Flammability Properties of Polymer–Layered-Silicate Nanocomposites. Polypropylene and Polystyrene Nanocomposites†

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Our continuing study of the mechanism of flammability reduction of polymer–layered-silicate nanocomposites has yielded results for polypropylene-graft-maleic anhydride and polystyrene–layered-silicate nanocomposites using montmorillonite and fluorohectorite. Cone calorimetry was used to measure the heat release rate and other flammability properties of the nanocomposites, under well-controlled combustion conditions. Both the polymer–layered-silicate nanocomposites and the combustion residues were studied by transmission electron microscopy and X-ray diffraction. We have found evidence for a common mechanism of flammability reduction. We also found that the type of layered silicate, nanodispersion, and processing degradation have an influence on the flammability reduction.

Introduction

Many issues are unresolved as to the mechanism(s) of the property enhancements observed for polymer–layered-silicate nanocomposites. To attempt to understand how the structural properties of these types of advanced materials influence their flammability properties, we have examined a range of nanomorphologies of polypropylene (PP)—and polystyrene (PS)—layered-silicate nanocomposites. These two commodity polymers are used in a number of commercial products which must be flame retarded. Although reduced flammability has been demonstrated for these nanocomposites, a fundamental understanding of both their unique physical properties and the reduced flammability properties is essential for nanocomposites to succeed as a flame retardant approach for virtually all polymers. This flame retardant approach via nanocomposites delivers the unique combination of reduced flammability with improved mechanical properties.

Nanocomposites. Polymer–layered-silicate nanocomposites were first reported in the literature as early as 1961, when Blumstein demonstrated polymerization of vinyl monomers intercalated into montmorillonite (MMT) clay.1 The most recent methods to prepare polymer–layered-silicate nanocomposites have primarily been developed by several other 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) in the polymer by addition of a modified silicate either to a polymerization reaction (in situ method),2-4 to a solvent-swollen polymer (solution blending),5 or to a polymer melt (melt blending).6,7 Additionally, a method has been developed

1 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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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 shown.

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or intercalated. In such cases, transmission electron microscopy (TEM) combined with XRD will more accurately characterize these materials.

Polymer–layered-silicate nanocomposites have unique properties when compared to conventional filled polymers.6 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 pure Nylon-6. The nanocomposite exhibits increases of 40% in tensile strength, 68% in tensile modulus, 60% in flexural strength, and 126% in flexural modulus. The heat distortion temperature (HDT) is also increased, from 65 to 152 °C, and the impact strengths are lowered by just 10%.11

The mechanical properties of aliphatic amine cured epoxy-layered-silicate nanocomposites, reported recently by Wang and Pinnavaia, reveal an improvement of 400% or more in tensile modulus and tensile strength and a substantial increase in the strain-at-break.12 Decreased gas permeability and increased solvent resistance also accompany the improved physical properties.8 Finally, polymer–layered-silicate nanocomposites often exhibit increased thermal stability13,14 and, as will be discussed below, reduced flammability.15–20

Thermal Stability. Blumstein first reported the improved thermal stability of a polymer–layered-silicate nanocomposite that combined poly(methyl methacrylate) (PMMA) and montmorillonite clay.21 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 (d spacing increase of 0.76 nm) between the lamellae of montmorillonite clay resisted thermal degradation under conditions that would otherwise completely degrade pure PMMA (refluxing decane, 215 °C, N₂, 48 h). These PMMA nanocomposites were prepared by free radical polymerization of methyl methacrylate (MMA) intercalated in the clay. Thermogravimetric analysis (TGA) reveals that both linear PMMA and cross-linked PMMA intercalated into Na⁺ montmorillonite have a 40–50 °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 types of materials appears in a 1976 Unitika patent application on Nylon-6-layered-silicate

