2009 BFRL Project Description

Project Title: Modeling the Dispersion and Agglomeration of Nanoadditives in Polymers

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Co-Investigator(s):

BFRL Program: Reduced Flammability of Materials

Objective: To develop a model of the agglomeration, exfoliation, and dispersion of carbon nanotubes and other nanoadditives in polymers.

Problem:

What is the problem? Small quantities of carbon nanotubes (CNTs) and other nanoadditives (e.g., alumina silicate clays, graphene oxides, and layered double hydroxides) are effective in reducing the flammability of polymeric materials. A reduction in heat release rates (HRRs) by as much as a factor of three (with respect to the untreated polymer) has been observed in favorable cases. BFRL scientists have shown that this improvement in fire performance is due to the presence of a network structure comprised of nanoadditives, which is left behind when the surrounding polymer gasifies in the fire. This network structure acts like a thermal barrier radiating energy away from the unburnt polymer in the interior of the burning object. Unfortunately, most nanoadditives are not fully compatible with hydrocarbon polymers and the network structures that form during processing are meta-stable. As a consequence, they can collapse when subjected to thermal and mechanical stress, which adversely affects the fire performance and other properties of nanocomposites. The current understanding of the structural characteristics (shape, aspect ratio, chemical functionality) of the nanoadditives and processing conditions (loading, dispersion) needed to ensure the formation of stable networks is incomplete. Without predictive measurement tools that can provide this guidance, industry cannot engineer products with required levels of performance and they will be reluctant to embrace the development and use of nanoadditives as fire retardants[1].

Why is it hard to solve? The major challenge is to develop an accurate representation of the nonbonded (Van der Waals) forces between the constituent atoms that determine the morphology of nanoadditive networks and integrate this description into a model that accounts

[1] An Assessment of the United States Measurement System: Addressing Measurement Barriers to Accelerate Innovation, Appendix B Case-Study Measurement Needs: A Compilation, NIST Special Publication 1048, 134, 2006.

for the variation of temperature, pressure, and composition that occurs when full-scale building materials burn in a fire.

How is it solved today, and by whom? The correlation between fire performance and the formation of nanoadditive networks was discovered by BFRL scientists who have approached the problem of identifying optimal formulations by trial and error. There are no reports of dynamic simulations of nanoadditive dispersion and agglomeration in the literature at the present time. However, several groups, including our collaborators on the University of Texas at Austin, are actively pursuing the development of similar models to explain rheological effects that result from CNT network formation.

Why NIST? Halogenated fire retardants have come under regulatory scrutiny and there is an urgent need for new approaches to reduce the flammability of hydrocarbon polymers. 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. Furthermore, since the US building and materials industries have just begun to commercialize products containing nanoscale materials, there is a window of opportunity for the introduction of a new generation of nano-fire retardants. A model that describes the dynamics of the mixing process will provide the scientific guidance needed to go beyond conventional trial-and-error approaches to the development of this technology. The National Nanotechnology Initiative report issued by the National Science and Technology Council as a supplement to the President's FY 2006 Budget specifically referred to NISTs role in the application of CNTs for improving the fire resistance of construction materials and the development of protocols for CNT dispersion[2].

Approach:

What is the new technical idea? The unique properties of polymer nanocomposites arise from interactions that are limited to a range of several nanometers. This is too small to be captured by continuum mechanics, but beyond the capabilities of conventional atom based molecular mechanics (MM) and dynamics (MD). Problems that fall into this domain (mesoscale) can be handled by Langevin dynamics, which can account for the explicit motion of the nanoadditives while treating the surrounding polymer as a continuous medium. We have adopted a multi-scale approach to model nanoadditive dispersion. A continuum description will be employed to account for the variation of the temperature (T), pressure (P), and composition (C_i) throughout the nanocomposite material, while the effects that these conditions have on the state of exfoliation/agglomeration of the nanoadditives will be determined by Langevin dynamics using course-grained potentials obtained from MM calculations.

Why can we succeed now? An atomistic model that describes the (static) thermodynamic compatibility of CNTs and polymers was developed at BFRL. However, a dynamical model, which integrates our atomistic approach with meso-scale and continuum modeling, is needed to simulate burning. We did not have this capability before initiating collaborations with UT-Austin (meso-scale) and the FAA (continuum).

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[2] The National Nanotechnology Initiative, Research and Development Leading to a Revolution in Technology and Industry, Supplement to the President's FY2006 Budget, National Science and Technology Council Committee on Technology Subcommittee on Nanoscale Science and Engineering, March 2005.

What is the research plan? The implementation of Langevin dynamics requires a description of the potential energy of interaction between the nanoadditives (as a function of their relative positions) that is resolved over length scales intermediate between atomic and continuum dimensions. Thus, the first step in our modeling effort was to develop a coarse-grained representation for the interaction between CNTs (and carbon nanofibers) modified by the presence of the polymer matrix. To accommodate their tendency to flex, fold, and entangle, the CNTs are represented by cylindrical segments connected by flexible joints. The angles between them are allowed to vary, but are restrained by a quadratic potential energy function. The separation distances between adjacent segments are fixed in the simulations to ensure that the lengths of the CNTs remain constant. During the first year of this project (FY08), we found that a simple function depending on the distance of separation between their outer walls and their relative orientations (measured by the degree of tilt from the parallel orientation) provided an accurate representation of MM calculations of the potential energy of interaction between pairs of CNTs. This function was modified to account for the interaction between the CNTs and the interstitial polymer. By employing this approach, the thousands of individual interactions between atoms contained within interacting CNT segments are integrated into a single energy contribution. Furthermore, by eliminating the need to resolve the high frequency vibrations associated with the motions of individual atoms, the time step for the dynamics can be increased by many orders of magnitude over what is required in MD calculations. These factors should enable simulations of CNT dispersion and agglomeration in model nanocomposites containing multiple CNTs for long periods of time; perhaps approaching experimental (millisecond) time scales. During FY09, this interaction potential will be incorporated into a multi-scale code in which Langevin dynamics is used to calculate the density of the CNT network in control volumes that reflect the temperature, pressure, and concentration gradients obtained from conventional continuum mechanics. The completed multiscale model will then be used to study the formation of carbon nanofiber networks, which are similar in structure to CNTs, during the processing and burning of polyurethane foams. This study will guide efforts in the development of low flammability foams for use in mattresses and furniture.

Recent Results: Insights gained during the first year of this project have been used to interpret experimental results obtained on epoxy/CNT composites and are guiding future work directed at identifying optimal formulations and processing conditions.

Output: Nyden, M.R. and Stoliarov, S.I., “Calculations of the Energy of Mixing Carbon Nanotubes with Polymers,” Polymer 49, 635-641, 2008.

Output: Nyden, M.R., Stoliarov, S.I., Ganesian, “Modeling The Dispersion And Agglomeration Of Carbon Nanotubes In Polymers,” Khounlavong, L, ACS PMSE Preprints, 2008.

Standards and Codes: None