

# Polymer Layered-Silicate Nanocomposites : Polyamide-6, Polypropylene and Polystyrene

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## ABSTRACT

In many of the cases studied, polymer-clay nanocomposites are materials that have improved thermal properties. Furthermore, most of the nanocomposite systems reported so far show reduced flammability. The delaminated versions of nanocomposites also offer measurable improvements in a variety of physical properties. The intercalated versions offer the reduced flammability benefits, but with less improvement in physical properties. Many issues are unresolved as to the mechanism of these property enhancements. We report here on our continuing study of the mechanism of flammability reduction with recent results for polypropylene-graft-maleic anhydride and polystyrene layered-silicate nanocomposites using montmorillonite and fluorohectorite.

## INTRODUCTION

*Nanocomposites.* Polymer-clay nanocomposites were first reported in the literature as early as 1961, when Blumstein demonstrated polymerization of vinyl monomers intercalated into montmorillonite (MMT) clay.<sup>1</sup> The most recent methods to prepare polymer-clay nanocomposites have primarily been developed by several groups. In general these methods (shown in Figure 1) achieve molecular-level incorporation of the layered silicate (e.g. montmorillonite clay, or synthetic layered-silicate) into the polymer by addition of a modified silicate either during the polymerization (*in situ method*)<sup>2,3,4</sup> or to a solvent-swollen polymer (solution blending),<sup>5</sup> or to the polymer melt (melt blending).<sup>6,7</sup> Additionally, a method has been developed to prepare the layered-silicate by polymerizing silicate precursors in the presence of a polymer.<sup>8</sup>

Two terms (*intercalated* and *delaminated*) are used to describe the two general classes of nano-morphology that can be prepared. *Intercalated* structures are self-assembled, well ordered multi-layered structures where the extended polymer chains are inserted into the gallery space between parallel individual silicate layers separated by 2 nm to 3 nm (see Figure

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2). The *delaminated* (or *exfoliated*) structures result when the individual silicate layers are no longer close enough to interact with the adjacent layers' gallery cations.<sup>9</sup> In the *delaminated* cases the interlayer spacing can be on the order of the radius of gyration of the polymer; therefore, the silicate layers may be considered well dispersed in the organic polymer. The silicate layers in a *delaminated* structure may not be as well ordered as in an *intercalated* structure. Both of these hybrid structures can also coexist both in intercalated in the polymer matrix; this mixed nano-morphology is very common for composites based on smectite silicates and clay minerals. X-ray diffraction measurements can be used to characterize these nanostructures. Diffraction peaks in the low angle region indicate the d-spacing (basal spacing) of ordered intercalated and ordered delaminated nanocomposites; disordered nanocomposites show no peaks in this region due to the loss of structural registry of the layers and (or) the large d-spacings (> 10 nm).

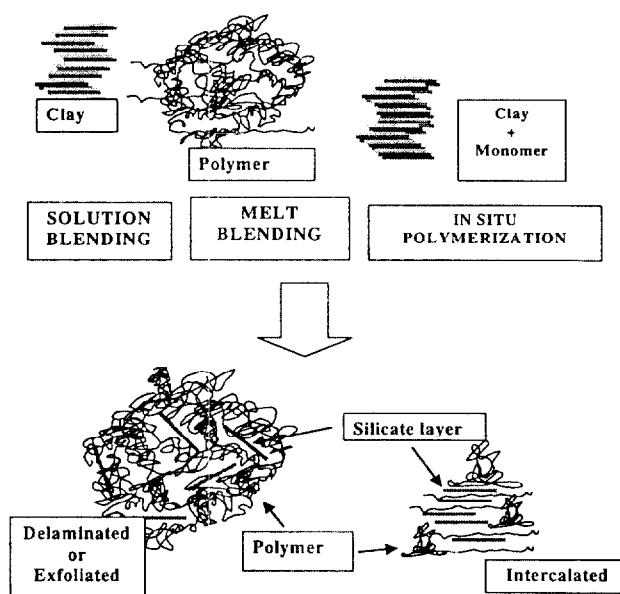


Figure 1. Schematic representation of various methods (solution blending, melt blending, and *in situ* polymerization) used to prepare polymer layered-silicate nanocomposites. The delaminated (or exfoliated) and intercalated morphologies are also shown.<sup>10</sup>

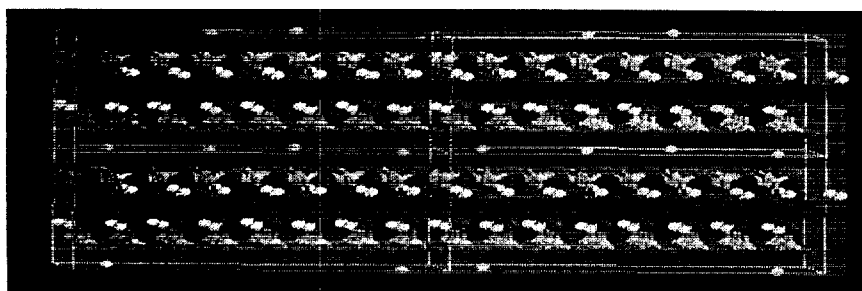


Figure 2. Molecular representation of sodium montmorillonite, showing two aluminosilicate layers with the Na<sup>+</sup> cations in the interlayer gap or gallery.

