2009 BFRL Project Description

Project Title: Metrologies for Characterizing Nanofiller Dispersion, Multi-scale Structure, and Optical Properties of Polymeric Materials

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Principal Investigator: Li-Piin Sung

Co-Investigator(s): Stephanie Watson

BFRL Program: Service Life Prediction of Nanostructured Polymeric Materials

Objective: To develop a suite of non-destructive, optical scattering techniques to (1) to characterize nanofiller dispersion in liquid (uncured) and in solid (cured) polymeric matrices over multiple length scales and (2) to relate nanofiller dispersion and physical properties to the service life of polymeric materials.

Problem:

What is the problem? Measurement science is lacking for non-invasively (1) measuring and quantifying nanofiller dispersions in liquid (uncured) and in solid (cured) polymeric matrices, (2) linking nanofiller dispersion state to the resultant multi-scale structure and its corresponding optical properties, and (3) correlating nanofiller dispersion to the service life of a nanostructured polymeric material. New construction materials containing nanofillers for improved performance properties have recently been introduced into the marketplace. However, poor filler dispersion is a universal problem inherent to NPMs that is known to qualitatively and adversely affect the performance properties (service life, mechanical performance) of polymeric systems. The inability to measure dispersion is a major barrier to more rapid introduction of new products in the nanotech/nanocomposites era (J. Coatings Tech, May 2004; NIST-NSAS sponsored "Nanomanufacturing workshop" Oct. 2006; as well as many nanotech-related workshops including 2003-2007 NIST-NASA sponsored workshops).

Why is it hard to solve? Nanofillers are small in nature and easily form aggregates or agglomerates of up to 100 microns. Current industrial measurement protocols for measuring dispersion are either indirect or destructive with narrow measurable size scales, and the measurement results are non-quantitative and inefficient. Furthermore, commercial color and gloss measurement methods are not adequate to fully characterize the optical property of a filler-polymer system, nor provide sufficient data to correlate the physical properties due to different filler dispersion states. The lack of accurate optical property measurements and an understanding of the link between optical and physical properties makes it difficult to improve

optical and durability properties of new materials. There is urgent need for practical, nondestructive methods specifically developed to solve this problem.

How is it solved today, and by whom? Current industrial methods for assessing filler dispersion in the liquid state include crude measures of particle dispersion including finesses of grind gauge, particle sizing in a very dilute state, or viscosity measurements at concentrated suspensions. These methods are indirect, subjective, and limited to micron-size particles. For solid products in their final form, industrial evaluation relies on color and tinting strength with respect to the reference standards. Again, this is indirect and subjective, and suitable only for ranking purposes. The direct dispersion measurement utilizes high resolution microscopy. However, most microscopy measurements are destructive, labor intensive and limited in sampling area. Scattering (x-ray, neutron) methods have been used to characterize nanostructure and filler distribution in nanocomposites. However, research facilities with these capabilities are difficult to access, and the measurement is highly technical and not always practical.

Why NIST? This research project is aligned with one of BFRL's core competencies- *performance, durability, and service life prediction of building materials*. Quantitatively measuring nanoparticle dispersion is also an articulated National Nanotechnology Need [NNI_Strategic_Plan_2004, NNI; R&D Supporting the Next Industrial Revolution, Supplement to President's FY 2004 Budget, 2003-2007 NIST-NASA sponsored workshops]. We have the in-house knowledge, expertise (experimental and modeling), and instrumentation to develop measurement science capabilities for quantifying filler dispersion, charactering mutli-scale structure, and relating to durability and optical properties of nanoconstructed materials. The measurement science development of the cutting-edge metrologies, modeling expertise and facilities, is a challenge uniquely suited to BFRL/NIST.

Approach:

What is the new technical idea? The new technical idea involves quantitatively measuring nanofiller dispersion using existing techniques with improved data processing in concert with new non-invasive metrologies. The following combined strategies will be developed: (1) characterize filler dispersion and multi-scale structure, from the liquid to solid states at various nanofiller concentrations, using both innovative and improved optical scattering metrologies; (2) use existing methods (high resolution microscopy, neutron scattering) with faster and better image and data analysis methods to construct realistic structure of filler dispersion and nanostructures in the final solid states; (3) validate the optical scattering results in complex nanocomposite suspensions and solid states with corresponding microscopy and neutron scattering results; (4) improve the optical scattering metrology and develop standardized measurement protocols for specified specimen conditions for practical industrial applications. In a parallel study, we will develop more accurate methods to quantify optical properties in terms of angular-resolved optical reflectance and color measurements from the resultant state of specified filler dispersion and multi-scale structure of the material. With the new capabilities for quantitatively measuring nanofiller dispersion and the corresponding optical properties from processing (liquid, uncured) to final products (solid, cured), an improved understanding of the mechanism of filler dispersion in a complex system and resultant performance (optical properties, durability) can be attained.