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pylene-silicate nanocomposites, with recent results for polypro-
anism of flammability reduction of polymer
ised in sodium
intercalation of silanol-
was not prepared by in situ polymerization in sodium
modified montmorillonite. In contrast to Blumstein’s
PDMS into dimethyl ditallow ammonium-
not prepared by in situ polymerization in sodium
improvement in thermal stability similar to that
PDMS and polyimide nanocomposites has also been
observed. In the case of PDMS, the nanocomposite was
formed by melt intercalation of silanol-
reported by Blumstein for both poly(dimethylsiloxane)
minated montmorillonite. However, not until
Figure 2. Molecular representation of sodium montmorillonite, showing two aluminosilicate layers with the Na
content, the disordered−delaminated nanostructure shows an
crease of 140 °C in decomposition temperature com-
important properties observed for other polymer
nanocomposites, this increased thermal stability was
attributed to hindered diffusion of volatile decomposi-
tions within the nanocomposite. The TGA data
proportion of layered silicate 3%, relative to PS) was ultrasoni-
ated for up to 5 min until a good suspension was created.
A mixture of a PS−graft-maleic anhydride (PPgMA) and polypropylene−graft-maleic anhydride (PPgMA, Aldrich, 0.4%25 mass fraction MA) were dried
for 2 h at 65 °C in an air-flow oven and then stored over silica
gel and P2O5 before use. Organically treated layered silicates
layered-silicate nanocomposites and the combustion
experiments, has also shown the improved flammability behavior of a number of other polymer−layered-silicate nanocomposites.

We report here on our continuing study of the mech-
anism of flammability reduction of polymer−layered-
silicate nanocomposites, with recent results for polyprop-
ylene-graft-maleic anhydride (PPgMA) and polypropylene−
layered-silicate nanocomposites using montmorillonite and
measure the heat release rate (HRR) and other flamm-
bility properties of the nanocomposites, under well-
controlled combustion conditions. Both the polymer−
layered-silicate nanocomposites and the combustion
residues were studied by TEM and XRD. We have found
evidence for a common mechanism of flammability
reduction. We also found that the type of layered
silicate, level of dispersion, and processing degradation
have an influence on the magnitude of the flammability
reduction.

Experimental Section

General Procedures. Polystyrene (PS, Dow Styron 612)
was dried in an air-flow oven prior to use. Polypropylene (PP,
6523, General Polymers) and polypropylene-graft-maleic an-
hydrdride (PPgMA, Aldrich, 0.4%25 mass fraction MA) were dried
for 2 h at 65 °C in an air-flow oven and then stored over silica
gel and P2O5 before use. Organically treated layered silicates
layered-silicate nanocomposites, level of dispersion, and processing degradation
have an influence on the magnitude of the flammability
reduction.

Preparation of PS−Layered-Silicate Nanocomposites.
PS−layered-silicate nanocomposite samples were prepared using one of the following three techniques.

A. Solvent Intercalation. A mixture of a PS−toluene solution
(Dow Styron-612, Mn27 100 000 g/mol, PS mass fraction
3−10%) and an organically treated layered silicate (mass fraction of layered silicate 3%, relative to PS) was ultrasoni-
cated for up to 5 min until a good suspension was created.
The solvent was then evaporated for several hours at ambient
temperature in a fume hood, yielding a very viscous gel. The
gel was placed in a vacuum oven at 70 °C for 2–5 h to
evaporate the remaining solvent.

B. Static Melt Intercalation. PS (dried, powdered) and
organically treated layered-silicate (dried) were mixed and

(22) Fujiwara, S.; Sakamoto, T. Kokai Patent Application, no. SHO
(23) (a) Gilman, J. W.; Kashiwagi, T.; Brown, J. E. T.; Lomakin,
S.; Giannelis, E. P.; Manias, E. Proceedings of 43rd International
SAMPE Symposium and Exhibition, May 1998, 1053. (b) Gilman, J.
W.; Kashiwagi, T.; Nyden, M.; Brown, J. E. T.; J ackson, C. L.; Lomakin,
S.; Giannelis, E. P.; Manias, E. Chemistry and Technology of Polymer

(25) All formulation percentages (%) are in mass fraction %.
1994, 6, 1017.
(27) According to ISO 31-8, the term “Molecular Weight” has been
replaced by “Relative Molecular Mass”, symbol M. Thus, if this
nomenclature and notation were used here, M, instead of the
historically conventional M, for the average molecular weight (with
similar notation for M, M, M) would be used. It would be called the
“Number-Average Relative Molecular Mass”. The conventional nota-
tion, rather than the ISO notation, has been employed here.
(28) Note: Most of the toluene must be removed prior to putting
the sample into the vacuum oven. If large amounts of toluene remain,
the vigorous boiling away of the solvent will result in an inhomoge-
neous sample.
ground together in a mortar and pestle. The mixed powder was heated at 170 °C for 2–6 h in a vacuum. The material was stirred once halfway through the annealing/melt intercalation process.

