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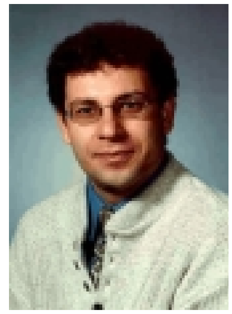
NANO-DISPERSION OF CLAYS MAKE BETTER, CLEANER PLASTICS



Dr. Evangelos Manias Assistant Professor Materials Science and Engineering/Polymer Science

Small amounts of well-dispersed natural clay can lead to environmentally friendly and inexpensive plastic composites with improved specialized properties, according to a Penn State researcher.

"Adding very small amounts of natural clays to plastics changes some of their physical properties," says Dr. Evangelos Manias, assistant professor of materials science and engineering. "While we can tune the chemical interactions between the clays and some polymers, it is the general changes due to the nanometer fillers in all plastics that may be the most interesting."

Addition of clay can make plastics less permeable to liquids and gases, more flame retardant and tougher. Lower permeability can make plastics like PET, the standard plastic used in soft drink bottling, suitable for bottling beer or wine. The clay-enhanced product would protect the beverages from the effects of oxygen. At the same time, the addition of small amounts of clay does not affect the transparency of plastics.

Adding clay to polymer blends is not a simple process as polymers and clays mix about as well as oil and water. However, if the clay is treated with an organic surfactant, a compound that allows the inert clay to mix with the polymers, much as soap allows oil and water to mix, the clays can be incorporated into the final product.

An inexpensive, more environmentally clean method of producing flame retardant plastics could eventually save lives. Because the addition of clay into plastics reduces flammability in a wide range of plastics, it may have universal application as a general flame retardant additive.

"Currently, chemicals used to make plastics

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flame retardant contain bromine, which produces poisonous combustion gases when burned," says Manias. "Using clay is a green alternative to current practices and reduces flammability in a wide range of plastics."

When polymers with clay incorporated in their structures burn, the clay forms a char layer on the outside of the plastic that insulates the material beneath.

"Natural clays are currently the most used because they are the same clays already used in many products," says Mania. "However, synthetic clays, because of their tailored properties, may prove essential for high added value products, such as in biomedical devices and space applications."

The natural clays Manias refers to are bentonites and montmorillonites that are already in use in paints to prevent dripping, cosmetics to prevent shine and in pharmaceuticals. Because the U.S. Food and Drug Administration already approve them for use, there is no problem incorporating them into plastics that come in contact with foods, medicines, beverages or plastics used in biomedical devices.

The polymer clay blends, while containing only 1 to 5 percent clay, are actually nanocomposites. The addition of clay into the polymer blend, does not alter the normal production and processing of the clayless polymer.

"The clay can be added at the final stages of polymer processing without any change in the current industrial practices," says Manias. "The thermodynamics drive the nanometer dispersion of the clay through the polymer and the small amounts of clay do not cause any wear in the equipment. Manufacturers can use the same equipment, timing and settings as in their normal process."

While natural and synthetic clays provide a broad possibility of enhances plastics, Manias is also looking at polymer nanocomposites that contain platelets of metal and ceramic nanoparticles instead of clay. These ultra-small fillers require different surfactants and offer much more flexibility in property tailoring, where cost can be slightly increased.

The Penn State researcher has reported on his work in a variety of journals including Advances in Polymer Science, Chemistry of Materials and Macromolecules.

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The Pennsylvania State University

Penn State MATSE Research Report

The Department of Materials Science and Engineering
in the
College of Earth and Mineral Sciences

October 12, 2000

Clay Fillers Point Way to Reducing Flammability in Many Polymers

University Park, Pa.--Clay fillers could become a popular "green" alternative to current flame-retardant additives for polymers, according to a multi-organizational team of researchers that includes a Penn State polymers expert. The team reports that clay fillers can greatly boost the flame-retardant properties of industrially valuable polymers, while retaining the polymers' low weight and eliminating the formation of toxic fumes upon burning.

"We have discovered evidence for a shared mechanism of flammability reduction for several polymers, including polypropylene, polystyrene, epoxies and Nylon-6, through nanocomposite formations based on montmorillonite clay fillers," says **Evangelos Manias,** assistant professor of materials science and engineering at Penn State. "Since polypropylene and polystyrene are commodity polymers, this could push the envelope of their applications, and thus lead to significant improvements in safety and cost effectiveness in many industries. For instance, the air transport industry relies greatly on low-weight, flame retardant materials, including polymers and composites that are much more expensive."