Polymer-clay nanocomposites have unique properties when compared to conventional filled polymers.<sup>6</sup> For example, the mechanical properties of a nylon-6 layered-silicate nanocomposite, with a silicate mass fraction of only 5 %, show excellent improvement over those for the pure nylon-6. The nanocomposite exhibits a 40 % higher tensile strength, 68 % greater tensile modulus, 60 % higher flexural strength, and a 126 % increased flexural modulus. The heat distortion temperature (HDT) is increased from 65 °C to 152 °C, and the impact strengths are only lowered by 10 %.<sup>11</sup> The mechanical properties of aliphatic amine cured epoxy layered-silicate nanocomposites, reported recently by Pinnavaia, reveal a factor of 4 or more improvement in tensile modulus and tensile strength, and substantial *increase* in the strain-at-break.<sup>12</sup> Decreased gas permeability, and increased solvent resistance also accompany the improved physical properties.<sup>6</sup> Finally, as will be discussed below, polymer-clay nanocomposites often exhibit increased thermal stability,<sup>13, 14</sup> an important property for high temperature applications and reduced flammability.<sup>15, 16, 17</sup>

*Thermal Stability.* Blumstein first reported the improved thermal stability of a polymer-clay nanocomposite that combined polymethylmethacrylate (PMMA) and montmorillonite clay.<sup>18</sup> Although this clay-rich nanocomposite (mass fraction ~10 % *intercalated* PMMA) undoubtedly exhibits mechanical properties dominated by the inorganic phase, the indications of enhanced polymer thermal properties are clear. Blumstein showed that PMMA inserted between the lamellae of montmorillonite clay resisted thermal degradation under conditions that would otherwise completely degrade pure PMMA (refluxing decane, 215 °C, N<sub>2</sub>, 48 h). These PMMA nanocomposites were prepared by free radical polymerization of methyl methacrylate (MMA) intercalated in the clay. X-ray analysis showed an increase of 0.76 nm in the basal spacing. Thermogravimetric analysis (TGA) reveals that both linear PMMA and crosslinked PMMA intercalated into Na<sup>+</sup> montmorillonite have a 40 °C to 50 °C higher decomposition temperature. Blumstein argues that the stability of the PMMA-nanocomposite is due not only to its different structure, but also to restricted thermal motion of the PMMA in the gallery.

The first mention of the potential flame retardant properties of these type of materials appears in a 1976 Unitika patent application on nylon-6 clay nanocomposites.<sup>19</sup> However, not until more recent studies of improved thermal stability were reported by Giannelis did the serious evaluation of the flammability properties of these materials begin.<sup>13</sup>

Giannelis found an improvement in thermal stability similar to that reported by Blumstein for both polydimethylsiloxane (PDMS) and polyimide nanocomposites. In this case (PDMS) the nanocomposite was not prepared by *in situ* polymerization in sodium montmorillonite, but by melt intercalation of silanol-terminated PDMS with dimethyl ditallow ammonium treated montmorillonite. In contrast to Blumstein's materials, this nanocomposite contained *primarily* PDMS (mass fraction 90 %) and only a 10 % mass fraction of montmorillonite. Furthermore, the nanocomposite had a featureless X-ray pattern indicating a disordered-delaminated nanostructure. In this case the nanostructure shows more than a 140 °C higher decomposition temperature than the pure PDMS elastomer. In view of the improved barrier properties observed for other polymer nanocomposites,<sup>13</sup> this increased thermal stability was attributed to hindered diffusion of volatile decomposition products within the nanocomposite. The TGA data for the aliphatic polyimide-clay nanocomposites also shows improved thermal stability. Self-extinguishing flammability behavior was reported while burning a 3 mm rod of the aliphatic polyimide layered silicate nanocomposites.<sup>13</sup>

Recent work done in our laboratory has also shown the improved flammability behavior of a number of polymer layered-silicate nanocomposites.<sup>15,16,20</sup> Using Cone Calorimetry and a radiative gasification device, we have measured the improved thermal stability and reduced flammability of these polymer nanocomposites.

