (PMMA-anh) layer were annealed for various periods. Significant reaction with the PMMA-anh, indicated by an interfacial excess, was observed with three molecular weights of dPS-NH₂. The measured growth of the interfacial excess with time for all three molecular weights could not be well described by recent theories of diffusion-controlled interfacial reaction. Furthermore, a novel trilayer sample geometry showed that the reactive dPS chains can diffuse throughout the PS matrix and sample the PS/PMMA 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 FF2.3

NMR STUDIES OF DYNAMICS OF PERFLUOROPOLYETHER THIN FILMS ON AMORPHOUS CARBON SUBSTRATES: CONFINED FLUIDS AND INFORMATION STORAGE.

Charles G. Wade, Gyunggoo Cho, Mark Sherwood, Bing Yen, IBM Almaden Research Center, Science and Technology Function, San Jose, CA; Chris Klug, Yoojin Kim, Stanford University, Dept. of Chemical Engineering, Stanford University, Stanford, CA.

19F and 13C NMR spectra and relaxation studies have been used to study the dynamics and microstructure of thin films of 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 interaction. In these experiments, the surface coverage 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 FF2.4

TIME-RESOLVED OBSERVATIONS OF FAILURE OF POLYMER-GLASS INTERFACES IN HUMID ENVIRONMENTS.

Tom Dickinson, Stuart Irwin and Steve Langford, 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 accelerated failure of strained adhesive bonds due to moisture is of considerable interest. By study of very small bonded zones (between nm and mm size scales) one greatly enhances the influence of environmental attack, allowing for accelerated testing. To measure failure kinetics, we compare videotaped micrographic records of failure along ethylene vinyl acetate/soda lime 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 (1-200 s) to failure decrease in a monotonic 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 assisted 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 detach strongly adhering nanometer particles from glass, 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 *FF2.5

MUSHROOMS AND BRUSHES IN THIN FILMS OF DIBLOCK COPOLYMER/HOMOPOLYMER MIXTURES. C. Toprakcioglu and D. Anastassopoulos, Department of Physics, University of Patras, Rio Patras, GREECE; S.H. Anastasiadis and H. Retsos, Foundation for Research and Technology-Hellas and University of Crete, Physics

Department, Heraklion Crete, GREECE; G. Smith, Los Alamos National Laboratory, Los Alamos, NM; G. Hadziioannou, Groningen University, Chemistry Department, Groningen, THE 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 the substrate/polymer interface from their mixtures with the respective homopolymers is investigated by neutron reflectivity; the adsorbed chain configuration was probed as a function of the ratio of block lengths. The segment density profiles of PV2P-PS diblocks adsorbed at the PS/substrate interface as a function of the size of the anchoring block are evaluated with the dangling block being kept constant. The composition profiles and conformational characteristics of all chain species present in the interfacial region are also investigated using a lattice-based self-consistent field model inspired by 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 experiment 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 FF2.6

STABILIZING COLLOIDS IN A POLYMER MELT BY END-GRAFTED CHAINS: A PROBLEM AND A SOLUTION.

Itamar Borukhov and Ludwik Leibler, Unité Mixte Recherche 167, CNRS/Elf-Atochem CAL, Levallois-Perret, FRANCE.

An important method of stabilizing colloidal mixtures against attractive van der Waals interactions is by covering their surface with a layer of end-grafted polymer chains. This method works well when the colloids are immersed in a regular solvent. However, when the surrounding media is a polymer melt, subtle entropic effects might lead to destabilization and flocculation. In this presentation we discuss this problem and suggest a mechanism for stabilizing the colloidal suspension. The model system 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 DeGrujin 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 contrast at the two particle-brush interfaces as well as that of the brush-melt interfaces.

4:00 PM FF2.7

ON THE INTERFACE BETWEEN HARD CHAIN FLUIDS AND A HARD PLANAR WALL. Frank van Swol, Sandia National Laboratories, Catalytic 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 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. To facilitate the future comparisons between exact simulation data for the surface tension 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 semi-dilute regime) we analyze the density profile in terms of a profile of universal shape, following recent suggestions based on the scaling behavior of thread like polymers.

4:15 PM FF2.8

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

Using scaling theory, we investigate the equilibrium behavior of a melt

of functionalized chains, non-functionalized polymers and two infinite, planar surfaces, which model clay sheets. The functionalized chains contain end-groups that are highly attracted 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 fraction of loops, tails, bridges 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 CROSS-LINKED MICROSPHERES ATTACHED TO WALLS USING OPTICAL MICROSCOPY. Selda Durmaz, Cigdem Sayil and Oguz Okay, Tubitak Marmara Research Center, Kocaeli, TURKEY; M. Naci Inci, Alpay Taralp and Burak Erman, Faculty of Engineering and Natural Sciences, Sabanci University, Orhanli, Istanbul, TURKEY.

The elastic properties of crosslinked swollen polyisobutylene polymers were determined in various solvents via 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 as 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 $\pm 10^{-9}$ 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 NEAR THE POLYMER/SOLID INTERFACE. Eric K. Lin, Darrin J. Pochan¹, Wen-li Wu, Sushil K. Satija, National Institute of Standards and Technology, Gaithersburg, MD. ¹Dept Materials Science and Engineering, Univ of Delaware, Newark, DE.

Polymer chain mobility near a solid surface is measured using neutron reflectometry by monitoring the rate of interdiffusion between bilayers of deuterated poly(methyl methacrylate) (d-PMMA) and hydro-gated PMMA supported on polished silicon wafers. Neutron reflectometry is a powerful technique for the non-destructive measurement of interfacial structures because of its high resolution and the opportunity to selectively label organic molecules with deuteration. 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 mean field theory. The effect of varying polymer/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. Sushil K. Satija, Robert Ivkov, Paul Butler, NIST Center for Neutron Research, Gaithersburg, MD; L.J. Fetters, Exxon Research and Engineering, Annandale, NJ.

We report recent results of neutron reflectivity studies of chemically end grafted polystyrene 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 profiles at 0/s and 130,000/s look identical indicating less than 2-3% change in the brush density profile. At these shear rates we do not observe any desorption of the chemically grafted brush in contrast to previously reported work where the brushes have a tendency to desorb at shear rates beyond ~ 10000 /s.

9:00 AM FF3.2

FRICTION OF POLYMER MELTS ON MODIFIED SOLID SURFACES. Hubert Hervet, V. Koutsos, T. Charitat, L. Léger. 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 50K to 135K, 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. Length and density of the attached surface chains are well controlled. In all force - displacement curves there is a transient followed by different stationary friction regimes 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 with the surface density of adsorbed chains and the molecular weight of the bulk and surface chains will be presented. Differences in reptation times could explain the changes observed between PDMS and SBR in the intermediate regime.

1) L. Léger, E. Rapháll, H. Hervet, Advances in polymer science, vol. 138, 185-225, 1999.

9:15 AM *FF3.3

EFFECT OF BORON NITRIDE IN THE PROCESSING OF METALLOCENE POLYOLEFINS. Savvas G. Hatzikiriakos, 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 200-1000 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 resins, 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 Klein, Eugenia Kumacheva¹, Rafael Tadmor, Dept. of Materials and Interfaces, Weizmann Institute of Science, Rehovot, ISRAEL. ¹present 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), a situation which can occur in areas from flow processing to lubrication . Using a surface force balance, we have examined the way in which solvated polystyrene chains end-attached 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 chains detach 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 from between the gap, illustrating qualitatively the chain-end detachment 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.

10:45 AM FF3.5

SHEAR AND LUBRICATION 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 mica surfaces immersed in dilute solution of poly(ethylene oxide) (PEO) in toluene have been carried out as a function of surface separation. Toluene is a good solvent for PEO and two different molecular weights were used: 37k and 112k. Following adsorption of the PEO force-distance law was indicated with repulsion beginning at a distance of $\sim(8\pm 1)R_g$ (where R_g is the unperturbed gyration radius), in agreement with earlier studies. In this study, uniform back and forth shear motion was applied in a series of separations. Shear response commenced at a distance of $\sim(2\pm 0.4)R_g$ and increased monotonically at shorter distances. In the lower molecular weight, 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 mica 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 $1.5R_g < D < 2.4R_g$. At shorter 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 tension was enough 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 FF3.6

MOLECULAR DRAG-STRAIN COUPLING IN BRANCHED POLYMER MELTS. Richard Blackwell, 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 relaxed and unrelaxed polymer segments at branch-points. This allows for localised displacements of branch-point within a quadratic potential before maximum extension is reached. Displacing the branch-point reduces the length of arm outside the tube and so reduces in 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 FF3.7

SHEAR-INDUCED DROPLET COALESCENCE IN IMMISCIBLE POLYMER BLENDS AND THE EFFECT OF INTERFACIAL MODIFICATION. S.D. Hudson, A.M. Jamieson, I. Manas-Zloczower, B.E. Burkhart, G.V. Prasad, 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 its rupture. Analysis of the experimental coalescence efficiency yields an independent measure for the probability of each step. Chesters film drainage 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

coalescence. 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 generated. Therefore, under these circumstances, the collision efficiency is reduced only slightly, and the primary effect of the block copolymer is to inhibit film drainage. Modifications of Milners collision-efficiency theory (2) to account for copolymer solubility, and of Chesters' theory (1) to incorporate the presence of copolymer have been developed and tested.

(1) A.K. Chesters, Chem. Engr. Res. & Design 1991, 69, 259.

