2009 BFRL Project Description

Project Title: Reliability Approach for Relating Outdoor and Accelerated Laboratory Aging for Nanostructured Polymeric Systems

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BFRL Program: Service Life Prediction of Nanostructured Polymeric Materials

Objective: To mathematically link field and laboratory exposure results using the reliability-based methodology and develop service life prediction models for nanostructured polymeric materials (NPMs).

Problem:

What is the problem? Critical measurement science is needed for characterizing the properties and for predicting service life of NPMs. Nanostructured polymeric materials (NPMs) (i.e., polymeric materials containing nanoparticles) potentially provide a very large market and competitive advantages to US industry. For example, GM reportedly used nearly 225,000 kg of NPMs in 2004 while PPG has commercialized scratch- and weather-resistant coatings containing nanoparticles. It is estimated that by 2010, 20 % of all NPMs produced will be used in construction and building applications.[1] However, due to the extremely small size of the nanoparticles and their extensive interfacial area, the incorporation of nanoparticles into traditional polymeric materials presents many technological and scientific challenges. [2] Metrologies for evaluating the dispersion of nanoparticles and their physical and chemical properties with nanoscale spatial resolution are limited; especially, for high volume, large products, like construction materials. Methodologies for generating accurate, precise, and timely estimates of the service life of NPMs are not available. The absence of such measurement science hinders product innovation, product development, and product acceptance of innovative and novel materials like NPMs.

Why is it hard to solve? Service life prediction of polymeric materials is an inherently complex phenomena. It involves numerous component interactions and multifunctional (chemical, physical, and mechanical) responses at multiple length and time scale ranges. Nanoparticles also possess unique properties (high surface area, high surface reactivity, large inter-particle forces) that will affect the processing, properties and performance of NPMs in unknown ways. Current metrologies lack spatial resolution and sensitivity in characterizing

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[1] *Nanocomposites: US Industry Study with Forecasts to 2010, 2015 and 2020*, The Freedonia Group, 2006.

[2] *MRS BULLETIN, 39,VOL. 32, APRIL 2007 • www.mrs.org/bulletin*

nanoparticles in the polymer matrix and their complex interfaces. Structure-property relationships developed for traditional filled systems may have to be further refined to be applicable to NPMs.

How is it solved today, and by whom? The problem of linking field and laboratory exposure and predicting long-term performance of NPMs has not been solved. BFRL was the first to successfully link field and laboratory exposure results for an unfilled polymer system. Extensive nanotechnology research efforts are underway within universities, industry and federal laboratories, both national and international. However, most work focuses on initial properties and simulations on polymer nanocomposites, simple end-application demonstrations and semi-quantitative performance test on end-products. None of this research is aimed at the development of a coordinated program for measurement and modeling of critical performance properties and for predicting the long-term performance of, and the release of nanoparticles from, NPMs.

Why NIST? This project is relevant to BFRL's mission and vision, and is aligned with BFRL's strategic priority of "Measurement Science for Sustainable Infrastructure Materials" and one of BFRL's five core competencies on "Performance, durability and service life prediction of building materials." Only BFRL at NIST is equipped to perform this work because it has a world-class multidisciplinary team in place, has established extensive national and international networks with industry and academia, and has successfully linked between field and laboratory exposure results for polymer systems. NIST is also recognized nationally and internationally for its advanced instrumentation, innovative exposure devices, and accurate characterization of the environments.

Approach:

What is the new technical idea? The new technical idea is that critical measurement science will be developed for characterization and prediction of service life of NPMs at multiple length and time scales. Reliability-based methodology will be applied to NPMs to link the field and laboratory exposures. Advances in measurement science in characterizations of nanoparticle dispersion, polymer-nanoparticle interactions, multiscale physical and chemical degradation will be developed. The nano-scale chemical, physical, mechanical and electrical properties of the nanostructured polymeric systems will be investigated using a number of advanced nanoscale techniques, including chemical force microscopy, electrical force microscopy, and scattering techniques (light scattering, x-ray, and neutron scattering) in an accurate, precise and timely manner. In addition, influence of nanoparticle-polymer interfacial interactions on nanoparticle dispersion, failure mechanism, and long-term performance of NPMs will be assessed. Mathematical predictive models for service life prediction of NPMs exposed to different controlled environments will be developed.

Why can we succeed now? NIST possesses the specialized facilities, interdisciplinary scientific and technical expertise, core knowledge, and technical exchange networks with industry, academia, and other national and international laboratories necessary to solve this problem. BFRL is the world's leader in developing the measurement science for service life prediction of polymeric material and was the first to successfully link field and laboratory

exposure results for an unfilled polymer system using its unique SPHERE facility, coupled with a reliability-based predictive methodology.

