Tuesday Morning, November 5, 2002

Applied Surface Science
Room: C-106 - Session AS-TuM

Polymer Characterization
Moderator: J.E. Fulghum, Kent State University

8:20am **AS-TuM1 Chemical Bonding of Perfluoropolyether End Group with Carbon Overcoat Surface by Irradiating Visible Laser Light**, ***L. Zhu***, *J. Zhang, T. Liew, K. Ye*, Data Storage Institute, Singapore

A thin lubricant film was applied on a magnetic hard disk carbon overcoat to reduce friction force, resist corrosion and minimize wear. Further treatment of the lubricant is to improve one or more of its properties for its compatibility with increasing magnetic recording densities. In this paper, we investigate the chemical bonding of perfluoropolyether lubricant molecules with carbon overcoat surface by irradiating visible laser light. A Nd:YAG laser with a wavelength of 532nm was used to irradiate the lubricant film (2 nm) on carbon overcoat surface in ambient environment. Samples were analyzed using the time-of-flight secondary ion mass spectroscopy. We found that with increasing laser energy, the ion yield of the end group CF2CH2OH decreases indicating the formation of chemical bonds of the end group with the active sites on the carbon overcoat surface. Secondary ion mapping of the laser irradiated area shows that fluorine and backbone fragments COF2 and C2OF4 are concentrated in the bonding area. This is in sharp contrast with our previous results with UV laser irradiation on the lubricant where the abundance of the end group remains almost constant with increasing laser energy and two unique backbone peaks are generated, indicating direct scission of the lubricant molecules in UV regime.

8:40am **AS-TuM2 TOF-HREELS and AFM Characterization of Highly Oriented Teflon (PTFE) Films**, ***Z. Yang***, *G. Bernhardt, R.L. Jackson, L.J. LeGore, P. Kleban, W.N. Unertl, B.G. Frederick*, University of Maine

Highly oriented polytetrafluoroethylene (PTFE) films are potentially useful as substrates for anisotropic growth of organic and bio-materials and as model surfaces for studying surface modification. High resolution electron energy loss spectroscopy (HREELS) has advantages of surface specificity, sensitivity and the possibility of non-dipolar interaction mechanisms, but has required relatively long data acquisition times. We have developed a novel time-of-flight (TOF-HREELS) spectrometer, which utilizes a throughput advantage to dramatically reduce acquisition times.[1] PTFE films were deposited onto sputtered films of gold and platinum on oxide-covered Si wafers by the friction transfer process.[2] The samples were studied by AFM to characterize the film roughness and thickness. The AFM images reveal long, straight ribbons of PTFE parallel to each other when deposited at a substrate temperature of 220 °C and a pressure of 1kg/8 mm^2. Comparisons are made between HREELS spectra obtained by the conventional instrument and the TOF-HREELS spectrometer.

[1] R. H. Jackson, et al., Surf. Sci. (2002), in press; L. J. LeGore, et al., ibid.

[2] P. Bodö, M. Schott, Thin Solid Films 286 (1996) 98.

9:00am **AS-TuM3 Surface Analysis of Poly (dimethylsiloxane) using Time-of-Flight Secondary Ion Mass Spectrometry**, *J.A. Gardella,* ***R. Rey-Santos***, The State University of New York at Buffalo

The study of polymer surface structures has become an important topic in surface chemistry. Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is one of the most powerful techniques for surface analysis. ToF-SIMS has been used to study the secondary and tertiary structures of polymers. The Langmuir-Blodgett technique has been used to prepare thin films of poly (dimethylsiloxane) (PDMS) monolayers. Reflection Absorption Fourier Transform Infrared Spectrophotometry (RA-FT-IR) has been used to identify the surface structure of PDMS films. The use of the statistical chain breaking model of poly (alkyl methacrylates) by Zimmerman, Hercules, and Benninghoven published in Analytical Chemistry in 1993, helped us to determine the statistical chain breaking model for PDMS. Our goal is to use polymers as model systems to investigate the ion formation mechanisms and provide information about the long-range forces between polymer chains.