C. Extrusion Melt Intercalation. PS (dried, powdered) and organically treated layered silicate (dried) were premixed and blended/extruded using a DSM miniextruder under N₂ at 150–170 °C for 2–4 min.

Preparation of PPgMA–Layered-Silicate Nanocomposites. PPgMA and an organically treated layered silicate (dimethylbis(hydrogenated tallow)ammonium MMT) were blended in a mixing head (Haake Rheomix 600 (69 cm³ capacity), Haake Rheocord 9000 system). The polymer and layered silicate were blended at 200 °C for 10 min. Upon completion of blending, the molten polymer was removed and allowed to cool. The PPgMA–layered-silicate nanocomposite (14–15 g) was then compression molded, at 180 °C and 3 kbar, to give a 7.35 cm diameter × 0.37 cm thick disk. These disks were then used for Cone calorimetry testing.

X-ray Diffraction Measurements. XRD data were collected on a Philips diffractometer using Cu Kα radiation, (λ = 0.1505945 nm). Powdered char samples were ground to a particle size of less than 40 μm.

Transmission Electron Microscopy. Bright field TEM images of PPgMA–layered-silicate nanocomposites and the corresponding combustion chars, were obtained at 120 kV, under low-dose conditions, with a Philips 400T. The PPgMA–layered-silicate nanocomposite samples were cyromicrotomed with a diamond knife at –110 °C to give sections with a nominal thickness of 70 nm. Combustion chars were broken into small pieces, embedded in an epoxy resin (Epofix), and cured overnight at room temperature. Ultrathin sections were prepared with a 45° diamond knife at room temperature using a DuPont-Sorvall 6000 ultramicrotome. The sections were transferred dry to carbon-coated Cu grids of 200 mesh. The sections were then used for TEM analysis.

Results

The Cone calorimeter is one of the most effective bench-scale methods for studying the flammability properties of materials. Fire-relevant properties, measured by the Cone calorimeter, such as heat release rate (HRR), peak HRR, and smoke and carbon monoxide yield, are vital to the evaluation of the fire safety of materials. We have characterized the flammability properties of a variety of polymer–layered-silicate nanocomposites, under firelike conditions, using the Cone calorimeter. We first observed reduced flammability for Nylon-6–layered-silicate nanocomposites. Subsequent preliminary investigations of polystyrene– and PPgMA–layered-silicate nanocomposites showed similar reductions in flammability, as did thermoset polymer nanocomposites made from vinyl esters and epoxies.

PP–Layered-Silicate Nanocomposites. In this work, we describe our most recent study of the flammability and structure properties of nanocomposites prepared from PPgMA, PS, and Nylon-6. We have prepared PPgMA–layered-silicate nanocomposites using PPgMA (mass fraction of MA 0.4%), known to be miscible with pure PP, and dimethylbis(hydrogenated tallow)ammonium MMT. Researchers at Toyota have also reported on PP–layered-silicate nanocomposites and have demonstrated their improved physical properties. These materials were also prepared using PPgMA to disperse the silicate.