## EXPERIMENTAL

*General Procedures:* Polystyrene (PS, Dow Styron 663) was dried in an air-flow oven prior to use. Polypropylene (PP, 6523, General Polymers), and polypropylene-graft-maleic anhydride (PPgMA, Aldrich, 0.4 % mass fraction MA) were dried for 2 h at 65 °C in an air flow oven, and then stored over silica gel and P<sub>2</sub>O<sub>5</sub> before use. Organically treated clays (tetradecyl ammonium fluorohectorite (C14-FH) octadecyl ammonium montmorillonite (C18-MMT) and dioctadecyldimethyl ammonium montmorillonite (2C18-MMT) were prepared using a literature procedure.<sup>21</sup>

*Preparation of Polystyrene (PS)/Layered Silicate Nanocomposites:* PS/layered silicate hybrid samples were prepared using one of following three different techniques. A. Solvent Intercalation. A mixture of PS- toluene solution (PS mass fraction 3 % to 10 % ) and an organically treated clay (mass fraction of clay 3 %, relative to PS) was ultrasonicated for up to 5 minutes until a good suspension was created. The solvent was then evaporated for several hours at ambient temperature, in a fume hood, until a very viscous gel was created. The gel was then placed in a vacuum oven at 70 °C for 2 h to 5 h until all the solvent was removed.<sup>22</sup> B. Static Melt Intercalation. PS (dried, powdered) and organically treated clay (dried) were mixed and ground together, by hand, in a mortar and pestle. The mixed powder was heated at 170 °C for 2 h to 6 h in a vacuum. The material was stirred once half way through the annealing/melt intercalation process. C. Extrusion Melt Intercalation. PS (dried, powdered) and organically treated clay (dried) were pre-mixed and blended/extruded using a DSM mini-extruder under N<sub>2</sub> at 150 °C to 170 °C for 2 min to 4 min.

*Preparation of Polypropylene(PPgMA)/Layered Silicate (Clay) Nanocomposites.* PPgMA and an organically treated clay were blended in a mixing head (Haake Rheomix 600 (69 cm<sup>3</sup> capacity), Haake Rheocord 9000 system). The polymer and clay were blended at 200 °C for 10 min. No process stabilizer was used. Upon completion of blending, the molten polymer was removed and allowed to cool. The PPgMA/clay nanocomposite (14-15 g) was then compression molded, at 180 °C and 3 metric tons pressure, to give a 7.35 cm diameter × 0.37 cm thick disk. These disks were then used for Cone Calorimetry testing.

*Transmission Electron Microscopy (TEM):* Bright field TEM images of PPgMA/layered silicate (clay) nanocomposites were obtained at 120 kV, at low dose conditions, with a Phillips 400T electron microscope. The samples were cryomicrotomed with a diamond knife at -110 °C to give 70 nm thick sections. The sections were transferred dry to carbon-coated (type B) Cu grids of 200 mesh. The contrast between the layered silicates and the polymer phase was sufficient for imaging, so no heavy metal staining of sections prior to imaging was required. Direct observation of PS/nanocomposite structure was realized by bright field TEM of nanocomposite films (0.5 μm to 1.5 μm thick) under strain in a JEOL-1200EX operating at 120 kV. The FH-based materials were microtomed from bars using a diamond knife to give 50 nm thick sections which were placed onto copper grids. MMT-based materials

were spin cast onto copper grids. The contrast between the silicon-containing phase and the polymer was sufficient for imaging, and no staining was required.

*Flammability Measurements.* Evaluations of flammability were achieved using the Cone Calorimeter. The tests were performed at an incident heat flux of 35 kW/m<sup>2</sup> using the cone heater. Peak heat release rate, mass loss rate, and specific extinction area (SEA) data, measured at 35 kW/m<sup>2</sup> are reproducible to within  $\pm 10$  %. The carbon monoxide and heat of combustion data are reproducible to within  $\pm 15$  %. The uncertainties for the cone calorimeter are based on the uncertainties observed while evaluating thousands of samples combusted to date. The cone data reported here are the average of two or three replicated experiments. The errors (one sigma) are shown as error bars on the plots of the Cone data. All mass fractions of clay or silicate represent the inorganic content in the nanocomposite.