9:20am **AS-TuM4 Surface Analysis of Novel PDMS-Containing Amphiphilic Graft Copolymer by X-Ray Photoelectron Spectroscopy**, ***L. Chen***, *P.L. Valint, J.A. Gardella*, State University of New York at Buffalo

The surface composition of a series of amphiphilic graft copolymers consisting of hydrophilic poly(2-hydroxyethyl methacrylate) [poly(HEMA)] backbones and hydrophobic poly(dimethylsiloxane) (PDMS) side chains prepared by both photoinduced-radical and anionic polymerization techniques has been determined by angle dependent X-Ray Photoelectron Spectroscopy (XPS). The effects of PDMS graft length, PDMS bulk content and Molecular Weight Distribution (MWD) on the surface composition were investigated. It was found that the PDMS surface concentration increased with the increase of PDMS bulk content, but the effect of the bulk content on PDMS surface concentration for copolymers with long graft chains is much smaller than that for copolymers with short graft chains. For a given PDMS bulk content, a longer PDMS graft gave a surface richer in siloxane. The dominating factor in defining the siloxane surface segregation is not bulk content but graft length for these copolymers. PDMS surface concentration of copolymers with narrow MWD was observed higher than that with broad MWD, this could be explained by the purification process the copolymers went through during preparation.

9:40am **AS-TuM5 Embedding of Noble Metal Nanoclusters into Polymers as a Potential Probe of the Surface Glass Transition : Study with XPS**, ***V. Zaporojtchenko***, Christian-Albrechts University of Kiel, Germany

Embedding of noble metal nanoclusters into polymers is introduced as a novel method with a strong potential to follow the polymer glass transition at the surface.[1] X-ray photoelectron spectroscopy (XPS) in combination with transmission electron microscopy (TEM) was used to characterize the formation of nanoclusters during the noble metals (Au and Cu) deposition onto different polymers and to study the embedding of nanoclusters into polymers. The size of the metallic clusters and an embedding depth were determined using a mathematical correction of the XPS intensity.[2] This procedure is based on the measurement of the ratio of two XPS lines of the same metal with different binding energies and their attenuation length. X-ray photoelectron spectroscopy (XPS) has been applied to study the embedding of Cu and Au nanoclusters into polycarbonate, nylon as well as polystyrene films with different molecular weight by annealing the polymer films above the glass transition temperature Tg . It is shown that the temperature dependence of the embedding depth is clearly correlated to the glass-transition temperature of the polymer. Our investigations strongly support a depression of Tg at the surface compared with that of the polymer bulk. This supports the view that the molecular motion is enhanced near the surface due to the additional degrees of freedom. The enhancement of the surface glass transition temperature was observed due to Ar ion treatment of the polymers. The changes of Tg , which are qualitatively related to cross-linking, depend on the ion fluencies in the range of 10E13 - 10E14 cm^{-2} .

[1] V. Zaporojtchenko, T. Struskus, J. Erichsen, F. Faupel, Macromolecules 34(5) (2001) 1125.

[2] V. Zaporojtchenko, K. Behnke, T. Struskus, F. Faupel, Surf. Interface Anal. 30 (2000) 439.

10:00am **AS-TuM6 Surface Composition in Isotopic Polymer Mixtures Based on ToF-SIMS and Neutron Reflectivity**, *A. Takahara, D. Kawaguchi,* ***K. Tanaka***, Kyushu University, Japan, *S. Tasaki,* Kyoto University, Japan, *M. Tozu, T. Hoshi,* Ulvac-Phi, Inc., Japan, *T. Kajiyama*, Kyushu University, Japan

Surface composition in blend films composed of monodisperse polystyrene (hPS) with the number-average molecular weight, Mn, of 19.7k and deuterated monodisperse polystyrene (dPS) with Mn of 847k was examined by time-of-flight secondary ion mass spectroscopy (ToF-SIMS) in conjunction with neutron reflectivity (NR). Although hPS has higher surface energy than dPS, ToF-SIMS and NR revealed that hPS was enriched at the outermost surface of the films. The surface segregation of hPS can be accounted for by the molecular weight disparity for both components, that is, an entropic effect.

10:20am **AS-TuM7 SPM Structural Study of Phase Segregation, Thermal Behavior, and Aging of Poly(Ester Urethane) Compression Molded Samples**, ***M.E. Hawley***, *E.B. Orler, D.A. Wrobleski, R.P. Hjelm*, Los Alamos National Laboratory