Why can we succeed now? A custom-designed, state-of-the-art optical scattering research facility has been designed and constructed with new capabilities for measuring particle size, microstructure, and optical properties of various sample forms and concentrations with flexible measurement configurations. Recently, a scanning wavelength illumination (SWI) system was added to enable the measurements of the high accuracy optical performance properties. With the new capabilities, array experiments can be carried out to quantify the filler dispersion, nano/ microstructure, and optical scattering properties of complex systems.

What is the research plan? Research will be carried out on model metal oxide nano-particulate systems, such as nanostructured titanium dioxide (TiO_2), due to their widespread commercial importance. The developed metrologies, however, should have generic application and will establish the metrological framework for determining structure-property relationships in nanofiller-polymer systems. In FY2009, we will focus on characterizing a series of samples of different filler sizes and dispersion states controlled by the interactions of polymer matrix and fillers, obtained from other researchers in the program or industrial partners. The effect of filler dispersion on the optical properties and UV durability of a filler-polymer system will be investigated and characterized using optical scattering, scanning microscopy (laser scanning confocal and atomic force microscopies), small angle neutron scattering (SANS), and new developed/improved optical metrologies. In addition to static and dynamic light scattering (SLS and DLS) methods, we will implement novel approaches such as multi-wavelength, backscattering, and diffusive scattering metrologies to probe and measure more complex nanostructured polymeric systems at a wide range of length scales. The DLS results from nanocomposite suspension such as auto-correction function will be compared to the theoretical modeling study conducted using the similar control parameters (PD 8665018 – Nyden), to provide fundamental understanding of nanoparticle dispersion mechanism. By correlating SANS measurements and microcopy measurements, an accurate filler dispersion measurement using optical scattering metrology can be developed. Measurement protocols for characterizing multi-scale structure and measuring filler dispersion (cluster size and the degree of dispersion) in various media will be refined and modified to more complex systems. In addition to developing metrologies for characterizing filler dispersion and nano-/micro-structure of polymeric materials, we will also focus on developing advanced measurement methods for accurately quantifying the optical properties with a wide range of incident illumination wavelengths. Optical scattering data as a function of UV exposure time will be measured and correlated to surface morphology/ microstructure of the test specimens or a given filler dispersion state.

We will extend the study to more complex nanocomposite systems using the improved/refined metrologies and measurement protocols. Detailed analyses from microscopic results will correlate to responding results from scattering metrologies using a statistical model/analysis to describe closely in real space, with whose 3D structural information can be used for modeling performance properties.

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

- 3 meeting proceedings
    - L. Sung, C. Clerici, H. Hu, and X. Gu, "Relating Optical Properties to Pigment Dispersion of Weathered Pigmented Polymeric Coatings," *FSCT·ICE 2007*

Proceedings of the 85th Annual Meeting Technical Program, Toronto, Ont, Canada, October 3-5, 2007.

- X. Gu, L. Sung, B. Kidah, M. Oudina, V. Delaurent, H. Hu, D. Stanley, W. E. Byrd, J. Y.C. Jean[1], T. Nguyen and J. W. Martin, "Multiscale Physical Characterization of a UV-degraded Polymeric Coating System," *FSCT·ICE 2007 Proceedings of the 85th Annual Meeting Technical Program*, Toronto, Ont, Canada, October 3-5, 2007.
- "Effects of Pigment and its Dispersion on UV Degradation of Epoxy and Acrylic Urethane Polymer Systems" S. Watson, A. Forster, I. Tseng, L. Sung, J. Lucas, and A. Forster, *Nanophase and Nanocomposite Materials V*, edited by S. Komarneni, K. Kaneko, J.C. Parker, and P. O'Brien (Mater. Res. Soc. Symp. Proc. **Volume 1056E**, Warrendale, PA, 2008), 05-HH03-67.

