2:00pm AS-WeA1 Changes in the Band Structure Across the Surface Ferroelectric Phase Transition in the Crystalline Ferroelectric Copolymer P(VDF-TrFE), J. Choi, P.A. Dowben, A.V. Bune, S. Ducharme, University of Nebraska, Lincoln; V.M. Fridkin, S.P. Palto, N. Petukhova, The Russian Academy of Sciences, Russia

Recently, the ferroelectric copolymer poly(VDF-TrFE, 70:30) LB films have been attracted because of the new surface ferroelectric phase transition and correlation of the surface ferroelectric transition with the electronic structure. @Footnote 1,2@ The relationship between the electronic structural and the conformational structural change of the crystalline 5 ML films of poly(VDF-TrFE, 70:30) has been studied in detail using several methods: angle resolved inverse photoemission spectroscopy, low energy electron diffraction, angle resolved X-ray photoemission, and work function across the surface ferroelectric transition. Their results indicate that the Brillouin zone size is doubled across the surface ferroelectric transition. This is a C-F bond reorientation across the ferroelectric phase transition. Most profound are the changes in the unoccupied (conduction band) structure. @FootnoteText@ @Footnote 1@A. V. Bune, V. M. Fridkin, Stephen Ducharme, L. M. Blinov, S. P. Palto, A. Sorokin, S. G. Yudin, and A. Zlatkin, Nature (London) (to be published) @Footnote 2@Jaewu Choi, P. A. Dowben, Shawn Pemble, A. V. Bune, Stephen Ducharme, V. M. Fridkin, S. P. Palto, and N. Petukhova, Phys. Rev. Lett. 80, 1328(1998)

2:20pm AS-WeA2 UV Photopolymerization of Methyl Methacrylate and Acrylic Acid on Pt(110) Using Time-Resolved FT-IRAS, J. Yan, K. Green, T. Jachimowski, J. Lauterbach, Purdue University

The adsorption and polymerization characteristics of methyl methacrylate (MMA) and acrylic acid on platinum were studied under varying conditions using time-resolved Fourier-transform IR reflection-absorption spectroscopy (FT-IRAS). Methyl methacrylate absorbs physically on Pt(110) at 100 K, while acrylic acid likely chemically adsorbs. Adsorption of these monomers results in broadening of features, peak shifts, and changes in the intensity ratios of different peaks in the vibrational spectra, as compared to their liquid phase values. The most significant observation in the FT-IRAS spectrum of adsorbed MMA is the absence of the vibrational bending mode of the @alpha@-CH3 group of the monomer in the adsorbed films. The FT-IRAS spectrum of acrylic acid shows that it adsorbs in both the cis and trans forms showing a relative increase in the cis form with coverage. The UV-initiated photopolymerization of MMA and acrylic acid were examined by monitoring the disappearance/appearance of characteristic absorption bands as the monomer was converted to polymer. MMA polymerization results in the expected decrease in intensity of the C=O bond of the monomer and also a decrease in the intensity of the carbonyl group of the monomer. Associated with the decrease in intensity of the carbonyl group is the observation of surface bonded CO. The most significant result of the photopolymerization of acrylic acid is the appearance of COO@sub 2@ on the surface as the polymerization proceeds. In contrast with MMA we did not observe large changes in the intensities of the carbonyl and C=C peaks indicating that although polymerization was occurring, decarboxylation was more likely.

2:40pm AS-WeA3 Correlations of the Structure and Mechanical Properties of Polymer Surfaces: Combined Sum Frequency Generation-Surface Vibrational Spectroscopy and Atomic Force Microscopy Studies, G.A. Somorjai, D. Gracias, D. Zhang, University of California, Berkeley

INVITED Vibrational spectroscopy by sum frequency generation (SFG) is a non-linear optical technique that is totally monolayer sensitive and can be employed for studies of solid-liquid, solid-solid, and solid-gas interfaces. It provides information about the surface structure and orientation of molecules at the interface. Atomic force microscopy permits measurements of the elastic moduli and the friction coefficient of interfaces with excellent spatial resolution. We utilized both techniques to investigate the surface (low and high density), polypropylene (atactic, isotactic) surfaces, and a polymer blend, Biospan-S, in air and in liquids and as a function of temperature. The structure and orientation of CH@sub 2@ and CH@sub 3@ groups at the interface readily identify polyethylene and polypropylene types. Structural changes that occur near and at the glass transition temperatures are detectable. The friction coefficients and elastic moduli correlate well with changes of surface structure. Biospan-S undergoes structural changes when placed in an aqueous solution from air resulting in the migration of the hydrophilic polymer components to the surface. Good correlations of these changes with variations of contact angle were found. AFM detects phase segregation as the composition of the polymer blend is altered.


