Material Characterization
Room 207 - Session MC-ThM

Polymer Characterization

Moderator: B.C. Beard, Akzo Nobel Chemicals

8:20am **MC-ThM1 Quantification of Polymer Surface Composition Based on ToF-SIMS Data*, P. Bertrand,*** Université Catholique de Louvain, Belgium **INVITED**

Time-of-Flight Secondary Ion Mass Spectrometry is nowadays intensively used for polymer surface characterization. The fingerprint nature of ToF-SIMS spectra acquired in static conditions is now well established. Characteristic molecular fragment ions can be used for identification of polymer and organic materials present at the surface. The aim of this presentation is to discuss some issues related to surface quantification with this technique. This is of special importance for applications where copolymers and polymer blends are involved. First, we will discuss the use of end group ToF-SIMS signals. Our recent results obtained on monodisperse polystyrene samples show that ToF-SIMS is very sensitive to end groups. Their intensity can be used, after appropriate calibration, to quantify molecular weight at the surface. Some end groups (sec-butyl) are seen to influence also the intensity of main chain fragments. This is due to a specific interaction with the first neighboring repeat unit. It consists in a mechanism of H transfer, with no long-range (intermolecular) influence. So, the end group signals allowed us to quantify the surface composition of polystyrene blends with close molecular weights but different end groups. Second, we will discuss the use of characteristic fragment intensity and intensity ratios for blend and copolymer surface quantification. For polystryrene / poly (2,6-dimethyl-1,4-phenylene oxide) blends, which are miscible and do not exhibit any surface segregation, the intensity of the characteristic ions is seen proportional to homopolymer bulk concentration, allowing a staighforward surface quantification. But for random copolymers, different situations are observed. For random styrene butadiene rubbers, an appropriate choice of ions leads to "bulk like" surface composition, as expected. However, styrene / methyl methacrylate random copolymers, exhibit strong matrix effects due to a specific interaction between adjacent species taking place during the secondary ion emission. This outlines the need of understanding the fragmentation pathways in order to use ToF-SIMS intensities for surface quantification. Another approach would be the use of "full spectrum" chemometrics multivariate methods.

9:00am **MC-ThM3 Characterisation of Polymer Additives by Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS)*, R. Kersting,*** *B. Hagenhoff,* TASCON GmbH, Germany*; D. Rading, E. Niehuis,* ION-TOF GmbH, Germany

In continuation of our ongoing studies concerning the characterisation of polymer additives in their respective host polymers we have concentrated on the investigation of the influence of the primary ion parameters on the emission behaviour of characteristic additive ions. The additives, mostly antioxidants, were incorporated into low densitiy polyethylene (LDPE) or spin coated onto virgin LDPE in concentrations between approx. 500 and 2000 ppm. Thus ion emission from thick polymer materials could be studied. Reference samples without the polymer host were prepared by spin coating the additives onto bare Si wafers. Both, monoatomic (Ga@super +@, Au@super +@) and polyatomic (SF@sub 5@@super +@, Au@sub 2@@super +@) ions were used for sample excitation. Additionally, the energy of the respective primary ions was varied between 1 and 10 keV. The talk will describe the influence of the respective primary ion parameter onto yield and efficiency of the desorbed secondary ions. The consequences for the quantification of polymer additives in "real world" samples will also be discussed.

9:20am **MC-ThM4 Surface Composition of Poly(imidesiloxane) Copolymers Containing Multiple Siloxane Lengths*, C.M. Mahoney,*** State University of New York at Buffalo*; J Rosenfeld, S.R. Rojstaczer,* Occidental Chemical Corporation*; J.A. Gardella,* State University of New York at Buffalo

Polyimidesiloxane copolymers (SIM) are becoming increasingly important materials for microelectronic applications due to their excellent adhesive properties, low dielectric constants and good overall thermal and mechanical properties. Hence it is of importance to study the surface and interfacial properties of this polymer system. More recently it has been shown through depth profiling using Electron Spectroscopy for Chemical Analysis (ESCA) that an increase in the siloxane chain length will result in an increase in the thickness of the siloxane layer at the surface.@footnote 1@ The effect of incorporating two or more different siloxane segment lengths into the same copolymer system, on the surface properties, has not been investigated. It is of importance to determine whether or not there is preferential segregation of certain segment lengths over others in SIM copolymers containing multiple siloxane lengths. A series of poly(imidesiloxane) (SIM) copolymers, based on a,w'-aminopropylpoly(dimethylsiloxane) (PDMS) of varying molecular weights, 2,2-bis(4-[4-aminophenoxyl]phenyl)propane (BAPP), and 4,4'-oxydiphthalic anhydride (ODPA) was synthesized in our laboratories. In this series, the total composition of PDMS was maintained at 10%, while the segment length composition of the PDMS was varied (e.g. 5% Mw = 252g/mol, 5% Mw = 832.5g/mol vs. 1% Mw = 252g/mol, 9% Mw = 832.5g/mol). This polymer series was analyzed using ESCA and Time of Flight Secondary Ion Mass Spectroscopy (ToF-SIMS). Angle-dependent ESCA results suggest that there is preferential segregation of the longer PDMS segment lengths to the surface. ToF-SIMS can be used to further confirm the occurance of this preferential segregation. The peel strength of the polymer series to a standard Ni/Fe alloy 42 was measured , and the results correlate well with the ESCA and ToF-SIMS data. @FootnoteText@ @footnote 1@ Zhao, J; Rojstaczer, S.R.; Chen, J.; Xu, M.; Gardella, J.A. Macromolecules. 1999, 32(2), 455.