- 7 book chapters (peer-reviewed, in press)
  - L. Sung, X. Gu, C. Clerici, H. Hu, V. Delaurent, "Metrologies for Characterizing Optical Properties of Clear and Pigmented Coatings," in Service Life Prediction for Polymeric Materials: Global Perspectives, Eds: J. Martin, R. Ryntz, J. Chin, R. Dickie, in press, Springer Press, 2008.
  - C. Clerici, X. Gu, L. Sung, Aaron M. Forster, D. L. Ho, P. Stutzman, T. Nguyen and J. W. Martin, "Effect of Pigment Dispersion on Durability of a TiO_2 Pigmented Epoxy Coating During Outdoor Exposure," in Service Life Prediction for Polymeric Materials: Global Perspectives, Eds: J. Martin, R. Ryntz, J. Chin, R. Dickie, in press, Springer Press, 2008.
  - L. Sung, X. Gu, C. Clerici, H. Hu, E. Loizou, and D.L. Ho, "Effect of Pigment Dispersion on Optical Properties and Durability of a TiO_2 Pigmented Epoxy Coating," in press, Chapter 23, ACS 1004 / Trends in Polymer Degradation and Performance, Eds: M.C. Celina, J. Wiggins, and N. Billingham, Oxford Press, 2008.
  - S. S. Watson, A. Forster, I.-H. Tseng, and L. Sung, "Investigating Pigment Photoreactivity for Coatings Applications: Methods Development", in Service Life Prediction for Polymeric Materials: Global Perspectives, Eds: J. Martin, R. Ryntz, J. Chin, R. Dickie, Springer Press, 2008.
  - S. Watson, A. Forster, I. Tseng, L.Sung, "Assessment of Spectrophotometric Assay Methods on Nanostructured Pigments", in press, ACS Symposium Series: Nanotechnology Applications in Coatings, Vol 1008, Eds: R. Fernando, L. Sung, Oxford Press, 2008.
  - X. Gu, L. Sung, B. Kidah, M. Oudina, D. Martin, A. Rezig, D. Stanley, J. Y.C. Jean, T. Nguyen and J. W. Martin, "Relating Gloss Loss to Nanoscale /Microscale Topographical Change for a Polymer Coating Exposed to UV Radiation," 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.

- 4 journal papers (1 published, 3 in press)
    - 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.
    - X. Gu, L. Sung, B. Kidah, M. Oudina, C. Clerici, H. Hu, D. Stanley, W.E. Byrd, J. Y.C. Jean, T. Nguyen and J. W. Martin, "Multiscale Physical Characterization of an Outdoor Exposed Polymeric Coating System," *J. Coat. Technol. and Res.*, in press, Oct. 2008.
    - N. J. Lin, H. Hu, L. Sung, and S. Lin-Gibson, "Quantification of cell response to polymeric composites using a two-dimensional gradient platform," C*ombinatorial Chemistry & High Throughput Screening*, in press, **2008**.
    - M. A. Tshabalala, and L. Sung, "Wood Surface Modification by In-Situ Sol-gel Deposition of Hybrid Inorganic-Organic Thin Film," *J. Coat. Technol. and Res*. **4** (4), 483-490**(2007)**.

- 7 meeting presentations (6 invited talks)

    - *"NIST Capability Overview: SLP and PSI Research Programs @ BFRL,"* BYK-USA, Wallingford, CT, August 20, **2008**. (Invited)
    - "*Multiscale characterization and Durability Study of Polymeric Coatings and Nanocomposites*," National Synchrotron Radiation Research Center, Hsinchu , Taiwan, June 18, **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 AC series on "Nanotechnology in Coatings Conference: Emerging Application" Orlando, FL, March 25-28, **2008**. (Invited)
    - "*Relating Optical Properties to Pigment Dispersion of Weathered Pigmented Polymeric Coatings*," FSCT·ICE 2007 Annual Meeting Technical Program, Toronto, Ont, Canada, October 3-5, **2007**.
    - "*Multiscale Structure and Dispersion Characterization,"* FSCT/ICE 2007 Pre-show one-day short Courses: Nanotechnology and Nanocomposities: Application in Coatings. Toronto, Ont, Canada, October 2, **2007**. (Invited)
- Grant for carrying out feasibility study for measuring and predicting appearance of a weathered coating using optical scattering and micro-physical data.

The major **outcomes** include:

- Establishment of a new measurement capability (SWI system) for color and multi-wavelength scattering;

- New knowledge gained and successful development of protocols for measuring high diffused composite suspensions using back scattering methods;
- New knowledge and methods to correlate the surface morphological results to physical measurements on a series of UV-exposed TiO_2 pigmented coatings.

Standards and Codes: Measurement protocols developed in this project may be submitted to ASTM subcommittee on nanoparticle dispersion characterization.