2009 BFRL Project Description

Project Title: Multi-scale Mechanical Properties of Nanocomposite Materials

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BFRL Program: Service Life Prediction of Nanostructured Polymeric Materials

Objective: To (1) develop measurement science tools that quantify changes in the micro- and sub-micro mechanical properties during the lifecycle of nanocomposite materials, and (2) link particle size, particle distribution, particle volume concentration, and aspect ratio to mechanical properties and service life of nanocomposites.

Problem:

What is the problem? The use of nanocomposites in structural components and adhesives for building and construction applications is rising rapidly, primarily because the large surface areas of the nanoparticle fillers influence composite mechanical properties at very low particle loadings (< 10 mass %). While mechanical properties and failure modes are well-known for polymer composites containing micrometer-sized particles and fibers, two main challenges remain for current research on the effect of nanofillers on composite mechanical properties: The majority of current studies are focused on (1) specific polymer/filler systems that do not attempt to elucidate the fundamental length scales that control specific performance gains, and (2) initial mechanical property improvements as opposed to changes in mechanical properties with time. Technical barriers to overcoming these deficiencies include a lack of understanding of the linkage between small scale mechanical property measurements and bulk measurements, and lack of data on the long term behavior of nanocomposites.

Why is it hard to solve? There are three hurdles that must be overcome to solve this problem. 1) It is difficult to measure mechanical properties at micron and sub-micron length scales. Small length scale mechanical property measurements are susceptible to non-linear material responses that reduce the accuracy and precision of the measurements. 2) It is not clear whether the large interfacial area of nanoparticles influences mechanisms or kinetics of failure in the long-term performance of nanocomposite materials. 3) It is difficult to reliably control morphology and microstructure of a nanocomposite at the nanometer length scale for large structural composites. Therefore, it is difficult to measure the length scale at which material heterogeneity becomes important.

How is it solved today, and by whom? A systematic study of the mechanisms involved in the enhancement of nanocomposite mechanical properties and service lives does not exist, to the

best of our knowledge. The majority of nanocomposite research in industrial, government and academic labs (national and international) has focused on optimization strategies for nanoparticle-matrix compatibility to facilitate uniform dispersion/stress transfer and increase the chances for improved short-term performance. MSEL is conducting research on the C_{60} cage (i.e., buckeyballs)-filled composites; however, these materials are not routinely used in structural applications.

Why NIST? This project addresses the development of measurement science tools for the U.S. building industry to link performance improvements to nanocomposite structure and determine service life of nanocomposites. BFRL is the appropriate organization to conduct this work because we possess world class environmental exposure capabilities and the expertise to carry out nanocomposite characterization at a wide range of length scales.

Approach:

What is the new technical idea? Measurement science tools and methodologies will be developed to characterize nanocomposite mechanical properties (initial and long term), using well-defined nanocomposite systems generated from model polymers and well-characterized inorganic nanoparticles (monodisperse silica, metallic oxides, clay platelets). The bulk mechanical properties of the samples will be characterized using accepted ASTM and ISO standards and the results fitted with existing theoretical models in order to predict composite behavior as a function of particle volume concentration, aspect ratio, and dispersion. The length scale dependence of mechanical properties will be investigated using depth-sensing indentation. The combined use of these tools will enable characterization of mechanical properties and failure modes of well-controlled nanocomposites from nanometer to millimeter length scales.

Different levels of dispersion, particle geometry and volume content will be employed to assess the influence of these changes on initial and long-term mechanical properties. Nanocomposite physical properties (concentration, anisotropy, dispersion) will be characterized using a combination of microscopy, scattering, and spectroscopy techniques. In particular, microscopic analysis of local nanocomposite microstructure will be coupled to depth sensing indentation measurements to link local mechanical properties to observed polymer/filler ratios.

Measurement tools developed to characterize the initial mechanical properties and failure modes of the nanocomposites will be used to examine their long-term performance. The NIST SPHERE and dark humidity cabinets will be used to environmentally age the nanocomposites, during which their mechanical and physical properties will be characterized as a function of aging time.