## RESULTS

*Flammability Properties.* The Cone Calorimeter is one of the most effective bench-scale methods for studying the flammability properties of materials. The Cone Calorimeter measures fire-relevant properties such as heat release rate (HRR), and carbon monoxide yield, among others. Heat release rate, in particular peak HRR, has been found to be the most important parameter to evaluate fire safety.<sup>23</sup> We have characterized the flammability properties of a variety of polymer-clay nanocomposites, under fire-like conditions, using the Cone Calorimeter. We have observed reduced flammability for several thermoplastic polymer-clay nanocomposites; *delaminated* nylon-6 clay nanocomposites, and polystyrene (PS) and polypropylene-graft-maleic anhydride (PPgMA) clay nanocomposites with a mixed *intercalated-delaminated* nanomorphology.<sup>16</sup> The Cone Calorimetry data (Table 1) shows that both the peak and average HRR were reduced significantly for nanocomposites with low silicate mass fraction (2 % to 5 %). Similar results were also obtained for thermoset polymer nanocomposites made from vinyl esters and epoxies.<sup>16,20</sup>

TABLE 1. CONE CALORIMETER DATA

Sample (structure)	Residue Yield (%) ±0.5	Peak HRR ( $\Delta\%$ ) (kW/m <sup>2</sup> )	Mean HRR ( $\Delta\%$ ) (kW/m <sup>2</sup> )	Mean H <sub>c</sub> (MJ/kg)	Mean SEA (m <sup>2</sup> /kg)	Mean CO yield (kg/kg)
Nylon-6	1	1,010	603	27	197	0.01
Nylon-6 silicate- nanocomposite 2 % <i>delaminated</i>	3	686 (32 %)	390 (35 %)	27	271	0.01
Nylon-6 silicate- nanocomposite 5 % <i>delaminated</i>	6	378 (63 %)	304 (50 %)	27	296	0.02
PS	0	1,120	703	29	1,460	0.09
PS silicate- mix 3 % <i>immiscible</i>	3	1,080	715	29	1,840	0.09
PS silicate- nanocomposite 3 % <i>Intercalated/ delaminated</i>	4	567 (48 %)	444 (38 %)	27	1,730	0.08
PS w/ DBDPO/Sb <sub>2</sub> O <sub>3</sub> 30 %	3	491 (56 %)	318 (54 %)	11	2,580	0.14
PPgMA	5	1,525	536	39	704	0.02
PPgMA silicate Nanocomposite 2 % <i>Intercalated/ delaminated</i>	6	450 (70 %)	322 (40 %)	44	1,028	0.02
PPgMA silicate Nanocomposite 4 % <i>Intercalated/ delaminated</i>	12	381 (75 %)	275 (49 %)	44	968	0.02

Heat flux : 35 kW/m<sup>2</sup>, H<sub>c</sub> : Heat of combustion, SEA : Specific Extinction Area. Peak heat release rate, mass loss rate and specific extinction area (SEA) data, measured at 35 kW/m<sup>2</sup>, are reproducible to within ± 10 %. The carbon monoxide and heat of combustion data are reproducible to within ± 15 %.

The HRR plots for PPgMA and PPgMA clay-nanocomposites (mass fraction 2 % and 4 %) at 35 kW/m<sup>2</sup> heat flux are shown in Figure 5, and are typical of those found for all the nanocomposites in Table 1. Comparison of the Cone Calorimeter data in Table 1, for the nylon-6, PS, and PPgMA nanocomposites, reveals that the heat of combustion (H<sub>c</sub>), specific extinction area (SEA, a measure of smoke yield) and carbon monoxide yields are unchanged; this suggests that the source of the improved flammability properties of these materials is due to differences in condensed-phase decomposition processes, and not to a gas phase effect. For comparison, the flammability properties of PS flame retarded with decabromo diphenyloxide (DBDPO) and Sb<sub>2</sub>O<sub>3</sub> are also shown in Table 1. These data show the typical gas-phase effect

of bromine. The incomplete combustion is reflected in a lower mean  $H_c$ , higher CO yield and higher mean SEA. The parameter primarily responsible for the lower HRR of the nanocomposites is the mass loss rate (MLR) during combustion. The MLR of the nanocomposite is significantly reduced from those values observed for the pure polymers. This data is shown in Figure 6.

Dispersion of the layered silicate in the polymer does seem to have an effect on the flammability of the polymer nanocomposite. A previous sample of PPgMA, made by compression molding, which gave incomplete dispersion of the clay, gave a 54 % lower peak HRR.<sup>16</sup> The sample presented in this paper was prepared using a mixing head, which dispersed the clay particles into the molten polymer under high shear. The TEM of the resulting PPgMA clay nanocomposite is shown in Figure 3 and Figure 4. These TEM show that the PPgMA nanocomposite has a mixed nano-morphology. Individual clay layers along with two and three layer particles are observed well dispersed (exfoliated) in the polymer matrix. In addition, intercalated tactoids (multi-layer particles) with a d-spacing of 3.5 nm (by XRD,  $2\theta = 2.5^\circ$ ) are observed. It is interesting to note that it is the small aspect ratio plates that are exfoliated, while the large plates remain only intercalated. This mixed nano-morphology for PPgMA gave a 70 % lower peak HRR for the nanocomposite with a clay mass fraction of 2 %, and a 75 % lower peak HRR for the nanocomposite with a clay mass fraction of 4 %.