(2) S.T. Milner and H.J. Xi, Rheol. 1996, 40, 663.

The authors gratefully acknowledge the financial support of the Goodyear Tire and Rubber Co., GE plastics, and NSF grant CTS-9731502.

11:30 AM FF3.8

SCALING BEHAVIOR OF POLYMER BRUSHES. Jürgen Rühle, Markus Biesalski, Martin Schimmel, University of Freiburg, Institute for Microsystem Technology (IMTEK), Freiburg, GERMANY; Diethelm Johannsmann, 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 macromolecules are terminally attached to a solid substrate. Several such systems were developed in the past, mostly in which functional groups of the polymers are reacted with appropriate surface sites (grafting to technique). To avoid some problems associated with this technique, we have generated the polymer molecules directly on the surfaces of the substrates by using self-assembled monolayers of initiators and polymerization in situ (grafting from). Following this grafting from approach polymer monolayers having a precisely controlled film thickness in the range between 2 and 1500 nm can 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 a solid surface will be described.

**SESSION FF4/DD4: JOINT SESSION:
POLYELECTROLYTES AND PROTEINS AT
SURFACES**

Chair: Alamgir Karim
Tuesday Afternoon, April 25, 2000
Metropolitan I (Argent)

1:30 PM *FF4.1/DD4.1

GRAFTED POLY(ACRYLIC ACID) BRUSHES FOR CELL-SURFACE INTERACTIONS. Jöns Hilborn, B. Gupta, L. Garamzeigy, A. Laurent, Polymer Lab, Dept Materials Science, Swiss Federal Inst Techn, Lausanne, SWITZERLAND; I. Bisson, P. Frey, Pediatric Surgery, Centre Hosp du Canton de Vaud, Lausanne, SWITZERLAND; J. Hedrick, IBM ARC, San Jose, CA.

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

BIO-LUBRICATION: 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 polymer brushes and of charged polyelectrolytes. 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 surface-attached chains, configurational entropy arising 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 chains - resembling the biological situation - there is the additional role of the counterions in solution, and in this case it is their translational entropy which leads to an osmotic repulsion between the mutually compressed and sliding surfaces. We present recent results on this effect which reveal the remarkable effect of these entropic factors in reducing friction, and which may point to possible strategies for better design of artificial joint implants.

2:15 PM FF4.3/DD4.3

NOVEL MICROPOROUS BIO-INTERFACE MATERIAL PREPARED FROM POLYELECTROLYTE MULTILAYERS. Jonas D. Mendelsohn, Anne M. Mayes and Michael F. Rubner, MIT, Department of Materials Science and Engineering, Cambridge, MA; Christopher J. Barrett, McGill University, Department of Chemistry, Montreal, CANADA.

A novel process has been developed to create large area, highly uniform microporous bio-interface materials. The relatively new layer-by-layer (LbL) self-assembly process, whereby oppositely charged polymers are sequentially adsorbed from dilute aqueous solutions onto an immersed substrate, was used to fabricate hydrogel multilayer thin films from the polyanion poly(acrylic acid) (PAA) and the polycation poly(allylamine hydrochloride) (PAH). It has been found that a substantial, irreversible phase separation will occur on PAA/PAH multilayers assembled at pH conditions of 3.5/7.5, respectively, simply by briefly exposing the films to aqueous solutions of a pH of ≈ 2.3 -2.5. AFM characterization shows that this pH-induced phase separation leads to a highly microporous morphology (up to a 2/3 volume of pores) with pore sizes of 100-500 nm. While PAA/PAH multilayers have been used as a model system to investigate this pH-driven porosity phenomenon, efforts are currently underway to create microporous films from charged biopolymers; the feasibility of incorporating charged drugs, enzymes, or other bioactive molecules, e.g., cell adhesion molecules for specific bio-interface activity, into the multilayers will be investigated. The LbL method also advantageously enables the in situ inclusion of nanoparticles of silver, a known antimicrobial, into the films. The pH-dependent porosity and swelling in these multilayers allow for controlled drug release capabilities, and these porous films are also foreseen as dialysis membranes and scaffold materials. Furthermore, this simple porosity transformation may lead to an alternative strategy to the polyelectrolyte complex coacervation technology routinely used to encapsulate cells or drugs. Since it assembles one molecular layer at a time with nanoscale precision, the LbL technique, coupled with this unique pH-induced phase separation, could be a novel approach to synthesizing porous biomaterials with highly tailorable features, including well-defined surface and interfacial properties.

2:30 PM FF4.4/DD4.4

POLYCATION-INDUCED STRUCTURAL REARRANGEMENTS IN NEGATIVE LIPOSOMAL MEMBRANES. Alexander Yaroslavov, Viktor Kabanov, Moscow State Univ, School of Chemistry, Moscow, RUSSIA.

Permanently growing biomedical applications of synthetic polyelectrolytes require to study their behavior in biological environment and especially, their interaction with cells. In the latter case, spherical bilayer vesicles composed of lipid molecules can be used as cell-mimetic objects. It is known that a cell membrane usually carries a net negative charge. Therefore, we focused on synthetic polycations, interacting with neutral and negative vesicles. Interaction of polycationic species with liquid vesicles can be accompanied, in certain systems and under certain conditions, by lateral lipid segregation (microphase lipid separation), highly accelerated transmembrane migration of lipid molecules (polycation-induced flip-flop), incorporation of adsorbed species into the liposomal membrane, aggregation of vesicles and their disruption. Electrically adsorbed polycation, if not additionally anchored by an attached hydrophob, can be completely removed from the membrane surface by recomplexation with polyanions. The above mentioned phenomena were examined depending on structure and linear charge density of polyelectrolyte molecules, content of charged lipids, vesicle phase state and size, as well as ionic strength of solution. It is likely that the observations we made might be useful to interpret biological effects of polyelectrolytes and multicharged polymeric constructs.

3:15 PM *FF4.5/DD4.5

BIOFUNCTIONALIZATION OF SURFACES WITH PEPTIDE AMPHIPHILES. Matthew Tirrell, College of Engineering, University of California, Santa Barbara, CA.

Peptides carry enormous capacity and versatility for participating in specific ligand-receptor binding interactions. As small fragments 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 lipidated synthetically by attaching a phospholipid-mimic, double-chain, hydrocarbon tail. Lipidation confers interesting amphiphilic and self-organization 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 generality 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 controller 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. Csajka, Roland R. Netz, Max-Planck-Inst of Colloids and Interfaces, Goltm, GERMANY.

Polyelectrolyte 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 promising tool to validate theoretical models, and to probe quantities 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, counterion sizes and Bjerrum lengths. The model includes counterions explicitly, and the full Coulomb interaction is treated using a direct summation technique proposed by Lekner and modified by Sperb. 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 regimes can be understood by an extended scaling model which includes Coulomb correlation between charged monomers and counterions. For partially charged chains we obtain a broad cross-over between the scaling regimes given by theory. Reducing the counterion size we find the osmotic regime in agreement with our scaling theory phase diagram. Varying the Bjerrum length we obtain a non-monotonic behavior of the brush thickness with a maximum at very small coupling where already a considerable part of counterions has left the brush.

4:00 PM FF4.7/DD4.7

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

We are interested by the adsorption of strongly charged polyelectrolytes (Polystyrene sulfonate with rate of sulfonation between 30 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 rate of sulfonation is observed. We invoke a *conformational barrier* effect to explain this phenomenon: chains with a low charge content are collapsed and form isolated globules which are repelled by a neutral surface. After rinsing adsorbed layers with pure water, the desorption is only partial, showing the existence of a *barrier that prevents complete desorption*. The existence of these energetical barriers leads to strong hysteresis 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 have been studied by a new technique of high-energy *X-ray reflectivity across water*: adsorbed layers are always very thin ($\approx 20\text{\AA}$) confirming the fact that the layers are monomolecular.

4:15 PM FF4.8/DD4.8

PROTEIN ADSORPTION ONTO CHARGE-REGULATED SELF-ASSEMBLED MONOLAYERS. Stella Y. Park, Anne M. Mayes, Michael F. Rubner, Massachusetts Institute of Technology, Dept. of Materials Science and Engineering, Cambridge, MA; Paula T. Hammond, Massachusetts Institute of Technology, Dept. of Chemical Engineering, Cambridge, MA.

Anomalous adsorption of poly(acrylic acid) onto charge-regulated self-assembled monolayers (SAMs) has been observed in recent experiments (Barrett and Mayes, submitted). In those 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 25 Å to 5 Å over a narrow pH range. Here we extend the investigation to include the adsorption of charged biopolymers *e.g.*, poly(lysine). 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 (Clark et al., *Advanced Materials*, **11**, 1031 (1999)) and polyelectrolyte adsorption on those modulated surfaces was investigated.

4:30 PM FF4.9/DD4.9

ENDOTHELIAL CELL GROWTH AND PROTEIN ADSORPTION ONTO HETEROGENEOUS SELF-ASSEMBLED INTERFACES. B.J. Tarasevich, Battelle Pacific Northwest National Laboratory, Richland, WA; C. Tidwell, B. Ratner, University of Washington, Seattle, WA; D.L. Allara, 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 cellular responses. 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 serum protein adsorption onto tailored chemically heterogeneous self-assembled interfaces composed of thiols on gold containing mixtures of COOH:OH and COOH:CH₃ 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:OH mixtures. The adsorption and elutability of albumin (Alb), vitronectin (Vn) and fibronectin (Fn) varied with mixed SAM surface composition. Cell growth was maximal on mixed surfaces which exhibited the highest surface fraction of adhesive proteins and the highest Vn elutabilities (*i.e.* decreased Vn binding strength). These results suggest that the mixed surfaces control the composition and binding strength of proteins in the adsorbed protein layer which affects cell receptor interactions and mitogenic activity.

