2009 BFRL Project Description

Project Title: Characterizing Particulate Emissions from Burning Polymer Nanocomposites

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BFRL Program: Reduced Flammability of Materials

Objective To determine the likelihood that nanoscale particles will be released into the environment when polymer nanocomposites are burned, develop techniques to quantify the yields, chemical compositions, morphologies, and size distributions of the aerosolized nanoparticulates and investigate how these quantities depend on materials formulation and combustion conditions.

Problem:

What is the problem? Because of their small size and ability to interact with biological molecules, there are potential health and environmental risks associated with the use of nanoscale materials[1,2]. There is the potential for nanoparticle aerosolization when these materials are exposed to heat and fire (either accidentally or during incineration). The nanoparticle morphologies and chemical compositions generated in this way may also be vastly different from the pristine nanoparticle structures due to oxidation and/or interactions with other decomposition products, possibly affecting health and environmental risks. The risks associated with particulates formed from polymer nanocomposite combustion are unknown and could differ from the hazards associated with non-filled polymer combustion. Measurement science needs include: understanding how chemical and physical modifications affect properties of nanomaterials, developing methods for standardizing assessment of particle size, size distribution, shape, structure and surface area, and the transformation of nanomaterials under different environmental conditions[2].

Why is it hard to solve? The quantification of aerosolized nanoparticles and characterization of their diverse morphologies is a more challenging problem than it is for pristine nanostructures. In the case of characterizing pristine nanostructures, it is common to

[1] Nanoscience and Nanotechnologies: Opportunities and Uncertainties, The Royal Society & The Royal Academy of Engineering, July, 2004, http://www.nanotec.org.uk/report/Nano%20report%202004%20fin.pdf

[2] The National Nanotechnology Initiative Strategy for Nanotechnology-Related Environmental, Health, and Safety Research, Subcommittee on Nanoscale Science, Engineering, and Technology, Committee on Technology, National Science and Technology Council, Feb. 2008, http://www.nano.gov/NNI_EHS_Research_Strategy.pdf

adopt unique, well-defined structures such as spheres, rods, layers and bundles. In flaming combustion, the soot produced may mask aerosolized nanoparticles, which themselves may undergo oxidation or growth. During non-flaming pyrolysis, nanoparticles may end up encapsulated by condensed pyrolyzate. A suite of measurement techniques will be needed to characterize the composition, morphology, size distribution and quantities of nanoparticulates so that assessment of health and environmental risks can be made.

How is it solved today, and by whom? Current research into the health effects of nanoscale materials has focused on pristine nanostructures, such as carbon nanotubes (CNTs), without consideration of morphological transformations that may occur during the lifecycles of materials containing them. There have been no studies directed at quantifying the release of nanostructures from nanocomposite materials and characterizing their morphologies. Prof. Kenneth Dawson, director of the Nanointeract program[3] at University College Dublin, agrees that this is an important problem and is willing to collaborate with us by evaluating aerosolized nanoparticles we provide.

Why NIST? Halogenated fire retardants have come under regulatory scrutiny creating an urgent need for new approaches to fire retardancy. BFRL's unique statutory role in fire research and expertise in service life and flammability prediction have enabled us to assume a leadership role in the international effort directed at investigating the potential of nanoscale additives as alternatives to halogenated fire retardants. However, industry will understandably be reluctant to commercialize products containing nanoscale fire retardants without a better understanding of the likelihood that these additives will be released into the environment where they can pose a significant threat to public health and safety. In view of these considerations, research directed at characterizing and quantifying nanoparticulate emissions is clearly aligned with our mission to increase the competitiveness of U.S. industry through technical innovation in ways that enhance economic security and quality of life.

Approach:

What is the new technical idea? Through a series of controlled combustion and pyrolysis experiments we will develop an aerosol sampling methodology and characterization protocol that will identify the presence of nanofiller materials (which may have been modified by the combustion/aerosolization process) in the sampled aerosols. Detailed measurements of the size distribution, morphology, chemical composition, and yield will be made to examine the effects of combustion mode and nanocomposite formulation (polymer and nanoparticle filler) on the potential for enhanced toxicity. A well-controlled combustion environment in the NIST well-stirred reactor will be explored as a means to produce bulk quantities of combustion modified nanoparticulates for toxicological studies and as potential standard reference materials. Molecular simulations will be conducted in an effort to formulate mechanisms to explain the observed morphological transformations and suggest modifications to mitigate aerosolization. Ultimately, a screening protocol or standard test method that evaluates the health and environmental risks associated with polymer nanocomposite combustion and the formation of combustion-modified nanoparticulates is seen as a potential outcome.

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[3] www.nanointeract.net, "Development of a platform and toolkit for understanding interactions between nanoparticles and the living world".

Why can we succeed now? BFRL has a unique mix of technical staff with the expertise to conduct a thorough investigation of the problem. Staff members are experienced in polymer nanocomposite formulation, combustion and flammability, combustion toxicity, aerosol characterization, molecular simulations, and have access to polymer processing equipment, aerosol characterization equipment, an electron microscope, and a well-stirred reactor.

What is the research plan? A set of experiments will be conducted to verify aerosolization of nanoparticles from a polymer matrix under heating and flaming conditions. The processes necessary to aerosolize these solid particles from a surface depend on the forces holding the particles to the polymer matrix and the gasification of the polymer which generates a blowing velocity from gaseous pyrolyzate. Aerosol samples taken above the surface will be examined to determine if nanoparticles are present in the various size fractions of the sample.

Analytical techniques to determine the presence of nanoparticles of interest will include electron microscopy (EM), and other conventional techniques depending on the nanoparticles and their concentration. Aerosol sampling techniques will be developed for collecting EM samples, and aerosol property measurements. Sampling techniques will consider the need for temperature control, dilution, and particle aerodynamics. We will characterize aerosol size distribution and aerodynamic properties with a range of instruments we have used for standard reference material (SRM) particle sizing and smoke aerosol measurements. Upon verification of nanoparticles in the aerosol during the initial experimental phase, additional nanocomposites will be investigated.

We will collect well defined samples for toxicity screening, and investigate the effects of altering materials formulation and combustion conditions in an effort to fully characterize the phenomenon and to identify strategies that mitigate nanoparticulate emissions. Molecular simulations will be conducted in an effort to formulate mechanisms to explain any observed morphological transformations.

We will formulate a test plan to use the NIST well-stirred reactor to produce quantities of combustion-modified nanoparticles for toxicity screening, and for the potential use as standard reference materials. The well-stirred reactor will be used to produce a range of combustion-modified nanoparticles. The particles will be characterized using the suite of instrumentation previously identified, and toxicity screening will be conducted by outside laboratories (Nanointeract- University College Dublin, National Institute of Occupational Safety and Health (NIOSH), Scripps Institute of Oceanography).

Results will be presented in the form of guidance to the industry on what polymer/nanofiller systems may exhibit enhanced toxicity over the base polymer when burned, and what actions may reduce the risk. A methodology for aerosol sampling and size, morphological, and chemical characterization to help quantify environmental, health and safety risks of combusted nano-composites will be proposed.

Recent Results: New Project

Standards and Codes: We expect that this research will become the basis for the development of standards for nanoparticulate emissions.