Biodegradable polymers have many applications such as controlled release for drug delivery and as wound healing devices. The characteristics of surface hydrolysis as a degradation mechanism for biodegradable polymers are crucial to the application. Time-of-flight secondary ion mass spectrometry (ToF SIMS) makes it possible to observe the in-vitro hydrolysis products directly as intact low molecular weight oligomers. In this study, we have investigated the hydrolysis degradation of important biopolymeric, polyelectrolytes such as poly(glycolic acid) (PGA), poly(lactic acid) (PLA), the copolymer poly(lactic-co-glycolic acid) (PLG) and various polyamides. The in-vitro hydrolysis reaction is conducted on polymer disc samples at 37 @super 0°C@ in a physiological buffer for a range of hydrolysis periods from one to twelve hours. The hydrolysis products are observed in ToF SIMS spectra as peaks assigned to intact molecular ions. The molecular weight distribution of hydrolysis products is then obtained. The capability of using ToF SIMS in direct characterization of surface degradation kinetics of biodegradable polymers is demonstrated.

3:40pm AS-WeA6 Effect of PDMS Segment Length on the Surface Composition of Polymidesiloxane Copolymers and its Role in Adhesion, J. Zhao, State University of New York, Buffalo; S.R. Rojstaczer, Occidental Chemical Corporation, J.A. Gardella, J. Chen, State University of New York, Buffalo

Polymidesiloxane (SIM) copolymers are becoming increasingly important materials in the microelectronics industry in applications, such as die attach adhesives, due to their attractive properties, such as good adhesion, low dielectric constant and low stress. In this study, a series of SIM copolymers, based on @alpha@-@omega@-aminopropyl(dimethylsiloxane)[PDMS] and 4,4'-oxypthalic anhydride(ODPA) was synthesized in our laboratories. We investigated the effect of siloxane segment length on the surface composition of the SIM copolymers and its role in adhesion. The aim is to elucidate the correlations between polymer structure, surface composition, and the adhesion strength, as evaluated by peel tests. In-depth compositional profiles of the near surface region to approximately 100Å depth were simulated from the results of angle-dependent Electron Spectroscopy for Chemical Analysis (ESCA) experiments by using a deconvolution computer program. The simulated in-depth compositional profiles show that the topmost surface of the copolymer is composed of a mixture of silicon and carbon, but also the 75Å thick SIM copolymer film consists of a siloxane-rich layer, even with the shortest siloxane segment. For a given siloxane bulk content, a longer siloxane segment gives a surface richer in siloxane. The adhesion strength was determined by peel testing of SIM copolymers-Fe/Ni Alloy-42 laminates. The peel strength decreases exponentially with increasing thickness of the surface siloxane-rich layer, which corresponds to a longer siloxane segment length. However, all values of adhesion strength of SIM copolymers are higher than that of pure polyimide. This confirms our previous results that both siloxane and polyimide are essential components to rendering the high adhesion strength. The siloxane component provides a good diffusive ability, while the polyimide component interacts with the substrate to give rise to adhesion strength. Longer siloxane segments in the SIM copolymers are found to be detrimental to adhesion strength by way of interference with the polyimide-metal interaction.

4:00pm AS-WeA7 Interface Characterization with Combined XPS and TOF-SIMS An Application to the Metalization of Plasma Modified Polymer Surfaces, D. Wolany, T. Fang, T. Guntenfort, L. Wiedmann, A. Benningenhooven, Universität Münster, Germany

In recent years, the combination of time-of-flight secondary ion mass spectrometry (TOF-SIMS) and X-ray photoelectron spectroscopy (XPS) has gained considerable importance for the analysis of technologically relevant surfaces and interfaces, e. g. for device technology or for surface modification of organic substances. The polymer-metal interface is of particular interest, because such compound materials are used e. g. for compact disks or flexible electronic circuit boards. The polymer-metal
interface itself, however, is not accessible by surface analytical techniques except in the case of adhesion failure. The combination of TOF-SIMS and XPS can help in this situation by characterization of the original polymer substrate, the surface of the plasma modified polymer, and the initial stages of metal deposition. In this way, one can obtain valuable insights into the interaction mechanisms between the metal and the substrate. We present results for Cu on polyimide modified in an oxygen plasma, and Al on polycarbonate modified in oxygen, argon and SF$_6$ plasmas, respectively. In both cases, XPS shows, after plasma modification, the occurrence of additional binding states within the polymer. In the initial stages of metallization, metal-substrate bonds can be identified which are characteristic for adhesion of the metal. The TOF-SIMS fragmentation patterns both after plasma treatment and after metallization allow the identification of specific interaction mechanisms between the polymer and the metal. In addition, standard technical adhesion tests (peel test, twist-off test) were applied to similar samples with thick metallic overlayers. In this way we established correlations between the plasma parameters used for substrate modification, the chemical and physical properties of the modified substrate and the polymer-metal interface, and the adhesion strength of the compound material.