4:45 PM FF4.10/DD4.10

PROTEIN INTERACTIONS WITH PDMS DURING INTERFACIAL 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 hydrophilic 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 recovery and increases protein adsorption. The recovery is attributed to oligomeric PDMS fragments that diffuse to the surface after its chemical treatment.

SESSION FF5: POSTER SESSION:
INTERFACES, ADHESION, AND PROCESSING IN
POLYMER

Chair: Spiros H. Anastasiadis
Tuesday Evening, April 25, 2000
8:00 PM
Metropolitan Ballroom (Argent)

FF5.1

PREPARATION OF MICROSTRUCTURED ULTRATHIN FILMS BY CONTROLLED DEWETTING ON MICROHETEROGENEOUS SURFACES. Evelyn Meyer, Hans-Georg Braun, Institute of Polymer Research, Dresden, GERMANY.

The preparation of ultrathin polymer layers by dip-coating or spin-coating is generally accompanied by dewetting processes if the film thickness decreases to the nanoscale level. Dewetting is caused either by nucleation or by capillary waves. Independent of the origin of the dewetting process the film ruptures in an unpredictable way. It will be demonstrated that surface heterogenization by micro-contact printing can be used to control the dewetting process. Geometrical features such as size, shape, periodicity and distances between adjacent motifs are some of the engineering parameters to control liquid flow and ultrathin film formation processes on micro scale. Characteristic morphological features of both amorphous (poly-styrene) and semi-crystalline polymers (polyethylene) were studied in detail by AFM and Low Voltage Scanning Electron Microscopy. Dewetting and crystallisation during film formation on micro-patterned surfaces are competitive processes. Size and shape of dendritic structures are a consequence of diffusion controlled crystal growth and dewetting processes in thin layers. Parameters changing the viscosity of polymers consequently influence the morphological features in thin films. Low molecular weight polyethylene crystallizes within single microdroplets in stacks of individual lamellae of identical thickness. Special morphological features can be generated in amorphous films by variation of polymer concentration. Some criteria which are relevant for the design of surface film patterns by controlled dewetting are discussed.

FF5.2

INTERFACIAL THERMAL RESISTANCE OF LOW DIELECTRIC CONSTANT THIN FILMS. Chuan Hu, Michael Kiene, Junjun Liu, Paul S. Ho, Microelectronics Research Center, University of Texas at Austin, Austin, TX.

Polymeric low dielectric constant (low-k) thin films are proposed as interlevel dielectrics (ILD) for microelectronic devices to improve density and performance. The thermal conductivity is one of the key issues for the application of polymers as ILD materials. Beside the bulk thermal resistivity the interfacial thermal resistance, which is due to the mismatch of phonon propagation between different types of materials, is an important aspect. Using the 3 omega technique, we have studied the thermal conductivity of spin coated polymeric thin films with thicknesses from 7 nm to about 1 micron at room temperature. The thickness dependency allows us to calculate the film and interfacial thermal resistance of an Al/ILD/Si stack. Three different polymers, which represent different polymer morphologies, were studied: BCB (crosslinked), PMDA-ODA polyimide, (semi-flexible) and BPDA-PDA polyimide (rigid-rod like). The mechanisms for the interfacial thermal resistance at room temperature are being investigated. Consideration of the acoustic anisotropy and phonon density provides some of the mechanisms to account for the interfacial thermal barrier. Our data indicate that the film roughness is also an important issue for the observed interfacial thermal resistance. Though rougher surfaces improve adhesion, they lower the thermal conductivity. This suggests that there is a general tradeoff between electrical, mechanical and thermal performance for polymeric thin films.

FF5.3

MAPPING PHASE DYNAMICS OF CONDUCTING POLYMER BLEND FILMS WITH NEAR-FIELD SCANNING OPTICAL MICROSCOPY. Jeeseong Hwang¹, Lori S. Goldner¹, Alamgir Karim², and Connie Gettinger³. ¹Optical Technology Division, Department of Physics, National Institute of Standards and Technology (NIST), Gaithersburg, MD, ²Polymers Division, NIST, ³Corporate Processing Technology Center, 3M Company, St. Paul, MN.

Conventional methods to fabricate small structures and patterns mainly employ high-resolution lithographic techniques which are costly and tedious. More recently, innovative techniques involving control and use of the molecular microenvironment in polymer blends have drawn much attention for generating submicron patterns and devices. Among those techniques, self assembly of macromolecules using phase separation in polymer blends is being investigated for this purpose. Some aspects of phase separation in these multi-component polymer systems have been studied by conventional optical microscopy techniques. However, these techniques have resolution that is diffraction limited so there is still little information available on the nanoscale electric, mechanical, or optical properties of phase

separated films. We report on the study of mapping phase dynamics of polymer blend films using near-field scanning optical microscopy (NSOM). NSOM uses the near-field interaction of light from 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 poly(styrene) and poly(3-octyl-thiophene). 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-octyl thiophene) molecules are mobile even below the glass transition temperature (T_g) of bulk polythiophene when these molecules are cast with poly(styrene) which has a lower T_g and acts as a plasticizer. Samples annealed at temperatures above or below the T_g of poly(3-octyl thiophene) showed that poly(3-octyl thiophene) covers the poly(styrene) in these films. Artifacts that appear in near-field data on samples with large or varying film thickness or topography were also identified, and their modeling is currently being pursued towards a correct quantitative evaluation of these films.

FF5.4
POLYMERIZATION KINETICS OF NORBORNENE ON GOLD NANOPARTICLES. Qinghong Fu, Dale L. Huber, Thomas A.P. Seery, 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. $^1\text{H-NMR}$ was used to determine the polymerization kinetics of norbornene on modified gold nanoparticles as well as in solution. 5-Norbornene-2-carbonyl chloride was synthesized in order to modify the gold nanoparticles that were previously prepared with hydroxyl end groups to introduce norbornene on the surfaces. Bis (tricyclohexylphosphine) benzylidene ruthenium(IV) chloride, was then used to react with the surfaces bound norbornene moieties. The concentration of the monomer left during the polymerization was calculated according to the changes of the areas between the protons on norbornene double bonds and the protons 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.

FF5.5
THERMOMECHANICAL RELIABILITY MODELING OF POLYMER/METAL INTERFACES IN MICROELECTRONIC APPLICATIONS. Seung-Yeop Kook, Reinhold H. Dauskardt, Stanford University, Department of Materials Science and Engineering, Stanford, CA; Amol 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 present in the atmosphere and perhaps in the layers themselves can lead to premature failure and reduced lifetimes. These fractures are driven by residual stresses remaining from processing, thermal cycling during use, and mechanical or vibrational loading. In this study, the effect of environmental and temperature variables was investigated on interfacial adhesion and subcritical debonding of a representative polymer/metal interface under both monotonic and cyclic fatigue loading conditions. While the steady-state interfacial fracture energy was found to be insensitive to moisture content, 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 in using chemical reaction rate theory and relaxation process at the debond tip. Activation energies were determined for the different stages of debond growth and a model is presented to account for the effects of loading, humidity and temperature on subcritical debond-growth rate behavior.

FF5.6
STUDY ON POLYSTYRENE ENCAPSULATED EXFOLIATED GRAPHITE/SBS COMPOSITES. Peng Xiao, Kecheng Gong, Polymer Structure & Modification Res. Lab, South China University of Technology, Guangzhou, PR CHINA.

In 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 filler's capsulation by polymerizing monomer in the presence of filler is put forward. Surface modification of exfoliated

graphite is carried out by encapsulating exfoliated graphite by styrene polymerization. Then we introduce the encapsulated exfoliated graphite into styrene/ butadiene/styrene triblock copolymer(SBS) by melt mixing. Result shows encapsulation benefits the dispersion of exfoliated graphite in the composite. The composite has a relative low threshold value of electrical conduction than that of unmodified exfoliated graphite filled SBS system. And also high mechanic strength, high thermal conductivity and low density composites are obtained.

FF5.7
NOVEL SILICON ORGANIC COMPOUNDS TO ENHANCE FILLERS INTERFACIAL ADHESION AND PROCESSABILITY OF POLYMER. Weixing 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 organosilane coupling agent coming from carbon-thermal reduction process to promote polymer-filler interaction via formation of covalent chemical linkage. However, organosilanes are expensive and significantly increase the cost of products. Here, we first present a novel, inexpensive type of silicon organic compounds containing hydrophilic and functionally hydrophobic groups through a new surface-modification 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 interphase region between fillers and polymer developed acting as binders, coupling agent, 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 be compared with the rubber filled with organosilane-modified fumed silica.

FF5.8
ADHESION MICROMECHANISMS OF SOFT POLYMERIC ADHESIVES ON SILICONE RELEASE COATINGS. Gwendal Josse, Costantino Creton, Laboratoire PCSM, 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 tack tester, 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, 2-ethylhexyl acrylate and acrylic acid. A layer approximately 100 μm thick was deposited by doctor-blading on a microscope glass slide. The release coatings were crosslinked elastomers of poly(dimethyl siloxane) and were deposited by spin-coating (thickness of about 1 μm) on the previously polished steel probe. The adhesion energy of the acrylate adhesive on a surface coated with a PDMS elastomer was very low. However when a rigid and relatively polar bulky resin was incorporated in the elastomer network, the adhesion energy increased significantly, while the surface tension of the silicone was hardly modified. We investigated the role of the resin in the debonding mechanisms and the coupling existing between the rheological properties of the adhesive (controlling the bulk dissipative 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 cavities at the silicone/adhesive interface, while its absence 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.

