2009 BFRL Project Description

Project Title: Surface Mechanical Characterization of Polymers

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Principal Investigator: Aaron Forster and Li-Piin Sung

Co-Investigator(s): Chris Michaels, CSTL

BFRL Program: Service Life Prediction of Nanostructured Polymeric Materials

Objective: To develop methodologies to (1) determine surface mechanical properties and scratch behavior in polymeric systems incorporating indentation, spectroscopy, and light scattering; and (2) evaluate the scratch resistance of filled, patterned (grainy), or colored polymeric systems.

Problem:

What is the problem? Several persistent measurement challenges exist for multi-layer polymer systems used in building components: (1) accurate, spatially resolved measurement of mechanical properties at the nanometer level, (2) in-situ hardness and modulus measurements during the curing process, (3) relating polymer relaxation behavior and scratch damage recovery, and (4) lack of a robust, quantitative scratch visibility assessment metrology. Current metrologies used in assessing the mechanical properties of these materials are designed for model coatings, and are not suitable for characterizing new materials with complex surface morphologies or microstructure. Industry attendees pointed out these challenges during the Polymer Interphase Consortium Workshop held at NIST in January 2008. Multi-layer polymer coating systems are the first line of defense against corrosion and appearance loss on the fascia of components in buildings. Customer demands for multifunctional (thinner coatings with high hardness and improved adhesion) coating systems continue to increase.

Why is it hard to solve? Quasi-static and viscoelastic mechanical property measurements of polymers at the micron-scale are difficult because micron-scale measurement techniques induce high strains and plasticity that impart non-linear behavior into elastic and time dependent measurements. For the visual assessment of scratch resistance, the complexities in surface morphology and microstructure result in multi-dimensional optical properties that are difficult to quantify accurately.

How is it solved today, and by whom? In general, industry measures the mechanical properties of coatings through pencil hardness measurements, cross-hatch or punch adhesion measurements, macro-scratch measurements, and other non-quantitative tests. All of these measurement techniques are qualitative or “rank and order” methods that convolute polymer and substrate properties, test conditions, and/or the specific bias of the tester. There has been ongoing work in the United States and Europe to address indentation standards for materials.

Scratch metrologies are currently developed by instrument manufacturers or academia, however, the methodologies and metrologies that have originated from these efforts are capable of inducing a controlled scratch into a material, but have not been successful in linking surface mechanical properties to scratch damage/delamination.

Why NIST? This research project is aligned with one of BFRL's core competencies- *performance, durability, and service life prediction of building materials*, and as well as a major strategic priority of *measurement science for sustainable infrastructure materials.* The PI's have knowledge, expertise, and instrumentation to develop surface mechanical and morphological measurement tools. BFRL/NIST has demonstrated the applicability of these tools to quantify scratch resistance and complex optical properties of constructed polymeric materials. Furthermore, industry has requested that NIST/BFRL assist them in the development of measurement science tools that link chemistry-mechanical-optical properties in multi-functional polymer coatings.

Approach:

What is the new technical idea? The new technical idea involves combining surface mechanical and optical scattering measurement tools to quantify scratch damage. Indentation methodologies will be refined to increase measurement resolution for modulus and hardness and define the onset of non-linear polymer behavior, in order to better relate indentation mechanical property measurements to scratch deformation. A difficulty often encountered in scratch testing is surface cracking during scratch at high strains and scratch velocities. Indentation with sharp indenter tips and higher loading rates will be used to propagate a crack in a polymeric material. The loads and strains required to induce cracking during indentation will be compared to scratch induced cracking to determine whether a correlation exists. We will modify scratch test methods based on the existing Polymer Interface Consortium (PIC) scratch test method (STP) (PIC-STP-PIC phase II) to provide a more accurate assessment of scratch resistance in complex surface morphology and microstructure materials.

Why can we succeed now? We have been successful in utilizing these methodologies for model polymeric systems in the previous PIC. The Polymer Surface/Interface (PSI) consortium will expand upon this experimental foundation to investigate more complicated and industrially relevant materials. Industry partners have shown support by providing industrially relevant and well-characterized polymeric systems to the consortium.

What is the research plan? Current indentation techniques are limited for polymeric materials because surface roughness and inaccuracies in tip shape calibrations require larger indentation depths for accurate mechanical property measurements. Accurate mechanical property measurements for shallow depths are important because these measurements best represent the elastic material response without the non-linear plastic response. Current metrologies will be refined using more accurate tip shape calibrations and improved surface find algorithms to achieve shallow depth mechanical property measurements. The expected outcome is the ability to compare mechanical properties from indentation at different strains (indentation depths) to scratch morphology.

