

Applied Surface Science Division

Room 6A - Session AS-ThA

Polymer Surfaces, Films, and Interfaces

Moderator: P.M.A. Sherwood, Kansas State University

2:00pm AS-ThA1 Conformation and Orientation Effects in the XPS Spectra of Thin Polymer Films, *G. Beamson*, Daresbury Laboratory, U.K., United Kingdom

INVITED

The conformation and orientation of polymer chains at surfaces and in thin films can play an important role in determining the properties of technological systems, and may be different from the bulk polymer. Techniques such as GIXS, NEXAFS, AFM, infrared spectroscopy, ellipsometry and XPS are currently being used to investigate the arrangement of polymer chains at surfaces. Conformational effects in the XPS spectra of polymers are small, but advances in instrumentation over the past decade have increased their probability of detection. The search for conformational signatures requires careful measurements on well characterised polymers as a function of conformational change. Changes in conformation often accompany a change in crystallinity or physical state. Polymers suffer x-ray induced degradation during XPS which can mask subtle conformational effects. Hence time dependent studies are required to establish upper limits on x-ray exposure times such that degradation is not a concern. Differential charging can also mask subtle spectroscopic effects and good charge compensation is crucial for the detection of conformational signatures. Orientation effects in polymer systems can be probed by angle dependent XPS studies. A conformational signature in the C 1s spectrum of PET will be discussed and comparison of XPS and infrared data will be used to demonstrate faster conformational change at the surface than in the bulk when the polymer is annealed above T_g . Conformational signatures in the valence bands of PEG, PTMG and nylon 12 will also be described. Angle dependent XPS studies of orientation effects in molecular overlayers on PTFE tribological transfer films will be discussed. Functional group orientation effects in acrylic polymers will also be described.

2:40pm AS-ThA3 Correlative XPS and FTIR Imaging Analysis of Polymer Blends, *J.E. Fulghum*, *K. Artyushkova*, *A.C. Ferryman*, Kent State University; *J.L. Koenig*, Case Western Reserve University

Phase segregation in blends of poly(vinyl chloride) and poly(methyl methacrylate) has been evaluated through correlation of photoelectron and infra-red images and small area spectra. Polymer surfaces which are heterogeneous on the scale of microns can be characterized by XPS if both imaging and small area spectroscopy are utilized. Polymer compositions in the bulk phase are routinely evaluated using FTIR spectroscopy. In this study, we take advantage of recent advances in the imaging capabilities of both techniques to improve characterization of heterogeneous organic samples. Surface-specific chemical information was acquired using a Kratos AXIS Ultra photoelectron spectrometer, while phase-segregation in the bulk was studied using a Biorad Stingray FTIR microscope. Images of comparable spatial resolution are readily obtained, allowing for a more complete characterization of lateral and vertical phase segregation than is possible with a single spectroscopic technique. Core and valence band XPS determinations of polymer blend composition in phase-separated regions will be compared to results based on small-area FTIR spectra. This work has been partially supported by NSF DMR89-20147 and 3M.

3:00pm AS-ThA4 Beam Induced Damage Effects in XPS Studies of Thin Organic Films, *H. Cohen*, *R. Maoz*, *E. Frydman*, *J. Sagiv*, The Weizmann Inst. of Science, Israel

Beam induced irreversible effects are frequently overlooked in XPS studies of thin organic films, mainly because of limitations in self testing capabilities of the technique. Minimization of such effects requires elaborated experimental procedures, and a fundamental understanding of the dominant damage mechanisms. Aiming at this goal, a thorough study of X-ray induced effects in layered self assembled organic films has been conducted using a number of complementary techniques, additional to the in-situ XPS measurements. Chemical functions particularly sensitive to the X-ray radiation have been identified. Structural and chemical modifications are discussed as a function of the initial film composition, and their significance for potential applications is indicated.

3:20pm AS-ThA5 Surface Analysis of Nitrogen Plasma-Treated Poly(ethylene-2,6-naphthalate) Films using XPS and Gas Phase Derivatization Reactions, *Y. Liu*, *L. Gerenser*, Eastman Kodak Company

Nitrogen plasma-treatment is a very useful technique for modifying the surface properties of polymers, including adhesion, wettability and biocompatibility, through the introduction of nitrogen functional groups. This presentation will focus on the characterization of nitrogen plasma-treated poly(ethylene-2,6-naphthalate) films using conventional XPS and gas phase derivatization reactions in combination with XPS. The selectivity and yield of trifluoroacetic anhydride for primary amines, and trifluorotoluene for secondary amines, were determined by reacting them with model compounds containing the nitrogen group of interest (e.g., primary and secondary amines, amides and nitriles). The quantity and depth distribution of primary and secondary amines for nitrogen plasma-treated PEN were evaluated as a function of gas composition (e.g. N@sub 2@, NH@sub 3@, and N@sub 2@O) and treatment conditions (power and pressure). Correlations were found between the plasma conditions and the resultant surface chemistries.