FF5.9
THE EFFECTS OF GRADED ELASTIC AND YIELD PROPERTIES ON ADHESION IN AN UNDERFILL-SILICON DIOXIDE SYSTEM. Dan Maidenberg, Reinhold Dauskardt, 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 cure conditions. Samples were tested using double cantilever beam fracture mechanics 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

layer. Published mechanical models were employed to determine the effect of the beads on yield strength and modulus. This information was used to predict the plastic zone size and plastic energy dissipated during debonding, which control the overall fracture resistance.

FF5.10
ADHESION STRENGTH AND PEELING ANGLE MEASURED ON THE POLYIMIDE/Cr INTERFACES. Jin-Won Choi, Kwang-Eung Lee, Tae-Sung Oh, Hong Ik Univ, Dept of Metallurgical Engineering and Materials Science, Seoul, KOREA.

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 peeling 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.

FF5.11
¹⁹F NMR INVESTIGATION OF THIN FILM ZDOL BACKBONE DYNAMICS ON CARBON SURFACES. Yoojin Kim, Christopher A. Klug, Department of Chemical Engineering, Stanford University, Stanford, CA; Charles G. Wade, Materials Analysis and Characterization, Almaden Research Center, IBM, San 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 these lubricants. Comparisons of ¹⁹F NMR spin-lattice relaxation time, T₁, and spin-spin relaxation time, T₂, for molecularly thin Zdol (HOH₂CF₂C(OC₂F₄)_p(OCF₂)_qOCF₂CH₂OH, p/q = 0.7, M_w/M_n = 1.5, MW=2000) film on carbon surfaces were made to obtain information about the backbone mobility of the surface bound polymer. The spin-spin relaxation time decreases and the line width increases with decreasing Zdol coverage, while the spin-lattice relaxation time stays constant as the coverage of Zdol 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 flat conformation of the polymer described by other studies using surface energy and TPD measurements and ab initio calculations.

FF5.12
CHEMICAL AND STRUCTURAL CHARACTERIZATION OF SILANE ADHESION-PROMOTING FILM FOR USE IN MICROELECTRONIC PACKAGING. Maura Jenkins, Dimitrios Pantelidis, John C. Bravman, Stanford Univ, Dept of Materials Science and Engineering, Stanford, CA.

We investigate the mechanism by which an aminosilane adhesion promoter strengthens the interface between benzocyclobutene (BCB) and an oxidized silicon wafer. The adhesion promoter film is characterized using AFM and angle-resolved XPS to identify surface bond density, morphology, and chemistry. Films produced from a range of adhesion promoter spin-coat solution concentrations have been characterized. The 0.083% solution produces a single monolayer on the surface, and the 0.14% concentration produces two monolayers. In both cases, the directionality of the films is preserved. That is, the amine functional group is oriented toward the BCB, and the silane groups are oriented toward the silicon oxide substrate. Finally, this solution concentration is optimized with respect to the mechanical strength of the interface. Additionally, there is evidence that a short cure of the adhesion promoter may significantly improve adhesion strength, and FTIR is used to identify the chemical mechanism of this enhancement. Characterization of this adhesion-promoting film and the interfaces it forms with silicon oxide and BCB allows us to correlate adhesion strength with processing conditions through an understanding of chemical and microstructural mechanisms.

FF5.13
INTERFACIAL FRACTURE OF THIN EPOXY FILMS ON ALUMINUM. A. Strojny, Xerox Corporation, Webster, NY; N.R. Moody, Sandia National Laboratories, Livermore, CA; J.A. Emerson, Sandia National Laboratories, Albuquerque, NM; W.W. Gerberich, University of Minnesota, Minneapolis, MN.

Interface structure and composition are two of the most important factors controlling performance and reliability of components where changes can lead to degradation and premature failure. They are particularly important factors in components with polymer interfaces for which susceptibility to interfacial failure can increase markedly with age and environmental exposure. Nevertheless, our understanding of failure in these systems is limited by the lack of established test techniques for measuring adhesion. We have therefore combined nanoindentation techniques developed for metal and ceramic thin film systems with mechanics based models to determine interfacial fracture energies in a 16 μm thick styrene acrylate coating on T-6061 aluminum sheet and a 1.6 μm thick epoxy coating on sputtered aluminum. The tests on the well-characterized styrene acrylate demonstrated that accurate interfacial fracture energies could be obtained from free surface polymer films using mechanics-based models for circular blister formation. These tests were then used to assess the effects of a silane interlayer on adhesion of epoxy to aluminum. The tests showed that without the interlayer, the epoxy film delaminated following nanoindentation at a fracture energy of 0.75 J/m². With the interlayer the films did not delaminate, even when the indentations exceeded the epoxy layer thickness. In this presentation these results will be used to show that interfacial fracture energies can be obtained from free surface glassy polymer films using nanoindentation test and analysis techniques. In addition, the results will be used to show that the use of adhesion enhancing interlayers can significantly increase resistance to interfacial fracture in epoxy film systems. This work supported by U.S. DOE Contract DE-AC04-94AL85000.

FF5.14
CHARACTERIZATION OF THE POLYMER-FILLER INTERFACE IN SILICA-REINFORCED POLYSILOXANES UNDER GAMMA IRRADIATION. Allen T. Chien, Robert Maxwell, David Chambers, Bryan Balazs and James LeMay, Chemistry and Materials Science Directorate, Lawrence Livermore National Laboratory, Livermore, CA.

Silica is an effective reinforcing agent for silicone polymers due to the hydrogen bonds that form between the polymer and the silica filler particles. While known to be important, characterization of the interactions at the polymer-filler interface in these systems is difficult. In this paper, a two-stage solvent swelling technique was employed to determine the individual contributions of the polymer matrix and filler phase to the overall crosslink density of the filled rubber. This technique can be used to determine the extent to which the polymer-filler interactions dictate the overall material properties. Changes in the apparent crosslink density of silica-reinforced silicone polymer composites were observed as a result of gamma radiation in air and inert environments. The results showed how hydrogen bonding at the polymer-filler interface dominates the overall properties of the composite material. Irradiation in air showed a decrease in hydrogen bonding at the polymer-filler interface, while vacuum-irradiated samples revealed the opposite effect. The polymer matrix exhibited an increased crosslink density upon irradiation in both air and vacuum. These results were supported by solid state NMR experiments that exhibited similar changes in T₂ relaxation times as a function of dose and environment. T₂ times were used to empirically correlate the motional dynamics of the polymer chains with crosslink density. Analysis of the volatile degradation species by GC/MS analysis revealed a number of unexpected species formed as a result of irradiation in the different environments. This work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract W-7405-ENG-48.

FF5.15
ADHESIVE BEHAVIOR OF LATEX PARTICLES. Maude Portighatti, Vasileios Koutsos, Liliane Léger, Laboratoire de Physique de la Matière Condensée, URA CNRS 792, Collège de France, Paris, FRANCE.

Nanometric latex particles are commonly used as binders in many industrial applications. Macroscopic adhesion tests on latex films show that the viscoelastic dissipation is the predominant contribution to the adhesion energy for a very large range of velocities. This dissipation develops in regions of the sample with dimensions large compared to the size of one latex particle. As the latex films have a particular structure due to the reminiscence of the interfaces existing between particles, there could be an interplay between this structure and the adhesive behavior, especially when the size of the sample becomes comparable to the particle one (isolated particle or small clusters). To gain information on these smaller length scales, we have investigated the rupture of contact between a single latex particle and the tip of an atomic force microscope, using force/distance curves. Strong elongation of the particle is then observed and the rupture proceeds in a stick-slip fashion. The elongation behavior, the minimal force of detachment and the separation energy depend strongly on the tip velocity and are sensitive to the particle neighborhood (i. e. to the

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 interpreted in terms of thermodynamical 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 nanoscopic one highlights that the adhesive behavior of latex at 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 LIQUID CRYSTAL POLYMER FIBERS. Jennifer E. Taylor, Matthew Libera, Stevens Institute of Technology, Dept of Chemical, Biochemical, and Materials Engineering, Hoboken, NJ.

A novel electron-optical approach has been developed to evaluate structure-processing relationships in liquid crystal polymer(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 position of the electron beam can be correlated with real-space image data. This paper describes the application of spatially resolved orientation mapping to as-drawn and annealed HBA/HNA fibers. The average orientational order parameter increases, as expected, when drawn fibers are annealed. Director maps constructed at a spatial-resolution of $\sim 100\text{nm}$ show variations in local orientational order. These can depart by as much as $\pm 10\%$ 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 moldings where gradients in shear flows are more pronounced. Some local regions ($\sim 100\text{nm}$) in the annealed fibers appear to have crystal-like order.

FF5.17

AMINE-QUINONE POLYIMIDES AS COATINGS THAT PROTECT IRON AGAINST CORROSION. Mijeong Han, Huimin Bie, Garry W. Warren and David E. Nikles.

