

Tuesday Afternoon, November 11, 2014

Applied Surface Science

Room: 316 - Session AS+MC+SS-TuA

Analysis of Modified Surfaces

Moderator: Xia Dong, Eli Lilly and Company, Carl Ventrice, Jr., University at Albany-SUNY

2:20pm **AS+MC+SS-TuA1 Analysis of Surface-oxidized Polypropylene Films**, *Mark Strobel, S.J. Pachuta, D. Poirier, H. Lechuga*, 3M Company
INVITED

The most widely used industrial processes for modifying the surfaces of polymer films are flame and corona (dielectric barrier discharge) treatments. While both of these processes oxidize a thin surface region of the treated films, there are significant differences between the surfaces generated by the two surface-oxidation processes. A principal difference between corona and flame treatments is the likelihood to form water-soluble low-molecular-weight oxidized material (LMWOM). LMWOM is formed by the simultaneous oxidation and chain scission of a polymer material. LMWOM is an important surface characteristic that has a large effect on the wetting and adhesion properties of polymer surfaces.

LMWOM can be investigated by a number of surface analytical techniques, including x-ray photoelectron spectroscopy (XPS or ESCA), static secondary ion mass spectrometry (SIMS), atomic force microscopy (AFM), and contact angle measurements. This presentation will demonstrate how surface analysis enables the detection and detailed characterization of the LMWOM formed by the flame and corona treatment of polypropylene (PP) film surfaces. The mechanism of LMWOM formation can be then determined from these analytical results when coupled with an understanding of the bulk photo-and-thermal degradation of PP materials.

3:00pm **AS+MC+SS-TuA3 XPS Analysis for Modified Fabrics**, *Christopher Deeks*, Thermo Fisher Scientific, UK, *M. Milošević, M. Radoičić, Z. Šaponjić*, University of Belgrade, Serbia, *T.S. Nunney*, Thermo Fisher Scientific, UK, *M. Radetić*, University of Belgrade, Serbia

Modifications of fabrics are becoming more important for a wide variety of applications. For example, loading TiO₂ onto cotton can improve many of the material properties, such as anti-bacterial effects, UV protection, and stain resistance.

The conformity of these modifications across sample surfaces are an important part of the application process. By using XPS in addition to other techniques, surface concentration and conformity can be determined and deduced whether the samples have met certain criteria, and how the uniformity, or lack thereof, can affect the desired outcome of the modifications.

This presentation will look at the possibility of in situ photoreduction of Ag ions on the surface of TiO₂ nanoparticles to create "active fabrics", and will utilize XPS imaging to determine whether deposition on the surface of different fabrics has been successful.

3:20pm **AS+MC+SS-TuA4 Characterization of Corona Treated Polymers**, *Michaeleen Pacholski*, The Dow Chemical Company

Corona treatment is often used to increase the surface energy and surface polarity of polyolefins and other polymers. In this study corona-treated, formulated polyolefin was characterized over the course of one year by SIMS, XPS and surface energy. The changes in surface chemistry could be fit to simple models to predict long-term behavior. This system is more complex than many others discussed in literature, as the formulation ingredients change in surface concentration with time, in addition to the typical decrease in surface oxygen concentration over time. SIMS and XPS measurements were used to characterize the complex surface changes as the surface energy was monitored. Additional examples of corona treated PET will also be presented.

4:20pm **AS+MC+SS-TuA7 Investigation of Atmospheric Pressure Plasma Jet as a Pre-Treatment for Adhesive Bonding of Structures Made of Carbon Fiber Reinforced Plastics (CFRP)**, *Timo Hofmann, J. Holtmannspötter*, Bundeswehr Research Institute for Material, Fuels and Lubricants, Germany, *T. Meer*, Airbus Group Innovations, Germany, *J. Rehbein, G. Härtl*, Bundeswehr Research Institute for Material, Fuels and Lubricants, Germany

Carbon fiber reinforced plastics (CFRPs) are increasingly employed in novel aircraft structures due to their high tensile strength, low weight, favorable fatigue behavior, and ruggedness against outer influences

(corrosion). Joining of CFRP structures is currently performed using rivets and bolts. In order to exploit further weight-saving potential, the usage of adhesive bonding is intended.

An important key factor for the success of adhesive bonding is the surface pre-treatment of the adherents. Peel-plies are commonly used for the fabrication of CFRP structures and, in theory, are said to create a pristine and uncontaminated fractured surface upon removal. In reality, the presence of release agents leads to contaminated surfaces that may cause unforeseeable failures of structures in service.

In this contribution, CFRPs (Hexcel 8552 / IM7) were produced using various peel-plies and release foils currently employed in aerospace manufacturing processes. Atmospheric pressure plasma jet (APPJ) was investigated as a method to further improve adhesion and to clean the samples from release agents.