The HRR plots for PPgMA and PPgMA–MMT nanocomposites (silicate mass fraction 2% and 4%) at 35 kW/m² heat flux are shown in Figure 3 and are typical of those found for all the nanocomposites in Table 1. The PPgMA–MMT:silicate (4%) nanocomposite has a 75% lower HRR than the pure PPgMA. Comparison of the Cone calorimeter data in Table 1, for the Nylon-6, PS, and PPgMA nanocomposites, reveals that the specific heat of combustion (Hₛ), 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 decabromodiphenyl oxide (DBDPO) and Sb₂O₃ are also shown in Table 1. These data show that the effect of bromine is primarily in the gas-phase, as evidenced by the lower heat of combustion and higher CO yield typical of incomplete combustion. The primary parameter responsible for the lower HRR of the nanocomposites, under firelike conditions, is the reduced heat release rate (HRR).
ites is the mass loss rate (MLR) during combustion, which is significantly reduced from those values observed for the pure polymers (Figure 4). Previously we reported a 54% lower peak HRR for a PPgMA–MMT nanocomposite made by compression molding. The samples presented here were prepared using a mixing head, which dispersed the layered-silicate particles into the molten polymer under shear. The TEM of the resulting PPgMA–layered-silicate nanocomposite in Figure 5 shows that the PPgMA nanocomposite has a mixed nanomorphology. Individual silicate layers, along with two and three layer stacks, are observed to be well-dispersed (exfoliated) in the polymer matrix. In addition, some larger intercalated tactoids (multilayer particles) are also visible in an enlarged region by TEM (Figure 6); this sample also showed a peak by XRD corresponding to a d spacing of 3.5 nm. This delaminated–intercalated PPgMA nanocomposite gave a 75% lower peak HRR.

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 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. However, 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 TEM and XRD analysis of chars from a variety of nanocomposites. TEM images of sections of the combustion chars from the PPgMA–MMT nanocomposite (4%) are shown in Figure 7. In the Nylon-6–layered-silicate char a multilayered carbonaceous–silicate structure is seen after combustion, with the silicate sheets forming a large array of fairly even layers. In the Nylon-6–layered-silicate nanocomposite the delaminated nanostructure appears to collapse during combustion and yields a peak in the XRD at 1.38 nm (Figure 8). The new nanocomposite

<table>
<thead>
<tr>
<th>sample (structure)</th>
<th>% residue yield (±0.5)</th>
<th>peak HRR, (kW/m²) (Δ%)</th>
<th>mean HRR, (kW/m²) (Δ%)</th>
<th>mean H₂O, MJ/kg</th>
<th>mean SEA, m²/kg</th>
<th>mean CO₂ yield, kg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nylon-6</td>
<td>1</td>
<td>1010</td>
<td>603</td>
<td>27</td>
<td>197</td>
<td>0.01</td>
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<tr>
<td>Nylon-6–silicate nanocomposite 2% (delaminated)</td>
<td>3</td>
<td>686 (32)</td>
<td>390 (35)</td>
<td>27</td>
<td>271</td>
<td>0.01</td>
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<tr>
<td>Nylon-6–silicate nanocomposite 5% (delaminated)</td>
<td>6</td>
<td>378 (63)</td>
<td>304 (50)</td>
<td>27</td>
<td>296</td>
<td>0.02</td>
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<tr>
<td>PS</td>
<td>0</td>
<td>1120</td>
<td>703</td>
<td>29</td>
<td>1460</td>
<td>0.09</td>
</tr>
<tr>
<td>PS–silicate mix 3% (immiscible)</td>
<td>3</td>
<td>1080</td>
<td>715</td>
<td>29</td>
<td>1840</td>
<td>0.09</td>
</tr>
<tr>
<td>PS–silicate nanocomposite 3% (intercalated–delaminated)</td>
<td>4</td>
<td>567 (48)</td>
<td>444 (38)</td>
<td>27</td>
<td>1730</td>
<td>0.08</td>
</tr>
<tr>
<td>PS w/ DBDPO/Sb₂O₃ 30%</td>
<td>3</td>
<td>491 (56)</td>
<td>318 (54)</td>
<td>11</td>
<td>2580</td>
<td>0.14</td>
</tr>
<tr>
<td>PPgMA</td>
<td>5</td>
<td>1525</td>
<td>536</td>
<td>39</td>
<td>704</td>
<td>0.02</td>
</tr>
<tr>
<td>PPgMA–silicate nanocomposite 2% (intercalated–delaminated)</td>
<td>6</td>
<td>450 (70)</td>
<td>322 (40)</td>
<td>44</td>
<td>1028</td>
<td>0.02</td>
</tr>
<tr>
<td>PPgMA–silicate nanocomposite 4% (intercalated–delaminated)</td>
<td>12</td>
<td>381 (75)</td>
<td>275 (49)</td>
<td>44</td>
<td>968</td>
<td>0.02</td>
</tr>
</tbody>
</table>