Amine-quinone dianiline monomers were prepared by reaction of benzoquinone with either 4,4'-methylene dianiline or 4,4'-oxydianiline. The monomers were used to prepare a series of amine-quinone polyimides by condensation with a tetracarboxylic acid dianhydride, either 3,3',4,4'-benzophenonetetracarboxylic dianhydride, 4,4'-(hexafluoroisopropylidene)diphthalic anhydride, to give the polyacid amide, followed by thermal imidization. The polyimides had thermal decomposition temperatures in excess of 500°C . An amine-quinone polyacid amide was coated onto iron squares, and then thermally imidized. For comparison, a conventional polyimide coating was prepared that contained 4,4'-methylenedianiline and 3,3',4,4'-benzophenonetetracarboxylic dianhydride. 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
Chairs: Peter F. Green and Sanat K. Kumar
Wednesday Morning, April 26, 2000
Metropolitan I (Argent)

8:30 AM *FF6.1/EE6.1

STRUCTURE, DYNAMICS, AND PROPERTIES OF POLYVINYL CYCLOHEXANE BASED PENTABLOCK COPOLYMERS. Frank S. Bates, Martin Vigild, Kim Chaffin, Chin Chu, University of Minnesota, Minneapolis, MN; Glenn Fredrickson, UC Santa Barbara, Santa Barbara, CA; Stephen Hahn, Dow Chemical Company, Midland, MI.

Polyvinylcyclohexane (V), which is produced by catalytically hydrogenating polystyrene, 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 ($M_e=40,000$ 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 triblock and VEEV pentablock copolymers where E refers to semicrystalline hydrogenated polybutadiene. The phase behavior (morphology and order-disorder transition), rheological, and room-temperature mechanical properties have been characterized revealing several dramatic effects associated with the change in architecture from triblock 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. Lapeña, Andrea J. Liu, UCLA, Department of Chemistry and Biochemistry, Los Angeles, CA; Sharon C. Glotzer, Stephen A. Langer, 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 POLYOLEFIN BLENDS. Yingying 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/ethylethylene) blended separately with two linear random copolymer poly(ethylene/ethylethylene). Molecular architecture is the only difference between the two components of the blends. The molecular weights of the two linear random copolymer poly(ethylene/ethylethylene) are 57 kg/mol and 200 kg/mol, respectively. The heavily branched polymer has a molecular weight of 750 kg/mol. Unlike many previous studies that concentrate on the short-branched species, this heavily branched random copolymer 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 (200 kg/mol) phase separate.

9:45 AM FF6.4/EE6.4

PHASE SEPARATION IN POLYMERIC FLUIDS SUBJECTED TO A TEMPERATURE GRADIENT. Minqin Li, Shengqing Xu, Eugenia Kumacheva, 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

PHASE BEHAVIOR AND TRANSITIONS IN POLYMERS COMPRISING MILDLY AMPHIPHILIC MONOMERS. H. Duan, S.D. Hudson, P. Kewswan, V. Percec, M.N. Holerca.

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 of their ordered phases. Polyoxazolines with pendant glyoxyphenyl groups were used. The phenyl groups were bisubstituted in the 3 and 4 positions, or trisubstituted in the 3, 4, and 5 positions, with alkyl 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

columnar clearing temperature. Cubic materials comprising quasi-spherical aggregates were also investigated. Electron diffraction and TEM imaging were used to identify their equilibrium structure, and relationships with the molecular structure are examined. The authors gratefully acknowledge the financial support of NSF grants DMR-9806684 and DMR-9708581.

10:30 AM FF6.6/EE6.6

THE MORPHOLOGY OF BLENDS OF LINEAR AND SHORT-CHAIN BRANCHED POLYETHYLENES IN THE SOLID STATE BY SMALL ANGLE NEUTRON AND 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 TN; R.G. Alamo, Florida Agricultural and Mechanical University and Florida State University, Department of Chemical Engineering, Tallahassee, FL; J.D. Londono, DuPont Central Research and Development, Wilmington, DE; L. Mandelkern, Florida State University, Institute of Molecular Biophysics, Tallahassee, FL; 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/LLDPE). SANS indicates that the mixtures are homogenous in the melt for all compositions when the ethyl branch content in the copolymer is low (i.e. < 4 branches/100 backbone carbon atoms for a typical molecular weight of 100,000). However, due to the structural and melting point differences between HDPE and LLDPE, the components phase segregate in the solid state and form a lamellar morphology with a periodicity, typically 10 nm. The degree of separation is controlled by the crystallization kinetics and DSC, TEM, SAXS and SANS 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 surround them.

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

10:45 AM FF6.7/EE6.7

CRYSTALLOGRAPHY, CURVATURE AND COORDINATION OF BICONTINUOUS BLOCK COPOLYMER NANOSTRUCTURES. H. Jinnai, Kyoto Inst of Technology, Dept of Polymer Science & Engineering, Kyoto, JAPAN; R.J. Spontak, North Carolina State Univ, Depts 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 the gyroid, perforated lamellar and sponge (microemulsion 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 interfacial 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 $Ia\bar{3}d$ symmetry. 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 area-averaged mean curvature for these systems is found to be sensitive to composition, whereas the area-averaged Gaussian curvature is not. Structural characteristics exhibiting evidence of universality are identified, and experimental results are compared to self-consistent field predictions for block copolymers in the intermediate segregation regime when possible.

11:00 AM *FF6.8/EE6.8

SURFACE SEGREGATION IN MISCIBLE BINARY POLYMER BLENDS. Christopher Forrey, 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-constituent polymer generally differs from that of the bulk material. In an immiscible polymer blend, this phenomenon is referred to as blooming, and depends on surface energy differences and wetting 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 segregate a particular polymer to the surface and the resultant decrease in interfacial free energy. In this paper, we examine surface segregation for miscible blends of polystyrene 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 blend melts. Surface composition depth profiles were determined by angle dependent x-ray photoelectron spectroscopy. Data are presented for blends containing either normal or perdeuterated polystyrene. Perdeuteration markedly changes 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-LaCombe-Balazs extension of compressible lattice fluid theory. The latter approach provides a more appropriate description of the bulk-phase behavior for LCST blends.

11:30 AM FF6.9/EE6.9

SOLID-STATE BLENDING AND COMPATIBILIZATION OF POLYMER BLENDS BY CRYOGENIC MECHANICAL ALLOYING. Archie P. Smith, Richard Spontak, Carl Koch and Harald Ade*, 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% polyisoprene (PI) and poly(ethylene-alt-propylene) (PEP). High-energy ball milling in the solid state is considered here as a highly non-equilibrium processing alternative to avoid 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-annealing 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 to 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 intimate (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-annealing of the blends above the T_g of PMMA (which is dependent on milling time) induces morphological evolution, which varies for blends with PI and PEP. In blends composed of PEP, thermodynamic incompatibility expectedly drives phase separation within the system so that the intimate mixing gained as a result of milling is largely lost. Conversely, PI crosslinking hinders molecular mobility so that the milling-induced nanoscale mixing between 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 constitutes a viable means of producing intimate blends of immiscible polymers that can, depending on interchain reaction, retain their nanoscale morphology.

11:45 AM FF6.10/EE6.10

STRUCTURE EVOLUTION DURING POLYMER DEWETTING AND DEMIXING. Manfred Stamm^{1,3}, Peter Mueller-Buschbaum², Jochen Gutmann³. ¹Institute fuer Polymerforschung Dresden e.V., Dresden, GERMANY, ²Technical University, Garching, GERMANY ³Max-Planck-Institute fuer Polymerforschung, Mainz, 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 interface segregation effects, and lateral phase separation will generally occur. Those phenomena can be used to generate nanostructures, where relatively regularly spaced droplets or regions of different materials form. Structures are investigated by scattering techniques as well as by direct imaging techniques, which are shown to be complementary. By Fourier transform of a scanning force microscope image a power density pattern is obtained, where a prominent length scale may be recognized. Scattering techniques on the other hand also provide information from the interior 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/DD7: JOINT SESSION:
MECHANICAL ASPECTS OF SOFT BIOMATERIAL
INTERFACES

Chairs: Samuel I. Stupp and Kenneth R. Shull
Wednesday Afternoon, April 26, 2000
Metropolitan I (Argent)

1:30 PM *FF7.1/DD7.1

BIOADHESIVE POLYMER FORMULATIONS THAT PROLONG DRUG DELIVERY ACROSS MUCOSAL SURFACES. Allan Hoffman, Chad Brown, Masashi Nakakura, Guohua Chen, and Yoshi Hayashi, Dept of Bioengineering, Univ of Washington, Seattle, WA; Wayne Gombotz, Dean Pettit, Lotte Kreilgard and James Matsuura, Immunex Corp, Seattle, WA; Michael Roberts and Milton Harris, Shearwater Polymers, Huntsville, AL.

Bioadhesive 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. However, this does not necessarily lead to prolonged drug release from such formulations, since the drug may still be released too rapidly as 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 residence times on the mucosal 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/DD7.2

THE INFLUENCE OF INTERFACIAL MECHANICAL BEHAVIOUR UPON DEFORMATION AND FRACTURE OF COMPOSITE BIOPOLYMER GELS. K.P. Plucknett, V. 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 structuring additives for foods, has been examined in both tension and compression. Composite gels were fabricated by phase separation from mixed biopolymer solutions, followed by gelation, which results in discrete 'included' particles that are contained 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/maltodextrin and gelatin/agarose. The mechanical response of these materials was primarily determined by the individual constituent behaviour and the interface fracture resistance. For the gelatin/maltodextrin 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 $\sim 0.25 \text{ J}\cdot\text{m}^{-2}$ 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 maltodextrin and subsequently peeled off. Conversely, debonding was not observed for the phase-separated gelatin/agarose system. However, it was possible to conduct peel tests with a gelatin layer cast onto agarose. The fracture energy obtained in this case was approximately 30 times greater than that for the gelatin/maltodextrin system. This dramatic increase in interfacial fracture energy for this system, relative to gelatin/maltodextrin, is believed to result in the lack of observed interfacial debonding noted for the actual composite structure.