We present a detailed investigation of the surface morphology and composition of CFRPs before and after treatment with APPJ. The peel-plies and the CFRP surfaces were examined by a combination of Field-Emission Scanning Electron Microscopy (FE-SEM), X-Ray Photoelectron Spectroscopy (XPS), and Energy-Dispersive X-ray spectroscopy (EDX).

We studied the approach of surface functionalization and contaminant removal by variation of the type of peel ply, release agent, and plasma treatment parameters. In the experiments particular focus was placed on determining changes in the chemical composition of the surface and morphology. We demonstrate that APPJ-processes offer limited cleaning capabilities for CFRP surfaces. Furthermore, the ability to induce morphological changes is highly dependent on the initial level of surface roughness and chemistry. Finally, we show that overtreatment leads to degradation of the epoxy component and enrichment of the thermoplastic portion of the matrix on the surface.

4:40pm **AS+MC+SS-TuA8 Thickness and Composition Determination of Thin Film Sn-Oxides Growth at Room Temperature using XPS Spectra**, *M. Bravo-Sanchez*, CINVESTAV-Queretaro, Mexico, *Jorge Huerta-Ruelas*, Instituto Politecnico Nacional, Mexico, *A. Herrera-Gomez*, CINVESTAV-Queretaro, Mexico

The knowledge of the tin oxidation process is important for the development corrosion-free coatings and the engineering of alloys and compounds with specific functional properties. Tin, pure and well controlled oxidized samples were characterized by X-ray photoelectron spectroscopy (XPS). All samples were prepared on Si (100) substrates with RCA treatment before Sn deposition. The thickness of the Sn layer was approximately 100 Å as measured by a thickness monitor. The pure Sn sample was measured without ambient exposure. The oxidized samples were obtained by exposing pure Sn samples to pure oxygen at a pressure of 1x10⁻⁴ Torr. Three different exposure times were used: 10, 180 and 1200 seconds. To fit XPS spectra, traditional and novel method (using a double-Lorentzian) were employed to calculate thickness and composition of the oxide layer. High resolution transmission electron microscopy measurements were performed to validate calculations. Structural parameters obtained with different XPS data fitting approaches were compared, showing a clear advantage of the double-Lorentzian method in the understanding of the initial stages of tin oxidation.

5:00pm **AS+MC+SS-TuA9 Understanding the Physicochemical and Ice-Nucleation Properties of Bare and Sulfuric Acid Coated Atmospheric Mineral Dust Aerosols**, *Manjula Nandasiri, N. Madaan, A. Devaraj, G.R. Kulkarni, T. Varga, V. Shutthanandan, S.A. Thevuthasan*, Pacific Northwest National Laboratory

The relationship between atmospheric aerosols and the formation of clouds is among the most uncertain aspects in our current understanding of climate change. Especially, ice and mixed-phase clouds have been less studied even though they have extensive global coverage and dominate precipitation formation. As a result, the climatic impact of ice-containing clouds is not well-understood and there is urgent need to improve ice nucleation formulations in climate models. In order to understand this phenomenon, ice nucleation experiments and parameterization development need to be carried out. Specifically, heterogeneous ice nucleation processes are sensitive to surface properties of atmospheric aerosols, which can accumulate sulfates and organics during atmospheric transport. Thus, here we investigated the physical and chemical properties on the surface of a mixed mineral dust aerosol: Arizona test dust (ATD) and kaolinite mineral dust aerosol particles that trigger ice formation.

In this study, bare and sulfuric acid coated ATD and kaolinite particles were characterized using advanced spectroscopy and microscopy techniques. These particles were reacted with sulfuric acid with different strengths in a systematic way to obtain uniform coatings on the particle surface.

Following the acid reaction, the surface composition, chemical state, and elemental mapping of ATD and kaolinite particles were studied using X-ray photoelectron spectroscopy (XPS) and XPS imaging techniques. XPS showed significant changes in composition, chemical state, and elemental distribution of Si and Al on the surface of ATD and kaolinite particles due to the acid reaction. These surface properties also depend on the strength and pH value of the sulfuric acid. The surface morphology, particle size and distribution, and composition of these samples were further studied using scanning electron microscopy (SEM) combined with energy dispersive X-ray spectroscopy (EDS). The high resolution SEM micrographs showed differences in surface morphology between bare and coated samples. X-ray diffraction was also carried out to study the changes in crystallinity of ATD and kaolinite particles due to the acid coating. The samples were further characterized using atom probe tomography and transmission electron microscopy to understand the 3-D chemical distribution and microstructure, respectively. Following the characterization of physiochemical properties, ice-nucleation experiments were also carried out on ATD and kaolinite samples, which will be discussed here.