What is the research plan? The scope of this research is to develop measurement science to enable industry to manufacture high performance NPMs with known service life. This program will identify, measure, model, and integrate physicochemical failure mechanisms at multiple length and time sales in determining the contributions of nanoparticles to the long-term performance of NPMs. The research consists of three major technical components:

- Measurements of the multiscale chemical and physical properties of the aged and unaged, unfilled and nanoparticle-filled polymers,
- Laboratory accelerated and field exposures, and
- Linking laboratory and field exposure results via appropriate scientifically-based predictive models.

Measurements: Advanced measurement techniques developed in other projects contained in the BFRL program *Service Life Prediction of Nanostructured Polymeric Materials* will be used to characterize the multiscale physical and chemical properties of polymeric systems filled with nanoparticles such as ZnO and SiO_2 during photodegradation. In addition to macroscale chemical characterization using traditional techniques, such as FTIR and UV-visible spectroscopies, the nanoscale chemical structures of NPMs, the distribution of the nanoparticles in the polymer matrix, and the interactions between polymers and nanoparticles will be characterized using advanced, high-resolution microscopic, spectroscopic and scattering techniques at different exposure times.

Exposures: Unfilled polymeric materials and NPMs will be exposed systematically on the NIST SPHERE to different combinations of panel temperature, relative humidity (RH), spectral UV wavelength, and spectral intensity. Laboratory experiments will be designed to assess the validity of additivity and reciprocity laws for both NPMs and unfilled systems. Field exposure experiments will be initiated in Gaithersburg, MD; specimens exposed outdoors will be characterized in the same manner that these materials are characterized in the laboratory.

Predictive Models: The starting point for mathematically linking field and laboratory exposure results will be a model derived in the previous phase of the consortium by Professor William Meeker of Iowa State University. The prediction model will be developed via reliability-based methodology and cumulative damage model. The validity of this model for both unfilled and filled nanocomposites will depend on whether the additivity law is obeyed over a wide range of exposure conditions.

Recent Results: In FY 2008, major **outputs** include:

- 15 publications that reflect completion of major milestones. Selected publications are listed below.
  - Xiaohong Gu, Lipiin Sung, Bouchra Kidah, Mounira Oudina, Cyril Clerici, Haiqing Hu, Debbie Stanley, Walter E. Byrd, Jerry Y.C. Jean, Tinh Nguyen and Jonathan W. Martin, "Multiscale Physical Characterization of a Polymeric Coating System Exposed to UV Radiation", J. Coat. Technol. Res. (In press)

- Xiaohong Gu, Chris A. Michaels, Peter L. Drzal, Joan Jasmin, David Martin, Tinh Nguyen and Jonathan W. Martin, "Probing Photodegradation beneath the Surface: A Depth Profiling Study of UV-degraded Polymeric Coatings with Micro-Chemical Imaging and Nanoindentation", J. Coat. Technol. Res., 4 (4) 389–399, 2007
- Xiaohong Gu, Lipiin Sung, Bouchra Kidah, Mounira Oudina, Vincent Delaurent, Haiqing Hu, Debbie Stanley, Walter E. Byrd, Jerry Y.C. Jean, Tinh Nguyen and Jonathan W. Martin, "Multiscale Physical Characterization of a UV-degraded Polymeric Coating System", 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, 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, 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.
- Xiaohong Gu, Lijiang Chen, Chang Xu, Duangrut Julthongpiput, Michael Fasolka, and Tinh Nguyen, "Effect of Relative Humidity on Chemical Heterogeneity Imaging with Atomic Force Microscopy", MRS Proceedings (2008)
- Juntao Wu, Minhua Zhao, Tinh Nguyen and Xiaohong Gu,"Effects of Relative Humidity and Nanoparticle Incorporation on Nanostructures of PS-b-PEO Diblock Copolymer", MRS Proceedings (2008)
- Xiaohong Gu, Debbie Stanley, Water E. Byrd, Brian Dickens, Iliana Vaca-Trigo, William Q. Meeker, Tinh Nguyen, and Jonathan W. Martin, " Linking Accelerating Laboratory Test with Outdoor Performance Results for a Model Epoxy Coating System," 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, 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, 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.
- T. Nguyen, A. Granier, C. Steffens, Hajin Lee, A. Sharpiro, and J. W. Martin,, "A Novel Method to Covalently Functionalize Carbon Nanotubes with Isocyanate for Polyurethane Nanocomposite Coatings", 2007 Proceedings of the 85th Annual Meeting Technical Program, Toronto, Ont, Canada, October 3-5, 2007.

- Establishment of collaborations with Chinese Academy of Science, Fudan University and Xiamen University in China.

- Recruitment of NIST/NIH postdoctoral research associate; personnel exchanges with Lyon University, France and SinoPEC, China.

Major **outcomes** include:

- Linked laboratory and outdoor exposures using data from the SPHERE and the outdoor test site incorporated into mathematical models, and
- Developed an AFM-based method to quantitatively detect the buried nanoparticles in the NPMs

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Standards and Codes: Participation in future ASTM G03.08 on Service Life Prediction from next January, for promotion of reliability-based service life prediction protocols and measurements at the multiscale.