2009 BFRL Project Description

Project Title: Nanoparticle Release During Life Cycle of Nanostructured Polymeric Materials

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BFRL Program: Service Life Prediction of Nanostructured Polymeric Materials

Objective: To develop metrologies for characterization and prediction of nanoparticle release from nanostructured polymeric materials (NPMs) over their life cycle. This project will provide essential data and knowledge for understanding the effects of weathering elements on the mechanisms and rates of release, chemical composition, and morphology of common nanoparticles released from nanostructured polymeric materials.

Problem:

What is the problem? Critical measurement science is needed for understanding mechanisms, measuring and modeling the rate, and characterizing properties of nanoparticles released from NPMs during service and post service. New construction and repair of our nation's ailing infrastructure will potentially use a large volume of innovative, multifunctional nanostructured polymeric materials (NPMs), such as high-performance protective coatings and fiber-reinforced polymer composites [1, 2]. However, nanoparticles may be harmful to human health and the environment [3,4,5]. Such fear would present roadblocks to innovation and commercialization of nanotechnology [6,7]. Current research on health effects of nanoparticles focus on exposure during the manufacturing

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[1] *Nanocomposites: US Industry Study with Forecasts to 2010, 2015 and 2020, The Freedonia Group, 2006.*
[2] *Investment in Federal Facilities, National Research Council (2004).*
Report Card for America's Infrastructure", American Society of Civil Engineers, 2006 (www.asce.org/reportcard).
[3] *Helland, A., Wick, P., Koehler, A., Schmid, K., Som, C., Reviewing the environmental and health knowledge base of carbon nanotubes, Environmental Health Perspectives, 115, 1125-1131 (2007).*
[4] *. Nel, A., Xia, T., Mädler, and Li, N., Toxic Potential of Materials at the Nanolevel, Science, 311, 622-627 (2006).*
[5] *Poland, C., et al., Carbon nanotubes introduced into the abdominal cavity of mice show asbestos-like pathogenicity in a pilot study, Nature Nanotechnology, May, 2008. (doi:10.1038/nnano.2008.111).*

[6] *Environmental, Health, and Safety Research Needs for Engineered Nanoscale Materials", National Science and Technology Council (2008).*
[7] *Maynard, A.D., Nanotechnology: Assessing the risks, Nanotoday, 2: 22-33 (2006).*

process. The release of nanoparticles over an NPM's life potentially poses greater risks due to the large volume of materials that will be exposed in-service and eventually disposed in landfills at the end of a product's useful life. This is because polymeric materials are prone to undergo degradation during service, and the nanoparticles imbedded in the polymer matrix will eventually be released via interaction with UV radiation, rain, condensed water, and wind. However, little information on the nanoparticles released from NPMs is available, and thus their potential harmful effects on the environment and health cannot be intelligently assessed.

Why is it hard to solve? Science-based models for predicting the degradation of NPMs and release of nanoparticles has not, as yet, been extensively studied. Such research requires advanced, high resolution tools for accurate measurement of airborne-particles[8], degradation of NPMs, and the loss of their constituents. Nanoparticle release from NPMs exposed in their end-use environments is tied closely to the degradation of polymeric materials, which is inherently a very complex phenomenon depending on environmental factors, processing, and materials properties. Nanoparticles also possess unique properties that will affect the degradation mechanism and their release rate from NPMs in unknown ways. For example, our preliminary results showed that polyurethane coating containing silica nanoparticles degrades at a much faster rate than that of the same coating containing carbon nanotubes.

How is it solved today, and by whom? The problem of nanoparticle release from NPMs during their life cycle is critical to the success of the nanotechnology revolution and it has not been solved. Over the past few years, BFRL has developed and validated a *reliability-based methodology* for predicting the service lives of *traditional* polymeric materials used in building and construction industries. Extensive nanotechnology research efforts on materials development, metrologies, and environmental and health risks of nanotechnology are underway within industry and federal laboratories. Studies dealing with nanoparticle release during compounding of nanocomposites [9] have been also reported. None of these research efforts, however, are aimed at the development of a coordinated program for measurement and modeling of nanoparticle release rate over the life cycle of NPMs.