5:20pm **AS+MC+SS-TuA10 A Study of the Effect of Deep UV (172nm) Irradiation on Polyimide Surfaces**, *Lopamudra Das, M.J. Kelley*, The College of William and Mary

Polyimides have a wide range of industrial and scientific applications where changes in surface structure due to UV radiation are of significant interest. Particularly in its use in spacecraft, the effect of deep UV is important to predict photo-degradation of the material. We investigated the response of commercial samples of PMDA-ODA (PI) films to 172nm UV from a xenon excimer lamp in the absence of oxygen, using XPS, ToF/SIMS, and AFM.

5:40pm **AS+MC+SS-TuA11 Small-Angle/Wide-Angle X-ray Scattering Investigation of Functional Materials at Inorganic-Macromolecular Interfaces**, *Ich Tran, T.W. van Buuren, T.M. Willey, J.R.I. Lee, M. Bagge-Hansen, A. Noy, R. Tunuguntla, K. Kim*, Lawrence Livermore National Laboratory

Development in nanoscale engineering has enabled bioelectronics that can mimic and/or interact with the biological systems. Lipid bilayer-functionalized Si nanowires are considered as a promising candidate for the construction of bio-nanoelectronic devices. These biomimetic lipid bilayers serve as a general host matrix for bio-functional components such as membrane proteins. Though meaningful technological advancements have been made, critical questions still remain, in particular on structural characteristics of lipid bilayers at the interface with inorganic nanomaterials. Small-angle and wide-angle x-ray scattering (SAXS/WAXS) techniques are used to investigate self-organizations of dioleoyl-phosphatidylcholine (DOPC) lipid bilayers on Si nanowires. Critical structural parameters of the lipid bilayers (lamellarity, bilayer thickness and packing order of lipid molecules) are obtained through analyzing SAXS-derived Electron Density Profile (EDP). A decrease in bilayer thickness and a packing disorder of the lipid head groups in adjacent to supported Si nanowires have been observed upon coating on Si nanowires. Furthermore, effects on the packing order of lipid hydrocarbon tails induced by the incorporations of proteins or carbon nanotubes into lipid bilayers (served as natural or artificial ion channels, respectively) have been identified and characterized. The results shed light on a number of unresolved questions that are crucial for the comprehensive understanding this class of materials.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

Authors Index

Bold page numbers indicate the presenter

— B —

Bagge-Hansen, M.: AS+MC+SS-TuA11, **2**
Bravo-Sanchez, M.: AS+MC+SS-TuA8, **1**

— D —

Das, L.: AS+MC+SS-TuA10, **2**
Deeks, C.: AS+MC+SS-TuA3, **1**
Devaraj, A.: AS+MC+SS-TuA9, **1**

— H —

Härtl, G.: AS+MC+SS-TuA7, **1**
Herrera-Gomez, A.: AS+MC+SS-TuA8, **1**
Hofmann, T.: AS+MC+SS-TuA7, **1**
Holtmannspötter, J.: AS+MC+SS-TuA7, **1**
Huerta-Ruelas, J.A.: AS+MC+SS-TuA8, **1**

— K —

Kelley, M.J.: AS+MC+SS-TuA10, **2**
Kim, K.: AS+MC+SS-TuA11, **2**
Kulkarni, G.R.: AS+MC+SS-TuA9, **1**

— L —

Lechuga, H.: AS+MC+SS-TuA1, **1**
Lee, J.R.I.: AS+MC+SS-TuA11, **2**

— M —

Madaan, N.: AS+MC+SS-TuA9, **1**
Meer, T.: AS+MC+SS-TuA7, **1**
Milošević, M.: AS+MC+SS-TuA3, **1**

— N —

Nandasiri, M.I.: AS+MC+SS-TuA9, **1**
Noy, A.: AS+MC+SS-TuA11, **2**
Nunney, T.S.: AS+MC+SS-TuA3, **1**

— P —

Pacholski, M.L.: AS+MC+SS-TuA4, **1**
Pachuta, S.J.: AS+MC+SS-TuA1, **1**
Poirier, D.: AS+MC+SS-TuA1, **1**

— R —

Radetić, M.: AS+MC+SS-TuA3, **1**

Radoičić, M.: AS+MC+SS-TuA3, **1**
Rehbein, J.: AS+MC+SS-TuA7, **1**

— S —

Šaponjić, Z.: AS+MC+SS-TuA3, **1**
Shutthanandan, V.: AS+MC+SS-TuA9, **1**
Strobel, M.: AS+MC+SS-TuA1, **1**

— T —

Thevuthasan, S.A.: AS+MC+SS-TuA9, **1**
Tran, I.C.: AS+MC+SS-TuA11, **2**
Tunuguntla, R.: AS+MC+SS-TuA11, **2**

— V —

van Buuren, T.W.: AS+MC+SS-TuA11, **2**
Varga, T.: AS+MC+SS-TuA9, **1**

— W —

Willey, T.M.: AS+MC+SS-TuA11, **2**