3:40pm AS-ThA6 Quantitative Analysis of Functional Groups with TOF-SIMS, *T. Fladung*, *D. Wolany*, *T. Gantenfort*, *L. Wiedmann*, *A. Benninghoven*, Universität Münster, Germany

The unique identification and quantitative analysis of functional groups from plasma treated polymer surfaces with XPS and TOF-SIMS is often difficult. In this case, derivatization and subsequent quantitative XPS is well-known for a number of important functionalities. We will show that the analysis of derivatization products with TOF-SIMS can extend the limited sensitivity of XPS by several orders of magnitude and, at the same time, be made quantitative by suitable calibration. After gas phase derivatization of hydroxide groups with trifluoroacetic anhydride (TFAA), the XPS results of monofunctional model polymers can be used as standards for the calibration of SIMS data. During TOF-SIMS analysis of the model polymers after derivatization, the intensity of a characteristic set of molecular ions containing fluorine is proportional to the concentration of OH groups as determined by XPS, and can thus be taken as a quantitative measure of the surface concentration of OH groups. For polypropylene and polycarbonate samples treated in an oxygen and argon plasma, respectively, the modified surfaces were derivatized with TFAA and analyzed with XPS and TOF-SIMS. The results were used to quantitatively distinguish the OH groups from other functionalities generated by the plasma such as carbonyl or carboxyl groups. Principal component analysis was used for the comparison of SIMS spectra before and after derivatization. This seems to be a promising way to establish a direct assignment of secondary ions to specific functional groups. In this way the quantitative chemical analysis of surface functionalities by TOF-SIMS should become possible without derivatization.

4:00pm AS-ThA7 Determination of Helical Conformation Effects in PTFE NEXAFS Spectra with FEFF8 Calculations, *D.G. Castner*, *L. Gamble*, University of Washington; *D.A. Fischer*, *B. Ravel*, National Institute of Standards and Technology

Near edge X-ray absorption fine structure (NEXAFS) experiments can provide information about the orientation of adsorbed small molecules, self-assembled monolayers and polymers. Long fluorocarbon chains are known to have a twisted (or helical) structure due to the steric interactions of the fluorine atoms. FEFF8 calculations of the C K-edge and F K-edge spectra of poly(tetrafluoroethylene) (PTFE) have been done to determine how changing the helical structure of the PTFE chains affects the NEXAFS spectra. Experimental NEXAFS spectra were obtained at beamline U7A of the NSLS on highly-oriented PTFE samples prepared by rubbing a block of PTFE across a gold-coated silicon wafer heated to 150°C. The helical chains in this well-ordered film are oriented parallel to the gold surface and along the rubbing direction. A large polarization dependence is observed at the F K-edge for the C-F @sigma@* peak and at the C K-edge for the C-F @sigma@* peaks (at 292.6eV and 299eV) and the C-C @sigma@* peak at (296.4eV). FEFF8 NEXAFS spectra calculated with self-consistent spherical muffin-tin potentials, a full multiple-scattering formalism, the structural coordinates for bulk PTFE, and no adjustable physical parameters are in good agreement with the experimental NEXAFS spectra. Variation of the F-C-F bond angle in the calculated spectra showed that when this angle is commensurate with the helicity of the chains, F atoms from adjacent CF2 groups become aligned in the axial direction. This alignment results in a large change in the NEXAFS spectra. Calculations that varied the radial distance of the carbon atom from the molecular axis showed that a "straight" backbone produces significantly different NEXAFS spectra than a

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helical backbone. Further calculations show that "stretching" and "compressing" the helical chain can also effect the widths, positions, and intensities of peaks in the NEXAFS spectra.

