2009 BFRL Project Description

Project Title: Nanoadditive Flame Retardants for Polyurethane Foam

June 2, 2008

Principal Investigator: Jeffrey W. Gilman

Co-Investigator(s): Mauro Zammarano (GR)

BFRL Program: Reduced Flammability of Materials

Objective: To develop flammability measurement science for fire-safe flexible foams used in furniture and mattresses. Bench-scale flammability tests, nanoadditive flame retardants and foam rheological models will be combined to provide the necessary measurement tools to enable fire safe products.

Problem:

What is the problem? The total cost of fire to the U.S. economy is estimated to exceed $200 B annually[1]. Reducing the flammability of materials used in products which are found in homes and businesses could reduce these costs, significantly enhance public safety, and provide a competitive advantage for US companies in international markets. US fire deaths attributed to the burning of polyurethane foam products remain a major fraction of the total fatalities recorded in home fires.[2, 3] The European Union's ban on two members of the poly brominated diphenyl ethers (PBDEs) class of flame retardants, one of the more effective classes of flame retardants used in polyurethane foam, and similar actions in Maine, Washington, and California coupled with the more stringent, new and proposed, national flammability requirements for residential furnishings provide incentive for a concerted effort to develop the measurement science that will enable industry to produce fire-safe polyurethane foam.

Why is it hard to solve? Development of the measurement science to enable industry to produce fire-safe polyurethane foam requires the combination of several complex technologies; 1-development of multi-scale flammability tests, 2-foam nanocomposite characterization and processing, 3-flame retardancy and 4-rheological modeling. Nanoadditive flame retardants may provide part of the solution to this significant fire problem, since they have been shown to enhance a number of polymer properties.[4] However, the foam manufacturing process is a delicate balance between the rate of polymer cure,

---

[1] John R. Hall, Jr. THE TOTAL COST OF FIRE IN THE UNITED STATES, Fire Analysis and Research Division National Fire Protection Association, February 2008

[2] M. J. Karter, Jr., *NFPA J.* **101(5)**, 64 (2007).

[3] Ahrens, M; "Home Fires that Began with Upholstered Furniture", NFPA One-Stop Data Shop Report, May 2008.

[4] 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.

bubble formation, network phase segregation and open-cell formation. Any change made in a foam formulation can have a dramatic effect not only on the foam's manufacturability but also on the foams structure and hence flammability. For the enhancements described above to be realized in polyurethane foams, the affect of nanoadditives on flammability, processing and mechanical properties of polyurethane foams must be characterized.

How is it solved today, and by whom? No organization is addressing all of the necessary issues associated with the development of fire-safe flexible foams used in furniture and mattresses. Industry develops foam products to meet current regulations. However, many groups focus only on some subset of the issues, e.g., foam flammability tests, new halogen-free, environmentally friendly flame retardant, or nanotechnology aspects. For example, in Europe, the PREDFIRE NNANO (13 member program) focuses on flame retardant nanocomposites but does not apply them to foams.[5] Underwriters Laboratories is considering working on furniture flammability, but no one is focused on development of foam flammability test methods, nano-based flame retardants and foam process modeling.

Why NIST? The goals of this project are aligned with the BFRL mission in terms of improving public safety and enhanced industrial competitiveness, specifically for the chemical, flame retardant, polymer and soft furnishings industries. This project is aligned with the BFRL strategic priority of Measurement Science for Sustainable Infrastructure Materials. It lies at the intersection of BFRL core competencies of fire protection and fire spread within buildings and communities, and the performance, durability and service life prediction of building materials.

Approach:

What is the new technical idea? Integrating methods for combining nanoadditives, conventional flame retardants, bench-scale flammability measurement methods, and foam process modeling into a single approach to enable highly flame retardant polyurethane foams. Each component task is critical: 1-rheological modeling of the foaming process; to assist in modifying the foam formulation and to understand the myriad of effects brought about by introducing the nanoadditives, and 2- continued refinement of bench-scale foam flammability tests to include more severe fire conditions. In previous work we have already correlated one bench-scale foam flammability tests with furniture-scale calorimeter tests. A new high flux test-rig will be designed, fabricated and evaluated. 3- Nanoadditive flame retardant evaluations. Specifically, we will use layered silicates (LS), layered double hydroxide (LDH), polyoligosilsesquioxane (POSS), carbon nanofibers (CNF) and other green and renewable nano-based flame retardants (cellulose whiskers, graphene, etc.) from the Sustainable Flame Retardants project. We will also continue evaluation of layer-by-layer nanocomposite coatings on the foam to stop dripping. To facilitate screening nanoadditive polyol (a foam precursor) combinations we will exploit using a fluorescent dye method of measuring rheological properties (viscosity) utilizing our recently installed small-scale automated high throughput liquid handling, fluorescence platform. Systems which exhibit suitable viscosity will be evaluated for low-shear gel behavior and meso-scale aggregation using our new ultra-low shear rheometer and new in situ shear-cell microscope. The resulting foam samples will be characterized (density, air-flow, XRD, TGA). Flame retardant foam formulations, which have