Figure 3. TEM of PPgMA-clay (mass fraction 4 %) nanocomposite: with exfoliated single, double and triple layers as well as a multi-layer tactoid.

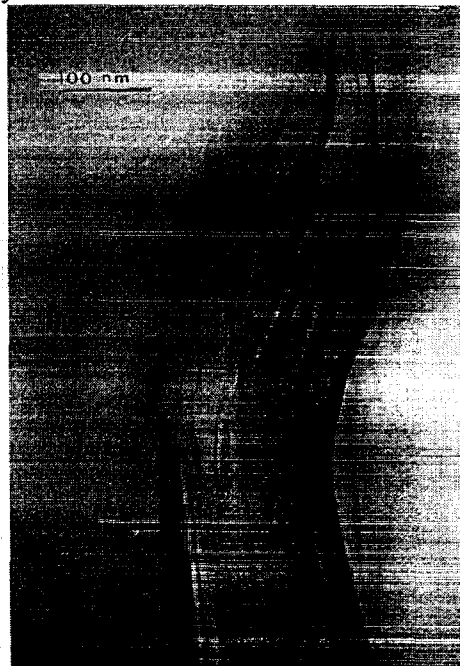


Figure 4. TEM of an intercalated tactoid (d-spacing 3.5 nm) of PPgMA-clay (mass fraction 4 %) nanocomposite.

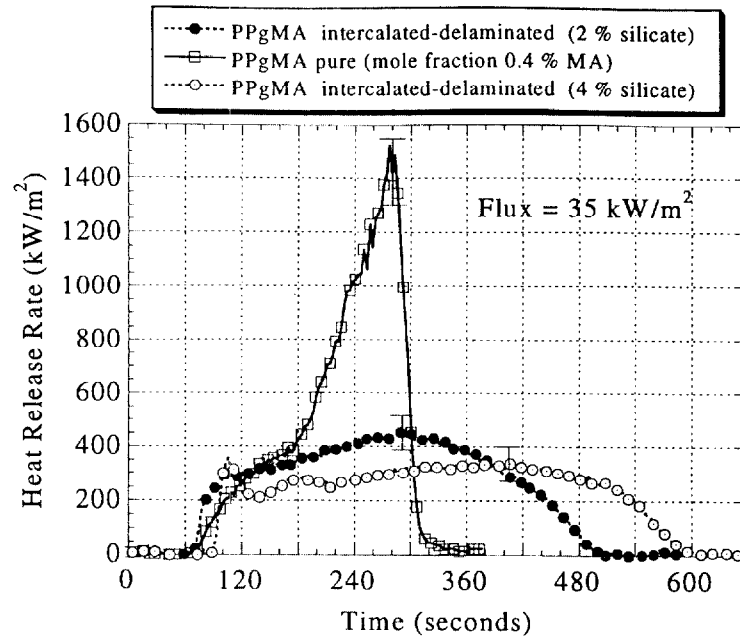


Figure 5. Comparison of the Heat Release Rate (HRR) plots for pure PPgMA, and two PPgMA-silicate (clay) nanocomposites, at  $35 \text{ kW/m}^2$  heat flux, showing a 70 % to 80 % reduction in peak HRR for the nanocomposites with only a mass fraction of 2 % or 4 % clay, respectively.

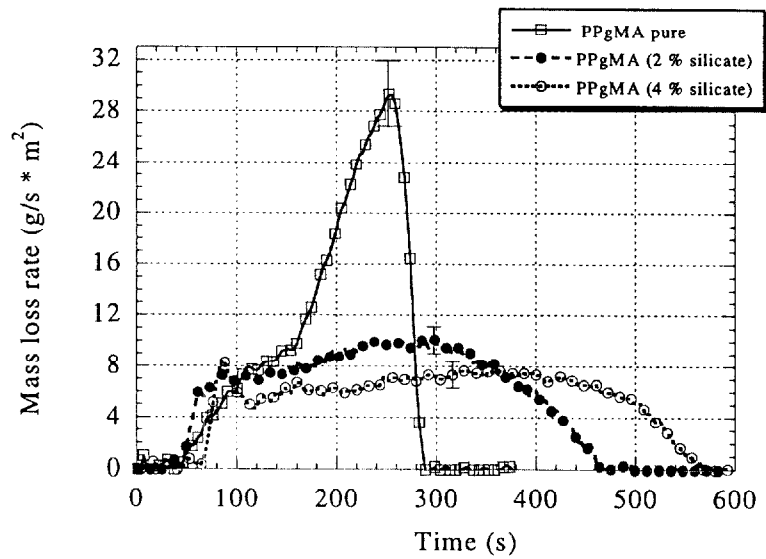


Figure 6. Mass loss rate plots for PPgMA, and two PPgMA-silicate (clay) nanocomposites.