9:40am **MC-ThM5 High Spatial Resolution XPS and FTIR: An Approach to 3-D Characterization of Polymer Blends*, K. Artyushkova,*** *G. Czwerniec, J.E. Fulghum,* Kent State University*; B. Wall, J. Koenig,* Case Western Reserve University

Correlative XPS and FTIR studies of the complex structure of PVC/PMMA polymer blends will be presented. The comparable lateral resolution and real-time imaging capabilities of both techniques allow for a direct comparison of surface (XPS) and bulk (FTIR) measurements of polymer blends. In order to eliminate substrate influence and film-to-film variations, the same areas on the polymer films were analyzed by both methods. The effect of PMMA molecular weight on surface separation and segregation was evaluated using six blends with a constant PVC molecular weight and a PMMA molecular weight varying from 75 kDa to 2,132 kDa. The imaging capabilities of both techniques were used for a qualitative comparison of the heterogeneous structure of the blends, while a quantitative comparison of bulk and surface compositions utilized small area spectroscopy from XPS and FTIR. Based on the quantitative analysis, we can conclude that surface segregation of PMMA increases with increasing molecular weight. Comparison of Attenuated Total Reflectance (ATR) FTIR, bulk FTIR and large area XPS analyses provides adiditional information about component distrubution in the blend. The combination of high-spatial resolution XPS and FTIR provides a more complete method for characterizing complex polymer films containing differing surface and bulk compositions. This work has been partially supported by NSF ALCOM (DMR89-20147)and 3M. The XPS was funded by a grant from the Keck Foundation and by NSF CHE-9613880.

10:00am **MC-ThM6 Iron Metallization of Fluorinated Organic Films; A Combined XPS and AFM Study*, S.R. Carlo,*** *A.J. Wagner, D.H. Fairbrother,* Johns Hopkins University

The evolution of the metal-organic interface during iron mediated metallization of fluorinated organic surfaces has been studied using X-ray Photoelectron Spectroscopy (XPS) and Atomic Force Microscopy (AFM). Poly(tetrafluoroethylene) (PTFE) and a semi-fluorinated self-assembled monolayer (CF@sub3@(CF@sub2@)@sub7@(CH@sub2@)@sub2@SH, CF-SAMs) formed on Au were used as substrates. Reaction of Fe resulted in defluorination of each film, production of a carbonaceous overlayer and exclusive formation of iron (II) fluoride. A metallic iron overlayer was formed concurrently with FeF2 during deposition on CF-SAMs and following extended iron exposures with PTFE substrates. X-ray treatment of metallized PTFE caused an increase of the FeF@sub2@ content in the metal-organic region. Ex-situ AFM measurements revealed that the frictional characteristics of the surface increase during the initial stages of metallization associated with defluorination and FeF@sub2@ formation. At higher Fe exposures the surface friction decreased as a metallic overlayer evolved. Results of metallization using other metals will also be presented.

10:20am **MC-ThM7 Interactions of Cu(I) with the Surface of a Novel Poly(imidazole)*, A.L. Marsh,*** *D.J. Burnett,* University of Michigan*; D.A. Fischer,* National Institute of Standards and Technology*; P.G. Rasmussen, J.L. Gland,* University of Michigan

The surface of a novel poly(imidazole), polyvinazene, was characterized using both X-ray Photoelectron Spectroscopy (XPS) and Near Edge X-ray Absorption Fine Structure (NEXAFS) at both the C-K-edge and N-K-edge.