Manias was a co-researcher on the nanocomposite project, which was partially funded by the Federal Aviation Administration and led to the featured cover article for the July 2000 issue of *Chemistry of Materials*, a publication of the American Chemical Society. He designed and synthesized the filler particles, and subsequently oversaw the preparation of the polypropylene-*graft*-maleic anhydride (PPgMA)/ and polystyrene (PS)/layered-silicate nanocomposite samples at Penn State. Various characterization studies of the samples before flame treatment were also performed in the Department of Materials Science and Engineering at Penn State. Other researchers on the project-from the National Institute of Standards and Technology (NIST), Cornell University and the Air Force Research Laboratory at Edwards Air Force Base-are listed below.

The PPgMA/layered-silicate samples were developed by melt blending PPgMA and an organically treated layered of montmorillonite in a mixing head, followed by cooling and compression molding. This preparation method had the effect of both delaminating and intercalating the clay layers in the samples. Various PS/layered-silicate samples were created using solvent intercalation, static melt intercalation and extrusion melt intercalation methods with either montmorillonite- or fluorohectorite-based organically treated layered silicates. These methods also resulted in delaminated and intercalated nanocomposite structures.

The researchers used Cone calorimetry to measure the heat release rates and other flammability properties of the nanocomposites under well-controlled combustion conditions at NIST's Fire Science Division in Gaithersburg, Md. The original nanocomposites and their resulting combustion residues were also studied using transmission electron microscopy and X-ray diffraction equipment at Penn State and NIST.

The results show that the PPgMA/layered-silicate nanocomposite had a 75 percent lower peak heat release rate than pure PPgMA, and the PS/layered-silicate nanocomposites that included montmorillonite had a 60 percent lower peak heat release rate as compared to pure polystyrene. Since the heat release rate quantifies the rate of combustion, these improvements are substantial, Manias says.
Furthermore, the clay does not release toxic fumes upon burning, which is a potentially fatal side effect of the bromine-containing additives typically used for flame retardant properties in polymers that are prized for their high strength-to-weight ratios in many industrial applications. The clay filler concentration needed is very low-typically less than 10 wt%-which keeps total material weights down and allows for ease of processing.

Besides its applications in nanocomposites, montmorillonite is used to slow the progress of water through soil or rocks, to give water greater viscosity in drilling muds, to purify and decolor liquids, and to serve as a base for cosmetics and for medicines for digestive disorders. Chemically, it is hydrated sodium calcium aluminum magnesium silicate hydroxide, and usually appears in nature as white, gray or pink. Fluorohectorite is a synthetic 2:1 alluminosilicate with a structure that is similar to that of montmorillonite.

"Our view of the flame retardant mechanism in the nanocomposites with montmorillonite is that a high-performance carbonaceous-silicate char builds up on their surface during burning, and that this insulates the underlying material and slows the mass loss rate of decomposition products," Manias explains. "This residue layer forms as the polymer burns away and the silicate layers reassemble into a multilayer char that can be observed with transmission electron microscopy."

The finding adds to a growing understanding of how the unique physical and reduced flammability properties of well-designed nanocomposites may someday be applied to a very wide range of polymers, the Penn State researcher notes. He adds that earlier research by the same group involved in this latest study found that a blend of the Nylon-6 polymer and montmorillonite displayed similar reduced flammability to the PPgMA/ and PS/layered-silicate samples.

"The understanding of the general mechanism that leads to flame-retardant properties in polymers, and the improvement of fire resistance in the diverse polymers that we have already studied, hold promise for finding a generally applicable filler that can become a 'green' alternative to the currently used flame-retardant additives," Manias says.

Manias continues to work on optimizing the mechanical and flammability properties of syndiotactic-polystyrene nanocomposites with **T. C. (Mike) Chung,** professor of polymer science at Penn State, through a recent grant from NIST.
Co-authors on the *Chemistry of Materials* article with Manias are **Jeffrey W. Gilman, Catheryn L. Jackson, Alexander B. Morgan,** and **Richard Harris, Jr.,** all of NIST; **Emmanuel P. Giannelis** and **Melanie Wuthenow,** of Cornell University's Department of Materials Science and Engineering; and **Dawn Hilton** and **Shawn H. Phillips,** at Edwards Air Force Base, California.

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If you are a subscriber to the web editions of the American Chemical Society publications, the full research article referenced in this story can be found here.

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The Department of Materials Science and Engineering is on the web at http://www.ems.psu.edu/MATSE/materials.html

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