Each of the thermoplastic nanocomposite systems we have examined shows essentially the same behavior when evaluated in the Cone Calorimeter. Furthermore, comparison of the residue yields (taken after combustion in the Cone Calorimeter) for the each of the nanocomposites in Table 1 reveals only a small improvement in the carbonaceous char yields, once the presence of the silicate in the residue is taken into account. These data indicate that the mechanism of flame retardancy may be very similar for each of the systems studied, and the lower flammability is not due to retention of a large fraction of fuel, in the form of carbonaceous char, in the condensed phase. Support for a common fire retardant mechanism comes from transmission electron microscopy (TEM) and x-ray diffraction (XRD) analysis of chars from a variety of nanocomposites. TEM images of sections of the combustion chars from nylon-6 clay nanocomposite (5 %) and cyanate ester clay nanocomposite (6 %) <sup>24</sup> are shown in Figure 7 and Figure 8, respectively. A multilayered carbonaceous-silicate structure is seen after combustion, with the darker, 1 nm thick, silicate sheets forming a large array of fairly even layers. The nanocomposite structure (intercalated and delaminated) appears to collapse during combustion. The nanocomposite structure present in the resulting char appears to enhance the performance of the char through reinforcement of the carbonaceous-char layer, just as the nanostructure enhances the properties of the pure polymer. This multilayered carbonaceous-silicate structure may act as an excellent insulator and mass transport barrier, slowing the escape of the volatile products generated during decomposition.<sup>16</sup> Analysis of combustion chars from nylon-6 and two epoxy nanocomposites, by XRD, shows that the interlayer spacing of all three chars is 1.3 nm.<sup>16</sup> The cyanate ester-clay nanocomposite char has an interlayer spacing of 2.1 nm from TEM (Figure 8) and XRD, possibly indicating that more carbonaceous char is captured between the silicate layers in this char than in the other nanocomposite chars. Presumably, this is due to the inherent higher char yields (70 %) of cyanate esters as compared to nylon-6 (1 %) or epoxies (10 % to 15 %).

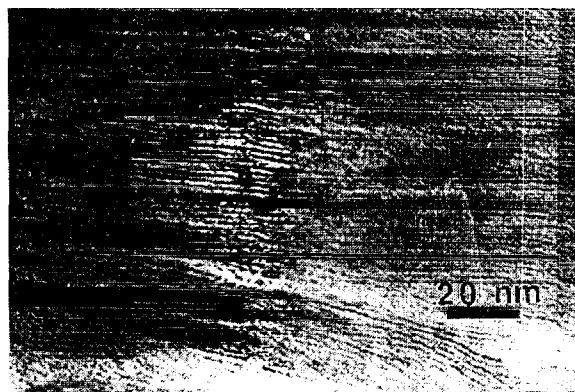


Figure 7. TEM of the combustion char from the nylon-6 silicate-nanocomposite (5 %) showing the carbon-silicate multilayered structure. Layer spacing = 1.3 nm.



Figure 8. TEM of the combustion char from the cyanate ester silicate-nanocomposite (6 %) showing the carbonaceous-silicate multilayered structure. Layer spacing = 2.1 nm.

*Flammability of PS layered-silicate Nanocomposites.* To attempt to understand how the structural properties of PS-nanocomposites influence flammability properties, we examined a range of nano-morphologies of PS-layered silicates. We looked at PS with a primary

ammonium fluorohectorite (PS 3 % C14-FH) and a PS with a quaternary ammonium MMT (PS 3 % 2C18-MMT). These two layered silicates disperse differently in PS. The TEM (Figure 10) of the PS 3 % C14-FH shows it is a neatly intercalated nanocomposite, while the TEM of PS 3 % 2C18-MMT shows it contains both intercalated MMT and delaminated MMT layers, similar to the PPgMA nanocomposite. TEM studies of the PS 3 % 2C18-MMT nanocomposites show that typically 25 % of the MMT layers are homogeneously dispersed in the PS matrix (in single, or 2-3 layer stacks), while the remaining organo-clay forms ordered-intercalated tactoids that consist of many parallel silicate layers (Figure 9). These PS nanocomposites also differ in that FH is a synthetic layered magnesium-silicate (unit cell formula:  $Z^{+}_{1.6}[Li_{1.6}Mg_{4.4}(Si_{8.0})O_{20}F_4]$  where  $Z^{+}$  is the exchange cation) with a high aspect ratio (4  $\mu\text{m}$  to 5  $\mu\text{m}$  plate diameter), while MMT, an aluminosilicate (unit cell formula:  $Z^{+}_{1.6}[Mg_{0.86}Al_{3.14}(Si_{8.0})O_{20}OH_4]$ ) has a lower aspect ratio (MMT plate diameter 0.1  $\mu\text{m}$  to 1  $\mu\text{m}$ ).