Why NIST? This project supports the National Nanotechnology Initiative (NNI) including NNI initiative on Environmental Health and Safety, and BFRL's strategic priority on Measurement Science for Sustainable Infrastructure Materials. NIST is recognized nationally and internationally for its advanced instrumentation and its world class expertise on service life prediction of polymeric building materials. Research that provides metrologies and models for measurement of nanoparticle release rate of NPMs is closely aligned with NIST's mission of advancing measurement science. Finally,

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[8] Lubick, N. "Risks of Nanotechnology Remain Uncertain" *http://pubs.acs.org/subscribe/journals/esthag-w/2008/feb/science/nl_nanorisks.html*

[9] *Tsai, S.-J., Ashter, A., Ada, E., Mead, J.L., Barry, C.F., and Ellenbecker, M.J.,Air-borne Nanopartcile Release associated with the Compounding of nanocomposites using Nanoalumina as Fillers, Aerosol and Air Quality Research, 8, 160-177 (2008).*

nanoparticle release is a very important environment and health issue of nanotechnology, and is a potential roadblock to US industrial competitiveness.

Approach:

What is the new technical idea? The new idea is that NIST will develop and apply measurement science to enable a comprehensive understanding and prediction of nanoparticle release rates of NPMs exposed to the environments. Research has demonstrated that besides concentration, physical and chemical properties of nanoparticles also play an important role in affecting the environments and health. Therefore, advances in measurement science will be developed for not only accurately measuring and modeling the release rate, but also for charactering the chemical composition, size, and morphology of the nanoparticles released from NPMs as these materials undergo degradation during exposures to various environments. This research will also critically assess the role of nanoparticles and their various chemically-modified forms[10] on the mechanism and rates of nanoparticle release during their life cycles. These data will be used in understanding the release mechanism and developing and validating models of nanoparticle release. This research will not address nanoparticles released during mechanical processing (sawing, polishing, etc.) and recycling of NPMs.

Why can we succeed now? Recent developments in nanoscale measurement tools, nanoparticle manipulation, well-controlled environmental chambers, and service life prediction modeling will enable the success of this work. 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. For example, NIST researchers have predicted the lifetimes of unfilled polymeric materials using its unique SPHERE facility, coupled with a reliability-based predictive methodology. Industry, through consortia, has identified NPMs life cycle performance as a high priority problem and has asked NIST to help solve it. The release of nanoparticles is a central part of NPM's degradation and service life.

What is the research plan? Release of nanoparticles occurs in-service via environmental degradation and incineration through thermal, chemical, and photolytic decomposition of NPMs. The goal of this research is to develop measurement science to characterize, measure, and predict the rate of nanoparticles released during in-service and life cycle of NPMs. The combination of experiments and models makes up the required measurement science. Specifically, this research will expose NPM samples to well-controlled environments or special devices, measure their chemical degradation and material mass loss, separate polymer loss from nanoparticle release, and model the nanoparticle release rates. Research will use nanosilica/epoxy and carbon nanotube/epoxy NPMs; the former is being used commercially, and the latter is being intensively investigated, for infrastructure applications.

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[10] *Majority of nanoparticles currently used in polymeric materials are chemically modified by non-covalent and covalent- bonding methods, and this treatment likely affects the rate and chemical composition of nanoparticles released from NPMs.*

Total mass loss, chemical degradation of NPMs, and nanoparticles release during exposures to different UV/relative humidity environments will be measured using high-resolution nano-gravimetry (quartz crystal balance and thermogravimetry) and Fourier transform infrared spectroscopy. In addition, the research will characterize chemical compositions, morphologies, and size distributions of aerosolized nanoparticles using a number of advanced methods, including helium ion microscopy (HIM) and particle mass spectroscopy. Combining the total mass loss and particle release data with aerosol data will provide information on the quantities and nature of the air-borne nanoparticles generated throughout the NPMs life cycles. Further, the roles of nanoparticle-polymer interactions (covalent bond or physically attached) and nanoparticle dispersion in the matrix on the release rate of nanoparticles will be assessed.

Nanoparticle release rate model will be based on cumulative damage concept and irradiation dosage (radiation absorbed by materials) as the metric. The model will incorporate both environmental (e.g., ultraviolet radiation, moisture, and temperature) and materials (e.g., matrix-nanoparticle adhesion) parameters.

Recent results: Although this is a new project, preliminary results from our research on functionalization of carbon nanotubes and nanoclays for NPMs have shown that the photo-degradation rates of NPMs exposed to UV light are markedly different for different nanoparticles. These results imply that the rates of nanoparticle released from NPMs are different for different types of nanoparticles and likely for different exposure environments.

Standards and Codes: none