4:20pm AS-ThA8 Monitoring the Kinetics of Migration/ Absorption/ Desorption/ and Cross-linking in a Curing Silicone Coating, using the QCM-D Technique, *P. Dahlgvist*, Q-Sense AB, Sweden; *M. Rodahl*, Chalmers, Sweden; *P. Bjoorn*, Q-Sense AB, Sweden; *M. Berglin*, *P. Gatenholm*, Chalmers, Sweden

The Quartz Crystal Microbalance - Dissipation (QCM-D) technique allows real time measurements of properties and processes in nm-um thin polymer and bio-films (M.Rodahl et al., Faraday Discuss. 107, 229 (1997)). Via changes in the resonant frequency, f , small mass changes (ng/cm²) are measured. Via changes in the energy dissipation factor, D , energy losses due to internal and interfacial friction in the polymer film are measured. This makes the technique a versatile tool to, e.g., phase transitions and polymerisation kinetics. In this work we studied the cross-linking kinetics of approximately 0.5 um thick films of silicone (PDMS) in the presence of various concentrations of catalyst and cross-linker (Tridecafluoro - 1,1,2,2, - tetrahydro - octyl triethoxysilane) (FTEOS), at varying humidity. The fluorine-rich FTEOS migrates to the surface due to phase separation and due to minimisation of the systems surface energy. The kinetics of the migration has been monitored and found rapid, most of the migration take place in the first 15 minutes. Water adsorption and ethanol desorption were monitored over time. The water absorption is dominant in the start of the reaction, but after a few minutes to hours, depending on relative humidity, catalyst and FTEOS concentration, the ethanol desorption becomes dominant. The cross-linking rate monitored with the dissipation factor, is highest in the beginning and slowed after 0.5 - 5 hours, depending on relative humidity and catalyst concentration.

4:40pm AS-ThA9 Angle Resolved XPS Study of Random Fluoromethacrylate Copolymers, *W.E. Kosik*, *S.H. McKnight*, *J.M. Deitzel*, *N.C. Beck Tan*, Army Research Laboratory

Design and control of polymer surface functionality is desirable for numerous applications. It is widely known that hydrophobic polymer surfaces can be produced on block-copolymers due to surface segregation of hydrophobic blocks, including fluoro and siloxane species. Less research has been performed on random copolymer compositions. In this work, we investigate the surface segregation of a random copolymer of polymethylmethacrylate (PMMA) and tetrahydrofurfuryl acrylate (PTAN). Copolymers containing different ratios of the two repeat units were examined. Thin films (150-200 nm) were solution spun-cast onto silicon substrates. As-deposited and samples annealed above the copolymer glass transition temperature were studied to assess the degree of surface reorganization that might occur. Angle resolved XPS was used to study the fluorine content of the thin films as a function of depth. It was observed that the concentration of fluoro groups increases near the surface of the film in all compositions. The degree of surface segregation was dependent on the PTAN to PMMA ratio of each copolymer. Furthermore, the segregation was enhanced after annealing of the films at elevated temperatures. Water contact angle measurements were in agreement with the angle resolved XPS results. Potential applications of these materials for selectively permeable membranes are discussed.

5:00pm AS-ThA10 Surface Analysis Characterization of Titanium/Sol-Gel/Polyimide Adhesive Systems, *J.T. Cherian*, Boeing Materials Technology & University of Washington; *D.G. Castner*, University of Washington

Bonded titanium alloys are being evaluated for use at an operating temperature of 175°C. Determining the locus of failure for bonded titanium lap-shear specimens is part of a larger effort to develop durable, environmentally safe surface treatments for titanium alloys. Surface-treated titanium alloy (Ti-6Al-4V, Ti3Al-2.5V, and Ti15V-3Al-3Cr-3Sn) plates are bonded in a standard lap-shear specimen configuration and exposed to temperature for specified intervals. The lap-shear bond joint consists of two etched titanium panels that are coated with a silicon and zirconium containing sol-gel, primed with a polyimide, and then bonded together with adhesive and supporting scrim material. The lap-shear specimens are tested for overall strength and failure modes. Specimens with cohesive failure modes were examined with ESCA and ToF SIMS to determine the composition of the bond joint failure layer. Although the failure was located closer to the sol-gel/polyimide interface than to the Ti/sol-gel interface, ESCA and ToF SIMS analysis revealed that the actual location (sol-gel, primer, etc.) of the failure varies from spot to spot across a given specimen. SEM analysis suggests that the rough surface of the titanium

oxide introduces stress at the interface and promotes the non-uniformity of the failure regimes. A model system is being used to investigate the interfacial bonding chemistry between the sol-gel and the polyimide primer. Pure titanium is deposited onto silicon wafers to create a smooth titanium substrate. Smooth, thin layers of sol-gel and polyimide coatings are then spun onto the Ti surface. AFM is used to measure the surface roughness of each layer. ESCA analysis in conjunction with pentafluorobenzaldehyde derivatization is used to follow the changes in the bonding chemistry at the sol-gel/polyimide interface as the sample is cured.

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