Figure 9. TEM of PS (3 % 2C18-MMT). About 25 % of the MMT layers are delaminated with the remaining MMT intercalated with a layer spacing of 3.1 nm.

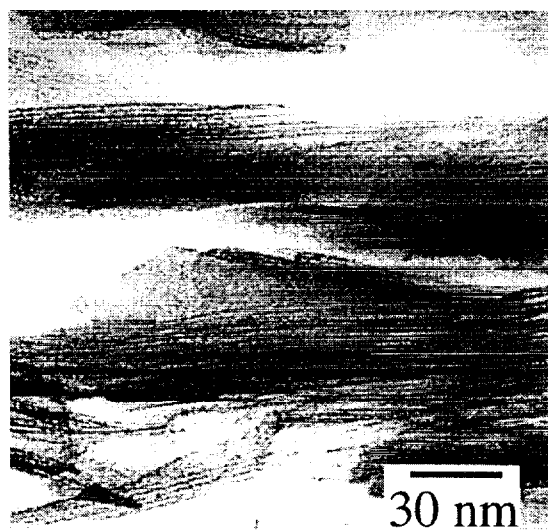


Figure 10. TEM of PS (3 % C14-FH) showing an intercalated nano-morphology with a layer spacing of 3.2 nm.

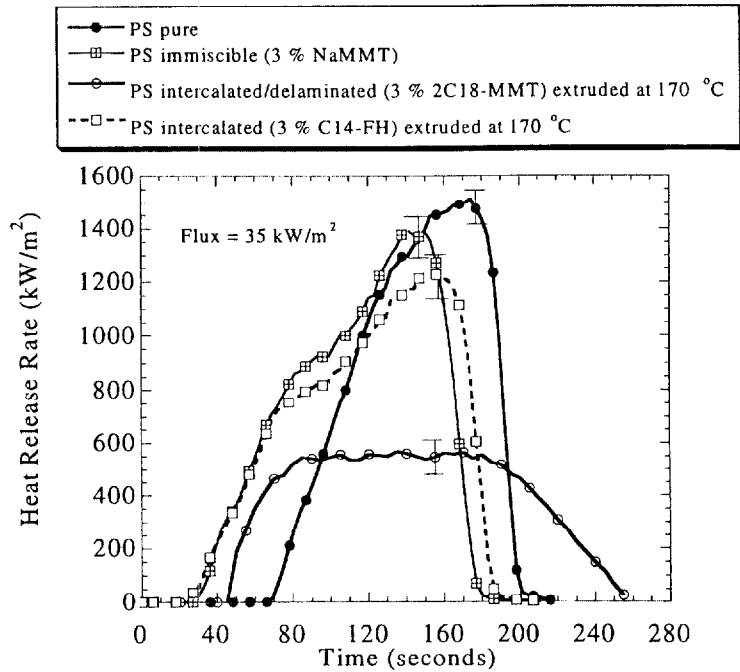


Figure 11. Heat Release Rate (HRR) plots for pure PS, PS w/NaMMT an immiscible-composite, PS w/ bis-C18 quaternary ammonium treated MMT and PS w/ C14 primary ammonium treated FH, at 35 kW/m<sup>2</sup> heat flux.