2:15 PM FF7.3/DD7.3

INTERFACIAL ADHESION OF BIOPOLYMER GELS MEASURED USING THE PEEL TEST. S.J. Pomfret, K.P. Plucknett, V. Normand, W.J. Frith, Unilever Research Colworth, Bedford, UNITED KINGDOM.

The adhesion between layers of biopolymer gels has been measured using the 90 degree peel test. Gel bilayers, including gelatin, agarose, maltodextrin and kappa-carrageenan, were prepared in several ways - simple contact between two pre-gelled layers; layers being cast on top of one another; and phase separation into bilayers. The force required to separate these layers was measured and the results allow the interfacial properties to be compared as a function of gel type, 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 attempts have been made to evaluate these terms and hence allow determination of the interfacial fracture energy of the systems involved. The value of approximately $0.2 \text{ J}/\text{m}^2$ for the interfacial fracture energy of a maltodextrin/gelatin interface, formed

by casting gelatin on maltodextrin, is in good agreement with values indirectly observed from particle/matrix debonding experiments performed on composite systems.

2:30 PM FF7.4/DD7.4

pH-DEPENDENT SWELLING BEHAVIOR OF HYDROPHILIC GEL WITH POLYSACCHARIDE. Xiaowei He, Jian Xiong, Nuo Lei, Faxing Luo, Liansheng Yang and Xiong 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 gels so far studied have poor bio-intermiscibility and probably have side effect 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 polysaccharide can be expected as a novel material like to biopolymer gels. In this study, the graft of polysaccharide and acrylonitrileStarch-g-PAN gel were prepared and also, the swelling behaviors of the gel with polysaccharide 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 region $\text{pH}=4$, the swelling ratio of the graft gel glucose group in starch: AN, 1; 6; molar ratio was almost constant. In a pH range above $\text{pH}=4.0$, the swelling ratio increased strikingly with pH up to $\text{pH}=6.0$, and showed a maximum at $\text{pH}=7.0$. Swelling and deswelling of the graft gel were induced by changing pH. For example, the swelling ratio of the graft gel decreased when the gel was immersed in water of $\text{pH}=4.0$ and then increased when it was performed in water of $\text{pH}=7.0$. The swelling ratio change for 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/DD7.5

ADHESION OF INJECTABLE SEMI-INTERPENETRATING POLYMER NETWORKS. Ranee A. Stile, Kevin E. Healy, Northwestern University, Departments of Biological Materials and Biomedical Engineering, Chicago, IL; Elizabeth Fabbioni, 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(N-isopropylacrylamide-co-acrylic acid) [P(NIPAAm-co-AAc)] hydrogels that supported bovine articular chondrocyte viability and promoted the formation of cartilage-like tissue in vitro. The aim 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 articular cartilage. The primary objective of this study was to determine the effect of synthesis conditions on the material properties of the semi-IPN. The solvent, the molar ratio of AAC:NIPAAm 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 temperature (LCST) of the semi-IPNs were determined. P(NIPAAm-co-AAc) hydrogels served as controls. The semi-IPNs demonstrated significantly smaller volume changes, as compared to P(NIPAAm-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:NIPAAm significantly affected the LCST and volume change of the semi-IPNs. To assess adhesive properties of the matrices, axisymmetric adhesion analyses were performed on thin (1 mm) layers of a semi-IPN using a coated hemispherical glass indenter. We observed a time-dependent increase in adhesion energy/elastic modulus as a function of displacement, consistent with data reported previously for a model system. Experiments are underway using this 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/DD7.6

ADHESION OF PRESSURE SENSITIVE ADHESIVES WITH APPLICATIONS IN TRANSDERMAL DRUG DELIVERY. Marc B. Taub and Reinhold H. Dauskardt, 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, necessitate 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 initial and long-term adhesion, clean removability, and skin and drug compatibility. In addition, their highly viscoelastic properties are necessary prerequisites for attachment to soft tissue. However, the adhesion of PSAs is not well understood with almost no reproducible test methods or quantitative adhesion data. This study utilizes a mechanics approach to quantify the adhesive properties of representative PSAs. Adhesion of PSAs is accompanied by cavitation in the PSA and the formation of an extensive cohesive zone. The presence of such large-scale bridging provides significant energy dissipation and increased resistance to delamination. The strain energy release rate (G) during debonding of a cantilever-beam sample, containing at its midline a thin layer of PSA, was utilized to quantify the adhesion of the PSA. The analysis accounts for both the work of adhesion as well as the viscoelastic constitutive behavior of the soft viscoelastic adhesive layer. Effects of adhesive chemistry, layer thickness, and strain rate will be discussed.

3:45 PM FF7.7/DD7.7

EFFECT OF PLASMA TREATMENT ON THE ADHESION OF AN ELECTROLESS SILVER FILM ON A BIOMEDICAL POLYURETHANE. Joy E. Gray, P.R. Norton, K. Griffiths, Dept. of Chemistry, Univ. of Western Ontario, London, Ontario, CANADA.

Bacterial growth on medical implants and devices is a common source of infection. There is a great deal of interest in the surface modification of polymeric materials to decrease infection rates without altering properties which affect their function. One possibility is to coat the material with a well known antibacterial agent such as silver. The adhesion of silver deposited on a biomedical polyurethane using a conventional electroless plating technique has been studied. Air plasma treatment of the polyurethane surface prior to electroless plating results in exclusive chemical modification of the surface and has been shown to dramatically improve silver adhesion. X-ray photoelectron spectroscopy indicates an increase in oxygen functionalities at the sample surface. Contact angle goniometry shows a significant increase in wettability. The absence of surface roughening or ablation has been confirmed by atomic force microscopy. The improved adhesion of the silver film following plasma treatment has been demonstrated using a standard tape test. Rutherford back-scattering spectrometry measurements show little change in the amount of silver on a plasma modified polymer surface after the tape test. The tape test results in almost complete removal of the silver from an unmodified polymer surface. Atomic force microscopy has been used to study the structure of the silver films produced. An unmodified polymer surface shows silver in loosely bound clusters while the plasma modified polymer film results in complete silver coverage as a uniform film. This work demonstrates the importance of chemical surface modification in the role of metal/polymer adhesion.

4:00 PM FF7.8/DD7.8

ADHESION AND MICROTRIBOLOGY OF POLYETHYLENE GLYCOL COVERED SILICA SURFACES. Norma A. Alcantar, Tonya L. Kuhl, Amy Stacy, Eray S. Aydil, Jacob N. Israelachvili, University of California, Dept of Chemical Engineering and Dept of Materials, Santa Barbara, CA.

A thin layer of polyethylene glycol (PEG) attached to a surface resist protein adhesion and biological attack. We have developed a direct method for chemically grafting low molecular weight PEG onto silica coated surfaces. The silica films are produced by plasma enhanced chemical vapor deposition (PECVD) and hydroxylated by exposure to water plasma. The end alcohol group of the PEG chain reacts with the silanol group on the silica surfaces to form an ester linkage, (Si-O-C). The adhesion and tribological properties of these surfaces were determined using the Surface Forces Apparatus (SFA) with friction device and bimorph slider. The measurements were conducted in dry air, 100% relative humidity and in bulk water. The presence or absence of water alters the frictional behavior from smooth sliding to stick-slip motion. We compare and discuss the differences between the friction, wear and lubrication properties of symmetric surfaces of PECVD deposited silica, hydroxylated silica and PEG grafted surfaces. Deposited silica surfaces have the highest friction and least resistance to wear. On the other hand, with PEG-covered silica surfaces the friction force dramatically increases with sliding velocity indicating possible "shear thickening" behavior under confined conditions.

4:15 PM FF7.9/DD7.9

NANOINDENTATION EXPERIMENTS TO PROBE THE SURFACE MECHANICAL PROPERTIES OF PLASMA TREATED POLYETHYLENES. C.M. Klapperich, K. Komvopoulos, Department

of Mechanical Engineering, Univ of California, Berkeley, CA and L.Pruitt, Departments of Mechanical and Bioengineering, Univ of California, Berkeley, CA.

Low-temperature plasma treatments have recently emerged as a popular method for the surface modification of polymers for biomedical and load bearing applications. These surface treatments have been shown to affect the surface chemistry of the material. Crosslinking by plasma treatment is also possible and can result in enhanced mechanical properties of the polymer surface. Since the plasma treatment only affects the surface or subsurface to a depth of a few microns, it is not possible to use traditional bulk tests to evaluate the mechanical properties. In order to characterize the surface mechanical properties, nano- and micro-mechanical tests were performed with a conventional atomic force microscope modified with a force-displacement transducer that utilizes a diamond tip to apply nano- and micro-Newton forces to localized regions of the polymer surface. The elastic modulus and hardness was determined by analyzing the data from these experiments using the compliance method. Since 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 energetically treated or mechanically altered polymers. Polyethylene was chosen as the material for this study because of its clinical and industrial importance. Further, polyethylene 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. Ultra-high-molecular weight (UHMWPE), high-density polyethylene (HDPE), and low-density polyethylene (LDPE) were treated in various low-temperature plasma environments. Indentations were made on all materials, and the resulting force-displacement curves were analyzed to determine the surface mechanical properties and adhesion behavior. The methods presented in this study provide a novel technique to study the surface mechanical properties resulting from controlled plasma treatments of polyolefins with varying degrees of crystallinity, molecular weight, and crosslinking.