Polyvinazene, which is based on the monomer 2-vinyl-4,5-dicyanoimidazole, is a novel polymer which has a high temperature stability and can be easily processed from solutions in concentrated aqueous ammonia into thin, yellow films. XPS was used to determine the chemical composition of the polyvinazene surface, while NEXAFS was used to determine the structure of the polymer surface before and after copper doping. Since NEXAFS probes unfilled molecular orbitals, it is capable of distinguishing between the specific bonds present in the polymer, so the bonding sites for Cu(I) can be determined. In addition, the orientation of the imidazole ring has been determined since resonance intensities for NEXAFS obey electric dipole selection rules. Based on NEXAFS experiments, Cu(I) interacts favorably with the amide N on the imidazole ring. Also, the imidazole ring is oriented close to the surface and away from the surface normal, which supports the claim that the polymer chains are linked together through hydrogen bonds. Determination of the bonding site of Cu(I) to the polymer and the structure of the polymer surface hopes to aid in design for materials such as sensors, catalysts, and metallized polymer films.

10:40am **MC-ThM8 Study of Semicrystalline Poly(ethylene terephthalate) by Atomic Force Microscopy**, *M. Kovar, U. Gorodzinsky, **P.R. Norton**,* University of Western Ontario, Canada

We studied the surface topography of isothermally crystallized polyethylene terephthalate (PET) films by atomic force microscopy (AFM). Annealing a flat amorphous PET film at 150 @super o@C produces a semi-crystalline film which is rough on several length scales. We found good correlation of the height (3.5 nm) of small topographical features with the lamellar thickness determined by small angle X-ray scattering in previous studies. It was shown that larger agglomerates (large peaks) are multiples of small ones. The phenomenon is known as lamellar stacking. We hypothesize that the surface corrugation originates as follows: elevated (more crystalline) areas are created at the locations of crystallization nuclei. The polymer chains fold to create lamellar structures and pull "loose" ends out of amorphous regions. Subsequently, lamellar stacks grow using a similar mechanism forming the elevated regions and leaving recessed (less crystalline) ones behind Surprisingly, the density of the small topographical features is the same in the recessed and elevated regions, apparently indicating similar crystallinity, while interfacial force microscopy (IFM) data [J. Mater. Res. 12 (1998) 3565] show the elevated regions to be more crystalline. This apparent conflict results from the sensitivity of AFM phase imaging to only the outermost surface of the film compared to IFM, even for IFM indentation depths of a few nm. Therefore, the variations in the density of crystalline domains (lamellae) that are visible in AFM phase images represent a surface phenomenon that cannot be simply correlated with the state of sub-surface regions.

11:00am **MC-ThM9 Morphology of Catalytically Formed Polyethylene on a Planar Model System for the Phillips (CrOx / SiO2) Catalyst**, *P.C. Thuene, J. Loos, P.J. Lemstra,* Eindhoven University of Technology, The Netherlands; ***J.W. Niemantsverdriet***, Eindhoven University of Technology, The Netherlands, Netherlands

One of the neglected topics of polymerization catalysis is the so called nascent morphology of polyolefins which is the result of polymer formation below the melting temperature and simultaneous crystallization. Nascent polyolefins have special physical properties, which might be controlled and manipulated to enhance the processability of certain high performance polyolefins. Using a planar model system for the chromium on silica catalyst for ethylene polymerization we have obtained AFM images of polyethylene in the state of nascent morphology. By diluting the number of catalytically active sites on the model, individual islands of polymer, produced by single sites have been observed.

11:20am **MC-ThM10 Nano-Mechanics of Polymer Surfaces**, *C. Steffan, H. Liu, **R.M. Winter**,* South Dakota School of Mines and Technology

We report on the nano-mechanical properties (elastic modulus and time dependent phenomena) of polymer surfaces as they relate to polymer matrix composites. This work is prompted by the desire to engineer macroscopic polymer matrix composite properties by systematic variation of nano- and micro-scopic properties of the interphase. The interfacial force microscope, a scanning probe microscope, which utilizes a non-compliant force sensor is employed to characterize the surfaces. Force-displacement curves are obtained, from which, elastic modulus is determined using contact mechanics analysis. Creep and relaxation experiments are performed to characterize the time dependent phenomena of the polymeric surfaces. The surfaces are comprised of epoxy, amine curing agent, and amine coupling agent of systematically varied epoxy-amine equivalence ratios. These ideal interphases model the interphase found in polymer matrix-inorganic reinforcement composites and are used to reveal the relationship between chemistry and nano-mechanical properties. Fourier transform infrared spectroscopy is used to analyze the model interphase chemical composition as a function of amine-epoxy equivalence ratio. The FT-IR analysis and nano-mechanical results are correlated showing how elastic modulus and time dependent properties can be controlled by varying the chemistry and reaction conditions of the system. These data are compared to previously obtained elastic modulus profiles of the interphase in fiber reinforced epoxy matrix composites where the modulus was found to vary by 100% in a ~5 micron region surrounding the reinforcing fibers.

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