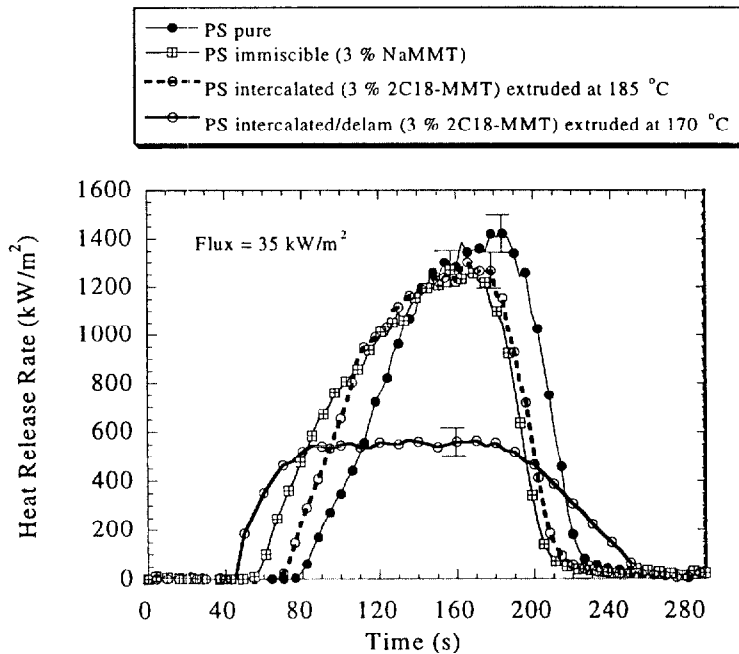


Figure 12. Heat Release Rate (HRR) plots for pure PS, PS w/NaMMT an immiscible-composite, PS w/ bis-C18 quaternary ammonium treated MMT and PS w/ bis-C18 quaternary ammonium treated MMT processed at 185 °C.

Figure 11 shows the heat release rate data for the PS nanocomposites (MMT and FH) and two control samples: pure PS and PS mixed with sodium montmorillonite, which gives an immiscible, conventional, filled, composite. Surprisingly, the PS 3 % 2C18-MMT and PS 3 % C14-FH behave very differently. The PS 3 % C14-FH has, within experimental uncertainty, no effect on the peak HRR, whereas the PS 3 % 2C18-MMT has a 60 % lower peak HRR as compared to the PS mixed with NaMMT. Since the two nanocomposites have different chemical formula of the layered silicate, different aspect ratios and different nanomorphologies, it is difficult to determine the exact reason for their very different flammability. However, in the aliphatic polyimide nanocomposite system, discussed above, both FH and MMT nanocomposites were found to have the same increase in thermal stability (by TGA).<sup>14</sup> The possibility exists that only the delaminated PS nanocomposites have reduced flammability. The lack of effectiveness for intercalated PS-FH nanocomposite is in agreement with the Showa-Denko patent work on synthetic fluorinated-synthetic-mica (FSM) polyamide-6 nanocomposites. The flammability of these nanocomposites was tested using the UL 94 test, and the results showed that more than 50 % of the FSM had to be uniformly dispersed (delaminated) in stacks of 5 or fewer layers for a V-2 or V-0 rating to be obtained.<sup>17</sup> Our view of the flame retardant mechanism is that a high performance carbonaceous-silicate char builds up on the nanocomposite's surface during burning, and that this insulates and slows the mass loss rate of decomposition products. This char layer forms as the polymer burns away and the silicate layers re-assemble into the multilayered, nanocomposite, reinforced carbonaceous char. We have shown reduced flammability for both delaminated and intercalated-delaminated MMT nanocomposites. However, it appears that for large aspect ratio silicates (FH and FSM) only the delaminated nanocomposites are effective. Possibly, the large aspect ratio of FH and FSM interferes with this re-assembly process. However, the potential difference in chemical reactivity of MMT versus FH can not be ruled out as a significant factor either.

Figure 12 shows the effect of processing conditions on the flammability of PS nanocomposites. When the PS 3 % 2C18-MMT nanocomposite is prepared via melt blending in an extruder (at 170 °C, under N<sub>2</sub> or vacuum) or by solvent (toluene) blending an intercalated/delaminated nano-structure results, which has reduced flammability. However, if the extrusion conditions include high temperatures, and if air is not excluded, the nanocomposite that forms has no improvement in flammability, as the data in Figure 12, for PS 3 % 2C18-MMT extruded at 185 °C, shows. This may be due to degradation during the extrusion.<sup>25</sup>

## SUMMARY

Polymer-clay nanocomposites are materials that in many of the cases studied have improved thermal properties for very moderate (mass fractions of <5 %) loading of the layered inorganic filler. Furthermore, all MMT based nanocomposite systems reported so far also show reduced flammability. The delaminated versions of nanocomposites also offer measurable improvements in a variety of physical properties. The intercalated versions may also offer the reduced flammability benefits, but with less improvement in physical properties. Many issues are unresolved as to the mechanism of these property enhancements. When they are resolved, nanocomposites may fulfill the requirements for a high performance additive-type flame retardant system; i.e., one that reduces flammability while improving the other performance

properties of the final formulated product. This may be accomplished either as a single flame retardant additive or more likely in combination with other flame retardant additives.<sup>17</sup>

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10. The "intercalated" cartoon is somewhat misleading; the polymer chains are **much** shorter than the silicate layers (for the PS/fluorohectorite a confined 2D chain would be 40-50 times shorter than the silicate layer).
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<sup>†</sup> Certain commercial equipment, instruments, materials, services or companies are identified in this paper in order to specify adequately the experimental procedure. This in no way implies endorsement or recommendation by NIST.

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