Only a limited number of structural studies have been performed on segmented poly urethanes using tapping mode scanning probe techniques to determine both the nanostructure and the corresponding nanophase segregation of hard and soft segments within the samples. This type of information is needed to better understand the mechanical and thermal properties of these materials and to facilitate modeling efforts. In order to address these issues, we have fabricated a compression molded segmented poly(ester urethane) samples with varying hard (HS) to soft segment (SS) ratios. Samples were examined using scanning probe phase imaging techniques to obtain the topography and map the corresponding HS and SS segregation before and after heating to over 100 °C both ex-situ and in-situ to and correlate those results with thermal absorption data. Changes in structure were followed as a function of time to address aging issues. A number of significant differences were observed before and after these thermal plastic samples were heat treated. Variations in structure and heat-induced morphological changes were directly related to HS content. Fine 10 to 10 nm thick lamellar- or fibril-like structures were most prominent in samples with lower HS content while harder, thicker elongated structures seen to a limited extent on all samples dominated the surface of high HS samples. The disappearance of the fine structures appears to be related to a peak in the endothermal data. The reappeared emanating from the large rod-like structures first as short branching then completely covering the surface after less than 2 days. Surface roughness increased in the process by approximately 10x.

10:40am **AS-TuM8 Surface-induced Ordering of Poly(ethylene terephthalate) Studied with In-situ Grazing Incidence X-ray Diffraction**, ***J.E. Macdonald***, *M. Durell, D. Trolley,* Cardiff University, UK, *P.C. Jukes, A.M. Higgins, R.A.L. Jones*, University of Sheffield, UK

Grazing incidence x-ray diffraction has been performed during in-situ annealing of a polymer thin film for the first time to investigate the molecular configuration at the surface of poly(ethylene terephthalate) (PET) films during crystallisation. The structural ordering at the surface of the film was compared directly with that in the bulk of the film by employing incident angles at and above the critical angle for total reflection. Ordering was observed at the surface at annealing temperatures of 85-95°C, while the bulk of the film remained amorphous. Parallel in-situ atomic force microscopy studies give direct images of the spherulites formed at the surface. Both techniques in tandem thus yield the structure and kinetics of ordering at the surface and in the bulk of the film.

11:00am **AS-TuM9 A Novel Micromechanical Platform to Measure the Surface Stress Produced by Electroactive Polymers**, ***V. Tabard-Cossa***, *M. Godin, O. Laroche, B. Seivewright,* McGill University, Canada, *A. Badia,* Universite de Montreal, Canada, *B. Lennox, P. Grutter*, McGill University, Canada

A novel platform to measure the surface stress produced by ionic electroactive polymer (EAP) materials is presented. In order for these materials to be used as conventional microactuators, it is important to accurately characterize them and, in particular, quantify the surface stress associated with the applied potential, so that their mechanical limitations and advantages can be determined. Micromechanical cantilever-based sensors, with their high sensitivity and fast response, are ideal tools for the characterization of these molecular scale electromechanical actuators. A standard, three-probe, electrochemical system is used, with an Ag/AgCl reference electrode and a Pt counter electrode, in a combined apparatus with a surface stress AFM cantilever-based sensor, where the cantilever simultaneously serves as the working electrode to obtain surface stress data in parallel with cyclic voltammetry (CV). The instrument, capable of integrating the electrochemical setup with the surface stress sensor requirements, will be described. The experimental setup, with the optimal cell geometry, necessary electronics and required software and hardware components will be shown. Dodecyl benzenesulfonate-doped polypyrrole (PPy(DBS)) in an aqueous solution of Na(DBS) is the EAP studied. Potentiostatic growth results of polypyrrole films on gold coated AFM cantilevers and their characterization by cyclic voltammetry and AFM/SEM will be presented. In addition, bending of the PPy/Au coated cantilever bilayer structure is measured as a function of applied potential. The equation used to calculate the surface stress induced during cyclic voltammograms circumvents the need to know the cantilever's Young's modulus by using readily measurable cantilever properties.[1] Finally, surface stress as a function of applied potential will be shown and its correlation with oxidation and reduction peaks addressed.

[1] M. Godin et al., Appl. Phys. Lett. 79, 4 (2001).

11:20am **AS-TuM10 Photoelectron Spectroscopy of Conjugated Polymers**, *R. Friedlein,* Linköping University, Sweden, *S.L. Sorensen,* Lund University, Sweden, *W. Osikowicz, M.P. de Jong,* ***W.R. Salaneck***, Linköping University, Sweden **INVITED**

Conjugated polymers have been studied by photoelectron spectroscopy and other related surface science techniques for over two decades. In the past few years, however, several advances have been made in classical techniques. Some aspects of X-ray and ultraviolet photoelectron spectroscopy (XPS and UPS), as applied to conjugated polymers, will be hilighted. New results on high quality conjugated polymers will be presented.

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