Why can we succeed now? There is a growing demand for nanoparticles in the coatings, adhesives, and composites communities. Inorganic particle manufacturers have restructured product lines to produce nanoparticle dispersions for use in organic and aqueous mediums to meet this demand from all of these industries. Often, one type of nanoparticle such as silica or metal oxides will see use in more than one industry. In addition, low polydispersity thermoplastics and highly purified thermoset resins are readily available. Therefore, it is feasible to reliably create model nanocomposite materials that can be well characterized across many length scales. In addition, the current understanding of depth sensing indentation for

polymers has improved to the point that fundamental measurements may be made on composite materials.

What is the research plan? A model structural thermoset (purified resin and crosslinker) and a thermoplastic (narrow polydispersity) matrix will be paired with three different classes of nanoparticle dispersions; sphere (Year 1), rods (Year 2), and platelets (Year 3). The dispersion (average cluster size) within the matrix will be quantified and mapped at millimeter and micrometer length scales using UV-visible spectroscopy, optical microscopy, light scattering, and/or SEM. Mechanical properties will be characterized using quasi-static, dynamic, and stress relaxation measurements at millimeter length scales. Existing analytical models for composites will be used to predict mechanical performance for the volume of material tested with each technique. The measurements mentioned above will provide the well-characterized nanocomposite samples needed to elucidate length scale dependent mechanical properties. Depth sensing indentation (DSI) can provide mechanical property measurements at sub-micrometer length scales, a wide range of frequencies, and a range of strain levels. This metrology will help determine whether linear and non-linear material behavior is related to indentation loading rate, higher strains, or nanoscale phenomena. DSI will be conducted using different tip shapes, loading rates, and loading depths on nanocomposite samples that possess a quantified dispersion of nanoparticle. This could lead to the development of protocols for measuring structural-property relationships in model nanocomposites.

Long term mechanical performance of the nanocomposites will be assessed as a function of cyclic thermal and hydrodynamic stresses. In this phase, the failure modes at different length scales are as important as the initial improvements in mechanical properties. The initial composite characterization, described above, is used to select the most critical measurements for monitoring mechanical performance during exposure. When possible, non-destructive metrologies for monitoring composite health will be explored. In addition, chemical measurements (IR or Raman spectroscopy) will be utilized to determine if/what chemical degradation mechanisms are present in the matrix. In addition, failure modes will be investigated by measuring fracture energies at multiple length scales via tension and compression loading.

Recent Results: In FY08, **outputs** include

<u>2 meeting proceedings</u>

- 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.
- 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.

<u>2 book chapters</u>

- A. M. Forster, S. S. Watson, J. White, "Elastic Modulus Characterization of Nanocomposite Latex Coatings," in press, ACS Symposium Series: Nanotechnology Applications in Coatings, Vol 1008, Eds: R. Fernando, L. Sung, Oxford Press, 2008.
- 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, 2008.2 book chapters (peer-reviewed, in press)

1 peer-reviewed journal publication

- A. M. Forster, C. A. Michaels, L. Sung, J. Lucas, "Modulus and Chemical Mapping of Multi-layer Coatings" to be submitted to ACS Applied Materials and Interfaces

2 meeting presentations

- C. Clerici, A. M. Forster, D. Hunston, "Microstructure Analysis of Fracture in Toughened Polymers" 31st Annual Meeting of The Adhesion Society, Feburary 2009
- 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

The major **outcomes** include:

- Protocols for creating dispersions of alumina oxide nanoparticles in acrylic urethane composites and titanium dioxide particles in latex composites,
- Protocols for fracture toughness measurements in nanocomposites and microscopy analysis of fracture surfaces, and
- New knowledge of the refinements needed in DSI metrologies to resolve the contribution of nanoparticles.

Standards and Codes: No current standards or code efforts for this project.