4:30 PM FF7.10/DD7.10

STRENGTH AND TOUGHNESS OF AN ORGANICALLY REINFORCED CARBONATED APATITE BONE MINERAL SUBSTITUTE. Victoria C. Jew, Reinhold H. Dauskardt, 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. Microstructural examination of the inorganic-organic composite materials reveals a number of toughening mechanisms. Most significant is the bridging of cracks in the apatite by the organic phase. Micromechanical models have been developed to account for strengthening and toughening effects. Implications for the integrity and reliability behavior of such synthetic bone mineral substitutes in load bearing applications are considered.

SESSION FF8: POLYMER COMPOSITES AND ADHESION

Chairs: Ramanan Krishnamoorti and Manfred Stamm
Thursday Morning, April 27, 2000
Metropolitan I (Argent)

8:30 AM *FF8.1

INVESTIGATION OF PRESSURE SENSITIVE ADHESIVES STRUCTURE THROUGH LATEX BLENDING. Francois Court, Christophe Verge, Christian Laurichesse, Karine Loyer, CERDATO, Elf Atochem, Serquigny, 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 PSA coatings are often prepared by spreading and drying a polymer latex dispersion. It is a key issue 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 is to introduce in the latex, monomers able to develop specific interactions 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 are of prime importance because of 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 latexes having the same particles size and the same glass transition temperature set far below room temperature to allow chain diffusion. The blends investigated are constituted of a non cohesive latex and a latex bearing controlled amounts of an ureido acrylic monomer. We find that even for low concentrations of latter latexes the static shear resistance increases meaning that significant chain interdiffusion is possible even for polymers able to form physical cross-links.

9:00 AM FF8.2

ADHESION OF TRIBLOCK COPOLYMER-BASED THERMO-REVERSIBLE GELS AND PRESSURE SENSITIVE ADHESIVES. Kenneth R. Shull, Alfred J. Crosby, Cynthia M. Flanagan, 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. These materials dissolve in a variety of alcohols at temperatures above 60 degrees C to form freely flowing liquids. At lower temperatures the PMMA end-blocks associate so that the solutions form ideally elastic solids. In our case the solvent is 2-ethylhexanol, polymer volume fractions vary from 0.05 to 0.3, 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 solvent. Very little adhesion hysteresis is observed in this case, although we do observe hysteresis associated with the frictional response of the gels. 2) Strongly adhering gels: By heating the gels in contact with a PMMA surface, 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: By removing 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. Resistance to adhesive failure, expressed as a velocity dependent fracture energy, greatly exceeds the thermodynamic work of adhesion. This energy is further magnified by "bulk" energy dissipation when the stress applied to the adhesive layer exceeds its yield stress.

9:15 AM FF8.3

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 of 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 adhesives (e.g. epoxy) on flat surfaces is much smaller 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. For two planar SAMs all the bonds must fracture simultaneously, but in the adhesives sequential bond breaking significantly reduces the instantaneous fracture stress.

9:30 AM FF8.4

SULFONATED WHOLLY AROMATIC PROTON EXCHANGE MEMBRANE FOR FUEL CELLS: ADHESION ISSUES.

J.E. McGrath, H.K. Shobha, F. Wang, S. Wang, N. Gunduz, W. Harrison, J.B. Mechem, G. Smalley, D.A. Dillard, Virginia Tech, Dept. of Chemistry, Blacksburg, VA; R. Formato and R. Kovar, Foster Miller, Waltham, MA.

Currently, the most important proton exchange membrane (PEM) for fuel cells is based on the statistical sulfonic acid fluorinated copolymer provided by DuPont under the trade name, Nafion. Although this is an excellent material in terms of many of the requirements, it is considered to be somewhat limited at elevated temperatures needed to limit the side reaction of carbon monoxide with the platinum catalyst. In addition to serving as a proton exchange membrane, the polyelectrolyte materials must also interact with the catalyst dispersed in carbon black and become part of the membrane electrode assembly (MEA). Thus, new PEMs will require further consideration of adhesion issues in the membrane electrode assembly. Our laboratory has investigated wholly aromatic poly(arylene ether)s, poly(thio ether sulfone)s, poly(arylene phosphine oxide)s, and specialty polyimides as candidate PEMs. This presentation will describe the fundamental characteristics of several of these new classes of materials, which are promising as new hydrolytic and oxidatively stable proton exchange membranes. The issues of adhesion and compatibility will be featured.

10:15 AM *FF8.5

INTERFACIAL WIDTH AND FRACTURE TOUGHNESS OF

INTERFACES BETWEEN GLASSY HOMOPOLYMERS. Ralf Schnell, Akzo Nobel Faser, Oberburg, GERMANY; Cornelia Lorenz, Manfred Stamm, Max-Planck Institut fur Polymerforschung, Mainz, GERMANY; Costantino Creton, Laboratoire PCSM, ESPCI, Paris, FRANCE.

We have investigated the relationship between the width a_I of interfaces between glassy monodisperse homopolymers, as measured by neutron reflectivity, and their fracture toughness characterized by the critical energy release rate G_c in a double-cantilever beam test. For a family of polymers with nearly identical crazing stresses and with molecular weights much larger than the average molecular weight between entanglements, we found a unique relationship between G_c and a_I . The fracture toughness increased with interfacial width following three regimes. For narrow interfacial widths (regime I), G_c was small and nearly independent of interfacial width, for intermediate values of a_I (regime II), a sharp increase in G_c was observed due presumably to the activation of plastic deformation mechanisms at the interface. Finally for thicker interfaces G_c was found to be again nearly independent of the width of the interface. For PS the transition from regime I to regime II occurred for $a_I = 6$ nm and that from regime II to regime III occurred at 11 nm. Most of the increase in toughness occurred in regime II and could be interpreted in terms of an increasing failure stress of a craze fibril with increasing interfacial width. Preliminary results with high-molecular weight PMMA-PMMA interfaces showed however a much sharper transition from low to high fracture toughness occurring around $a_I = 12$ nm. Since PMMA has a lower average distance between entanglements, this result is surprising and will be discussed in terms of microscopic mechanisms of deformation.

10:45 AM FF8.6

ADHESION ENHANCEMENT VIA INTERFACIAL ENTANGLEMENTS. Phillip J. Cole and Christopher W. Macosko, University of Minnesota, Department of Chemical Engineering and Materials Science, Minneapolis, MN.

Considerable research has focused on strengthening immiscible polymer-polymer interfaces through the addition of an adhesion enhancing molecule, such as a block copolymer. It may be possible to dramatically alter the interface integrity through carefully tailoring the properties of the homopolymers themselves, even eliminating the need for an adhesion enhancing species. This would be done by maximizing interfacial entanglements, which are largely responsible for the interfacial strength. In semicrystalline polymers, an additional improvement could also be achieved by end-anchoring an interfacially entangled chain in the crystalline regions of the homopolymer(s). In order to study the role of interfacial entanglements, and the additional variable of crystallinity, a series of crack propagation tests were performed on compression-molded, bilayer structures. These structures included glassy-glassy, glassy-semicrystalline, and semicrystalline-semicrystalline pairs with varying interfacial widths. Specifically, the polymer pairs included polystyrene-poly(methyl methacrylate), polystyrene-polyethylene, polystyrene-polypropylene, and others. In addition, commercial available polyethylenes synthesized with different catalyst technology were used, introducing a varying amount of non-crystallizable material at the interface. This permits an assessment of the importance of crystalline-anchored,

interfacially entangled chains. Initial crack propagation results have confirmed our expectations in the compression-molded samples, demonstrating the importance of interfacial entanglements. 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 multilayer 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 polymer components with appropriately tailored properties cannot be overlooked.

11:00 AM **FF8.7**

THE EFFECT OF SURFACE CONTAMINATION ON ADHESIVE FORCES AS MEASURED BY CONTACT MECHANICS.

John A. Emerson, Gregory V. Miller, Christopher R. Sorensen, Sandia National Laboratories, Albuquerque, 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 mate 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 practical work of adhesion (W_a) were determined by the contact mechanics, via the JKR model, using a model siloxane network for the elastomeric contact sphere. Variations in the thickness of the hexadecane were determined by ellipsometry. As the film thickness of hexadecane increases, W_a decreases as expected. We found that the W_a plateaus as the film thickness increases. However, for small amounts of contamination, there is no decrease in W_a . This work supported by U.S. DOE Contract DE-AC04-94AL85000.

11:15 AM ***FF8.8**

THE ROLE OF FIBER/MATRIX INTERFACE AS A STRESS TRANSFER MEDIUM IN POLYMERIC COMPOSITES.