- Determined. The optical data were also
- National Space Station and Hubble
- has been evaluated by x-ray photoelectron
- sma modification, the results of field exposure, and were found to
- , J.N. Hilfiker, J. A. Woollam Co., Inc.; J.A. Woollam, University of Nebraska, Lincoln
- Polymers used on spacecraft are often susceptible to environmental degradation in Low Earth Orbit (LEO). Therefore, the behavior of materials used on spacecraft such as the International Space Station and Hubble Space Telescope (Hubble) must be well characterized to ensure long term survivability of the spacecraft. Optical methods are favorable to study space application materials because they are non-contact and non-destructive. However, polymer films are often biaxially anisotropic and this anisotropy is usually not accounted for when optical measurements are acquired. In this work FEP Teflon (pristine and exposed to the LEO environment on Hubble) are studied using various optical measurements, including transmission ellipsometry, reflection ellipsometry and transmission intensity. By acquiring a series of different optical measurements the optical constants in three orthogonal directions and their optical axis orientations were determined. The optical data were also studied to help determine the extent of degradation of aluminized FEP returned from the first and second Hubble servicing missions.

### 4:20pm AS-WeA8 XPS Evidence of Redox Chemistry Between Cold Rolled Steel and Polyaniline, B.C. Beard, P. Spellane, Akzo Nobel Chemicals, Inc.

The electrochemical response of polyaniline (PANI) in its undoped form (emeraldine base, EB) oxidation state coated on cold rolled steel (CRS) or glass substrates has been evaluated by x-ray photoelectron spectroscopy (XPS). The oxidation state of the polymer was determined from the ratio of amine to imine nitrogen chemical states observed in the N(1s) photoelectron spectrum. A room temperature air dried PANI coating cast from NMP solution onto CRS was found to be reduced relative to its as-synthesized, air stable state. Heating the PANI coated on CRS in the absence of air (165°C, in ultra high vacuum) produced an even deeper reduction, resulting from the transfer of electronic charge to the polymer from the metal substrate. Subsequent brief exposure of this reduced PANI coating to air at elevated temperature (165°C) reoxidized the PANI to the EB state. Analogous treatment of a PANI coating on glass caused no such change in oxidation state of the polymer. Unlike steel which provides a redox couple with PANI, glass is electro-inactive.

### 4:40pm AS-WeA9 Evaluation of the Degradation Mechanism(s) Associated with Acid Rain Exposure of Acrylic Melamine Based Automotive Clearcoats, P.J. Schmitz, J.W. Holubka, L.F. Xu, Ford Motor Company

Environmental exposure of clearcoats to ambient conditions of low pH can result in visible surface pitting. The degradation phenomenon associated with this localized loss of material is thought to occur primarily through crosslink hydrolysis as a result of acid rain exposure. Although this phenomenon has been studied quite extensively, limited chemical data has been presented that confirms the mechanism(s) of the degradation process. Most conclusions that have been made are largely based on empirical considerations involving observations that degradation is most prevalent in areas having low pH rain, and the results of field exposure studies that indicate the sensitivity of a particular coating to environmental degradation is directly associated with the ease of hydrolysis of the crosslink. In this study, we have used XPS to monitor changes occurring at the clearcoat surface as a result of field exposure, to attempt to more clearly define degradation products, and therefore the mechanism(s) associated with the degradation phenomenon. Changes were observed in the N, C, and O core level spectra after field exposure, and were found to be consistent with the modification of melamine crosslinkers following laboratory acid treatment. Bulk elemental analysis and XPS core level results, obtained from sulfuric acid treated crosslinkers, were found to be consistent with melamine salt (sulfate) formation. The confirmation of residual melamine sulfate on the clear coat surface following field exposure, strongly suggests that the prominent degradation pathway is acid rain induced crosslink hydrolysis. The identification of degradation products associated with environmental exposure could prove useful in the development of laboratory testing for the evaluation of clearcoat hydrolysis resistance, to verify that exposure conditions reproduce field degradation pathways.
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