[5] PREDFIRE NANO- Predicting Fire Behaviour of Nanocomposites from Intrinsic Properties, http://www.engj.ulst.ac.uk/predfire/project.php

promising properties, good homogeneity and meet foaming requirements, will be scaled up and evaluated for flammability behavior utilizing the methods developed in the Fire Retarded Polyurethane Foam Flammability project (melt-drip bench-scale foam flammability tests). Successful concepts will be scaled up through our foam consortium and flammability testing done at furniture calorimeter scale in collaboration with the Reduced Risk of Fire Spread in Buildings Program.

Why can we succeed now? Halogenated fire retardants have come under regulatory scrutiny creating an urgent need for new approaches to fire retardancy. BFRL has extensive experience in flammability test method development, polymer modeling, nanocomposite processing and characterization, and novel flame retardant approaches, the combination of these efforts will produce the necessary tools for industry to develop fire-safe polyurethane foam.

What is the research plan? An integrated approach is critical for the success of this project, therefore the three main tasks will be done in parallel. Each component task will feed information to the others.

The primary tasks are: 1- Rheological modeling of the foaming process; dozens of experimental matrices are often required to re-design a foam formulation when a new additive is under evaluation. This is necessary because of the often dramatic effect nano-additives have on the chemistry and physics of the foaming process. The rheological foam process modeling should assist us in modifying the foam formulation and to build a knowledge-base on foam-nanoadditives interactions.

2- Bench-scale foam flammability tests. In previous work we have already correlated one bench-scale foam flammability tests with a larger scale “Vee” test of foam and a chair mock-up furniture-scale calorimeter test. A new high flux test-rig will be designed, fabricated and evaluated, so as the fire performance of the foams improves we will be able to measure their flammability under realistic, more severe fire conditions.

3- Nanoadditive flame retardant evaluations. Specifically, we will continue to use layered silicates (LS), layered double hydroxide (LDH), polyoligosilsesquioxane (POSS), and carbon nanofibers (CNF). In addition we will include other green and renewable nano-based flame retardants (cellulose nanofibrils, graphene, etc.) from the Sustainable Flame Retardants project. To facilitate screening nanoadditive-polyol (a foam precursor) combinations we will exploit using a fluorescent dye method to measure the rheological properties (viscosity) utilizing our recently installed small-scale automated high throughput liquid handling, fluorescence platform. Systems which exhibit suitable viscosity will be evaluated for low-shear gel behavior and meso-scale aggregation using our new ultra-low shear rheometer and new in situ shear-cell microscope.

The resulting foam samples will be characterized (density, air-flow, XRD, TGA). Flame retardant foam formulations, which have promising properties, good homogeneity and meet foaming requirements, will be scaled up and evaluated for flammability behavior utilizing the methods developed (melt-drip bench-scale foam flammability tests).

We will also continue evaluation of layer-by-layer nanocomposite coatings on the foam to stop dripping. This effort is part of our collaboration with Texas A&M through a fire grant awarded this year. Successful concepts will be scaled up through our foam consortium, which we are reforming.

Flammability testing will be done at furniture calorimeter and room scale in collaboration with the Reduced Risk of Fire Spread in Buildings Program.

Recent Results: Output: M. Zammarano, R.H. Kramer, R. Harris, Jr., T.J. Ohlemiller, J.R. Shields, S.S. Rahatekar, S. Lacerda, J.W. Gilman, Polym. Adv. Technol. 2008; 19: 1–8.

Output: T. Ohlemiller and J. Shields, "Aspects of the Fire Behavior of Thermoplastic Materials", NIST Technical Note 1493, January, 2008

Output: M. Zammarano, J. W. Gilman, R. H. Krämer, R. Harris Jr., T. J. Ohlemiller, J. R. Shields, Effect of nanpoparticles on flammability of flexible polyurethane foams, a novel approach to bench scale flammability testing of foams, in Proceedings of 19th BCC Conference, Stamford, CT; 2008.

Standards and Codes: The ASTM E5.15 (Contents and Furnishings) sub-committee would be most interested in the development of foam flammability tests and of methods for cost effectively reducing the flammability of foam. The PI is participating in this sub-committee.