Costas Galiotis, 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 (s). The stress build-up in the broken fiber (s), as well as, the magnitude and local stress distribution in the intact fibers are governed by the material properties and, most importantly, by the strength and toughness of the fiber/matrix interface. Practical experience has long guided composite manufacturers and users to produce tough composites by tailoring the interface in such a way so as to balance the beneficial reduction of stress concentration with the resulting detrimental increase of the transfer length. The complexities of the mechanisms of stress transfer and fiber stress redistribution combined with the statistical aspects of both fiber and interfacial strength make the modelling of the strength of fibrous composites a very difficult endeavour. In this paper the link between interfacial characteristics such as fiber surface treatment, fiber sizing, 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 tows. In all cases, the point-by-point stress in the fiber was measured with the technique of remote laser Raman microscopy (ReRaM). The composite specimens were loaded incrementally in tension and the stress transfer profiles emanating from fiber breaks, were closely monitored. The stress or strain along individual fibers at 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/ positive 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 filament break in the 2D and full composite geometries were determined as a function of distance from the fiber fracture.

11:45 AM **FF8.9**

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 (SFFT). In the SFFT, a single fiber is aligned along the axis of a dog bone cavity and embedded in a resin having an extension-to-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. This point is termed saturation. The fiber-matrix interface strength 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 viscoelastic deformation 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 distribution change with testing rate 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 Jahankhani and Galiotis (1991) and finite element calculations performed by Carrara and McGarry (1968). These authors concluded that 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 SFFT testing rate can lower the magnitude of these stress concentrations and minimize failure of the fiber-matrix interface.

SESSION FF9: POLYMER SURFACES AND SURFACE MODIFICATION

Chairs: Gregory S. Ferguson and Costantino Creton
Thursday Afternoon, April 27, 2000
Metropolitan I (Argent)

1:30 PM ***FF9.1**

STRUCTURE AND RHEOLOGY OF INTERCALATED POLYSTYRENE-POLYISOPRENE LAYERED-SILICATE NANO-COMPOSITES. Ramanan Krishnamoorti, Jiaxiang Ren, University of Houston, Department of Chemical Engineering, Houston, TX.

The structure and viscoelastic properties of a series of polystyrene-polyisoprene block copolymer (PS-PI) based nanocomposites with varying amounts of dimethyl dioctadecyl ammonium modified montmorillonite (2C18M) are studied. The layered structure of the nanocomposites, with a gallery height of 2.5 ± 0.1 nm and independent of the silicate loading, is verified by X-Ray diffraction. The melt rheology of PSPI-2C18M nanocomposites is systematically studied in terms of linear oscillatory shear measurement, linear and non-linear stress relaxation tests, steady shear rate response and dynamic strain sweeps. It is found that the nanocomposites display unique rheological properties that depend on the amount of silicate incorporated. The linear viscoelastic dynamic moduli are found to be quantitatively consistent with the linear stress-relaxation modulus. While the pure polymer exhibits liquid-like characteristics, a nanocomposite with 6.7 wt% silicate exhibits pseudo-solid like behavior. The unique rheology is a consequence of the mesoscopic and nanoscopic structure of these nanocomposites.

2:00 PM **FF9.2**

MODELLING SURFACE AND INTERFACIAL PROPERTIES OF LINEAR AMORPHOUS POLYMERS. Sylvain Goudeau, Jocelyne Galy, Jean-Francois Gerard, Laboratoire Materiaux Macromoleculaires, INSA Lyon, Villeurbanne, FRANCE; Rene Fulchiron, LMPB, Universite C. Bernard, Villeurbanne, FRANCE; Jean-Louis Barrat, Dept. Physique des Materiaux, Universite C. Bernard, Villeurbanne, FRANCE.

Much attention has recently been 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 interfacial properties, i.e. interfacial tension and interface 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 intersegmental or intermolecular interactions. PS and PMMA were selected as references and the methodology was applied to high-Tg polymers such as PPE, PEI, PES, epoxy prepolymers, and their binary mixtures. The first approach relies on PVT (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-Orwoll-Vrij or Prigogine models) to extract the cohesive energy density, CED, as well as surface tension. The surface properties of polymer blends, 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 MSI Cerius2 & InsightII with accurate force-field designed especially for polymers. Both bulk and surface cells were simulated. The simulation of thin films allows us to observe chain re-orientations and the increase of surface mobility. The comparison between bulk and surface simulations leads to the surface tension of polymers.

2:15 PM *FF9.3

SWITCHING OF SURFACE PROPERTIES WITH POLYMER BRUSHES. Manfred Stamm^{1,2}, Sergiy Minko^{2,3}, Alexander Sidorenko^{2,3}. ¹Institut fuer Polymerforschung Dresden e.V., Dresden, GERMANY, ²Max-Planck-Institut fuer Polymerforschung, Mainz, GERMANY, ³Physical Chemistry Institute, National Academy of Sciences, Lviv, UKRAINE.

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-vinyl pyridine), where a switching between a hydrophobic and hydrophilic behaviour is possible. This is achieved by a structural rearrangement of the brush-like surface layer, where either one or the other component occupies the outermost layer. The surface is analysed by photoelectron spectroscopy, scanning force microscopy, contact angle measurements and optical techniques. Potential applications of reversibly switchable and environmental adjustable surface layers in the area of materials science and biocompatibility are discussed.

3:15 PM *FF9.4

ELECTROGRAFTING OF CONDUCTING POLYMERS ONTO ITO SURFACES. David Labaye, Christine Jerome, Robert Jerome, Center for Education and Research on Macromolecules, University of Liege, Liege, BELGIUM; Viktor Geskin, Roberto Lazzaroni, Service des Materiaux Nouveaux, 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 (Fe, Ni) to ITO glass (1-2). The cathodic electrografting of the acrylate of thiophene will be discussed followed by the anodic polymerization of thiophene. The electroactivity of the organic film will be analyzed and the dependence of the film thickness on the electrosynthesis conditions, as well. A series of properties of the electrografted film will be compared to polythiophene films prepared by traditional anodic electropolymerization, including morphology, adhesion, optical and electroluminescence properties.

(1) M. Mertens, C. Calberg, L. Martinot, R. Jérôme, *Macromolecules*, 29, 4910 (1996).

(2) N. Baute, P. Teyssié, L. Martinot, M. Mertens, P. Dubois, R. Jérôme, *Eur. J. Inorg. Chem.*, 1711 (1998).

3:45 PM FF9.5

SURFACE MODIFICATION OF POLY(ALKYL/ARYL-PHOSPHAZENE) THIN FILMS. John V. St. John, Patty Wisian-Neilson, Southern Methodist University, Dallas, TX.

Poly(alkyl/arylphosphazenes) are a unique class of inorganic polymers. The alternating $-(PR_2=N)-$ backbone provides for stable bulk properties of the materials while allowing latitude for 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, disulfides, thiols, esters, ferrocene, and a variety of substituted silyl groups. This research demonstrates studies of surface modification of poly(phosphazene) thin films with the goal of enhancing specific surface chemical functionality while maintaining bulk properties of the films. Functional groups such as alcohols, thiols, and carboxylic acids can be used to enhance the adhesive properties of poly(phosphazene) 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 photoreactive substituents allows the potential for patterned polymer surfaces which have regions containing different chemical functionality. This yields the possibility of thin films which can be

used to assemble ordered arrays of nanostructures which have specificity for different chemical

4:00 PM FF9.6

RADIATION ENHANCED POROSITY AND ROUGHNESS OF BIOMATERIALS. A.L. Evelyn, D. Ila, R.L. Zimmerman, Center For Irradiation of Materials, Alabama A&M University, Normal, AL; M.G. Rodrigues, University of São Paulo, DFM-FFCLRP, Ribeirão Preto/SP, BRAZIL; D.B. Piker, D.K. Hensley, Oak Ridge National Laboratory/SMAC, Oak Ridge, TN.

Glassy polymeric carbon (GPC), made from cured phenolic resins, is sufficiently chemically inert and biocompatible that it is suitable for medical applications, such as heart valves and other prosthetic devices. We have used energetic ion bombardment of the partially and fully cured precursor phenolic resins to enhance biological cell/tissue growth on, and to increase tissue adhesion to, prosthetic devices made from GPC. GPC samples were bombarded with energetic ions ranging from 1 keV to 10 MeV. The surface topography and increased surface roughness were observed using optical microscopy and atomic force microscopy (AFM). The increased porosity was measured by introducing lithium from a molten LiCl salt into the GPC and using (p, α) 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 FF9.7

SURFACE INITIATED POLYMERIZATION FROM GaAs. Hanrong Gao, Thomas A.P. Seery, Institute of Materials Science, University of Connecticut, Storrs, CT.

Polymer layers attached to GaAs wafers were prepared by polymerization from a surface-tethered organometallic catalyst. As an example, thiols with terminal alcohols 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 polyhexylisocyanate 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 polynorbornene layer on the surface. Attached polymer layers were characterized by IR, XPS and ellipsometry analysis.

4:30 PM FF9.8

SURFACE-ATTACHED POLYMER NETWORKS. Oswald Prucker, Kristin Müller, Jürgen Rühle, University of Freiburg, Institute for Microsystem Technology (IMTEK), Freiburg, GERMANY.

The modification of surfaces with thin films of polymer networks is of great interest in many 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 structures to the solid support is mandatory as otherwise the networks would be depleted 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 FF9.9

MICROCELLULAR POLYMERIC FOAMS PRODUCED IN SUPERCRITICAL CARBON DIOXIDE. Srinivas Siripurapu, Yvon Gay, Joseph R. Royer, Joseph DeSimone, Richard J. Spontak and Saad A. Khan, Department of Chemical Engineering, North Carolina State University, Raleigh, NC.

Foamed 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 world-wide 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 viscosities, 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.