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Book of Abstracts
November 2-5, 1998

Kellie Ann Beall, Editor

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Gaithersburg, Maryland 20899

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Flame Retardant Nanocomposite Materials

Emmanuel P. Giannelis
Department of Materials Science and Engineering
Cornell University

As use of synthetic polymers has grown dramatically over the past thirty years so have efforts to control polymer flammability. Developments to that end include intrinsically thermally stable polymers, fire retardant fillers and intumescent fire retardant systems. Brominated polymers that prevent flame spread have the significant disadvantages of producing dense smoke and corrosive combustion by-products. Furthermore, the effectiveness of fire retardant fillers tends to be limited since the large amounts of filler required make processing difficult and alter the mechanical properties. Therefore there exists a need for new, more effective, and environmentally benign approaches are needed that combine flame resistance and mechanical robustness with processability and low cost.

Solventless, melt intercalation of high molecular weight polymers is a powerful new approach to synthesize polymer-layered silicate (PLS) nanocomposites. This method is quite general and is broadly applicable to a range of commodity polymers from non-polar polystyrene to strongly polar nylon. PLS nanocomposites are thus processable using current technologies and easily scaled to manufacturing quantities. In general, two types of structures are possible: intercalated, in which a single, extended polymer chain is inserted between the silicate layers resulting in a well ordered multilayer with alternating polymer/inorganic layers, and disordered or delaminated, in which the silicate layers (1 nm thick) are uniformly dispersed, with random orientation throughout the polymer matrix.

Polymer nanocomposites, especially polymer-layered silicates nanocomposites, represent a radical alternative to conventionally filled polymers. Due to their nanometer size dispersion, the nanocomposites exhibit markedly improved properties when compared to the pure polymer or conventional composites. The improved properties include increased modulus, decreased gas permeability, increased solvent resistance, and decreased flammability. For example, a doubling of the tensile modulus and strength is achieved for nylon-layered silicate nanocomposites containing as little as 2 vol.% of inorganic. In addition, the heat distortion temperature of the nanocomposites increases by up to 100°C, extending the use of the composite to higher temperatures environments, such as automotive engine applications. Furthermore, the heat release rate in the nanocomposite is reduced by up to 63% at heat fluxes of $50 kW/m^2$ without an increase in the CO and soot produced during combustion (see Figure 1).

There are several proposed mechanisms as to how the layered silicate affects the flame retardant properties of polymers. The first is the increased char layer that forms when nanocomposites are exposed to flame. This layer is thought to inhibit oxygen transport to the flame front and therefore reduce the heat release rate of the burning polymer. Another possible mechanism is the catalytic ability of layered silicates. At higher temperatures, the inorganic has the ability to act as a radical sink due to adsorption to lewis acid sites. This interupts the burning cycle as radical species are needed to break polymer chains into oligamer fuel. The disordered nanocomposites also inhibit oxygen and combustible oligomer species transfer by increasing the path length of these species to the flame front. The path length is dramatically increased due to the large surface area inherent in the silicates (approximately 760 $\frac{m^2}{g}$ for Na^+ Montmorillonite).

An excellent example of fire retardency in nanocomposites appears in the figure below. The heat release rate of pure Nylon 6.6 is compared to that of Nylon containing 5 wt% of the layered silicate, montmorillonite. It is clear from the plot, that with only a minute addition of silicate, it is possible to decrease the heat release rate by almost a factor of two. While the exact mechanism is still in question, a combination of the previously described causes is likely.