The current protocol for measuring the response of a polymeric material to indentation or scratch involves indentation followed by off-line microscopy or spectroscopy measurements. During the time between measurements, the polymer recovers some of the scratch damage. The lag in measurement time creates difficulties in directly linking scratch penetration profiles to morphology. Measurement tools will be developed to reduce the time lag for different measurements on scratches with an ultimate goal of in-situ optical or spectroscopy measurements during scratch and indentation.

Severe scratch damage leads to cohesive failure within the coating. This is evidenced by highly visible surface cracks emanating from the scratch walls. The complex stress and strain induced by scratching makes it difficult to predict the energy required to form a crack. High strain and strain rate indentation can be used to induce surface cracks similar to those observed during scratch. Recent literature developments provide methods to calculate the energy required to fracture a glass using indentation. This technique could be applied to multi-layer polymers in order to calculate the energy required to fracture a coating.

New experimental techniques and procedures for scratch testing will be developed and applied to more complex samples. The effect of microstructure, surface texture, optical properties, and other material properties on scratch behavior and will be evaluated through controlled specimens provided by industrial partners. This is a three-year project that will address multi-phase, filled systems with different filler dispersion states, different color pigments, different degrees of surface roughness and grainy patterns. The study will proceed from simpler systems to more complex systems from year 1 to year 3.

Recent Results: In FY08, this project successfully accomplished all PIC Phase II milestones and produced a number of **major outputs**, including:

- A NIST-industrial one day workshop (January 2008) – 13 companies, 27 non- NIST attendees
- A draft ASTM standard test method based on PIC scratch protocol, "Test Method for Measuring Scratch/Mar Resistance of Polymeric Coatings via Nanoscratching and Optical Scattering."

<u>2 meeting proceedings</u>

- A. M. Forster, P. Krommenhoek, L. Sung, C. A. Michaels, K. Wood, "Instrumented Indentation for Quantifying Quasi-static and Transient Properties of Polymeric Coatings" FutureCoat! Conference Proceedings, Characterization and Nanotechnology Track, 2008.
- A. M. Forster, C. A. Michaels, L. Sung, J. Lucas, "Interfacial Characterization of Multiple Layer Coatings on Thermoplastic Olefins (TPO)" MRS Proceedings Symposium AA, 2008.

<u>1 book chapters</u>

- L. Sung, J. Comer, A. M. Forster, H. Hu, B. Floryancic, L. Brickweg, and R.H. Fernando, "Impact of Nanoparticles on the Scratch Behavior of a Polyurethane

Coating," in press, ACS Symposium Series: Nanotechnology Applications in Coatings, Vol 1008, Eds: R. Fernando, L. Sung, Oxford Press, 2008.

1 journal paper

- L. Sung, J. Comer, A. M. Forster, H. Hu, B. Floryancic, L. Brickweg, and R.H. Fernando, "Scratch Behavior of Nano-Alumina/Polyurethane Coatings," *J. Coat. Technol. and Res*., in press, 2008.

6 meeting presentations

- "*NIST Capability Overview: SLP and PSI Research Programs @ BFRL*," BYK-USA, Wallingford, CT, August 20, **2008**. (Invited)
- "*Durability Study of Polymeric Coatings and Nanocomposites*," Materials and Chemical Research Laboratories, Industrial Technology Research Institute (ITRI), Hsinchu, Taiwan, June 17, **2008.** (Invited)
- "*Durability of Fluoropolymer/Acrylic Blends: Effect of Composition and Processing Condition*," International Symposium on Polymer Physics- PP'2008**,**" Xiamen, China, June 11, **2008**. (Invited)
- "*Effect of Nanofillers on the Surface Properties of Nanocomposites*," 2008 ACS series on "Nanotechnology in Coatings Conference: Emerging Application" Orlando, FL, March 25-28, **2008**. (Invited)
- "*An Overview of NIST/Industry Polymer Interphase Consortium (PIC*)" Arkema Inc., King of Prussia, PA, Dec 11, **2007**. (Invited)
- A. M. Forster, C. Michaels, J. Lucas, L. Sung, " Interfacial Characterization of Multiple Layer Coatings on Thermoplastic Olefins (TPO)" Fundamentals of Nanoindentation and Nanotribology IV, MRS Meeting: Symposium AA, November **2007**

A major **outcome** is the development of measurement protocols to: (1) measure spectral reflectance from scratched specimens of different colors; (2) correlate surface mechanical properties and scratch morphology to optical properties of polymeric materials; and (3) combine chemical imaging and mechanical measurements to determine interfacial modulus and interfacial diffusion in multilayer polymer systems.

Standards and Codes: The measurement protocols (scratch test and nanoindentation) developed in this project will contribute to standard test methods as requested and supported by consortium members.