* Heat flux, 35 kW/m². H₂O, specific heat of combustion; SEA, specific extinction area. Peak heat release rate, mass loss rate, and SEA data, measured at 35 kW/m², are reproducible to within ±10%. The carbon monoxide and heat of combustion data are reproducible to within ±15%.

Figure 4. Mass loss rate plots for PPgMA and two PPgMA–layered-silicate nanocomposites.
structure present in the resulting combustion residue appears to enhance the performance of the residue through reinforcement of the carbonaceous char layer. This is analogous to the enhancement of 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. Analysis of combustion residues from two epoxy nanocomposites, by XRD, shows that the interlayer spacing of both chars is 1.3 nm. A few layered carbonaceous-silicate structures are also observed in the PPgMA-MMT char, but as Figure 7 shows, individual silicate layers are also dispersed throughout the carbonaceous char and no peak in XRD is observed (Figure 8).

**Effect of Structure on Flammability of PS-Layered-Silicate Nanocomposites.** To understand how the structure of PS nanocomposites influences flammability properties, we examined a range of nanomorphologies of PS-layered silicates. We looked at PS with a primary ammonium-treated fluoroctorite (PS C14-FH, silicate mass fraction 3%) and PS with a quaternary ammonium-treated MMT (PS 2C18-MMT, silicate mass fraction 3%). These two layered silicates disperse differently in PS. The TEM image (Figure 9) of the PS C14-FH, prepared by static melt intercalation, shows that it is a neatly intercalated nanocomposite. The TEM image for the PS 2C18-MMT sample, prepared by static melt intercalation (Figure 10), shows that it contains both intercalated MMT and delaminated

**Figure 6.** TEM of an intercalated tactoid (d spacing 3.5 nm) of PPgMA-layered-silicate (mass fraction 4%) nanocomposite.

**Figure 7.** TEM of the combustion char from the PPgMA-MMT nanocomposite (4%) showing the carbonaceous-silicate multilayered structure.

**Figure 8.** XRD of the combustion chars from the Nylon-6 MMT nanocomposite and the PPgMA-MMT nanocomposite.

**Figure 9.** TEM of PS (3% C14-FH) showing an intercalated nanomorphology with a layer spacing of 3.2 nm.
MMT layers, similar to the PPgMA nanocomposite. TEM studies 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-layered silicate forms ordered–intercalated tactoids that consist of many parallel silicate layers. We note that the MMT plates with shorter aspect ratios were better dispersed, i.e., in single or 2–3 layer stacks, and the larger aspect ratio plates were found in the intercalated tactoids. These PS nanocomposites also differ in that FH is a synthetic layered magnesium silicate with fluorine substituted for hydroxyl groups (unit cell formula \( \text{Z}^+ 1.6\text{Li}_{1.6}\text{Mg}_{4.4}(\text{Si}_{8.0}\text{O}_{20}\text{F}_4) \), where \( \text{Z}^+ \) is the exchange cation) with a high aspect ratio (500:1 to 4000:1, FH plate diameter 4–5 \( \mu \text{m} \)), while MMT, is a layered aluminosilicate (unit cell formula \( \text{Z}^+ 0.86(\text{Mg}_{0.86}\text{Al}_{3.14-}(\text{Si}_{8.0}\text{O}_{20}\text{OH}_4) \) with a lower aspect ratio (100:1 to 1000:1, MMT plate diameter 0.1–1 \( \mu \text{m} \)).

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 2C18-MMT and PS C14-FH behave very differently. The PS C14-FH has, within experimental uncertainty, no effect on the peak HRR, whereas the PS 2C18-MMT has a 60% lower peak HRR as compared to the pure PS or the PS mixed with NaMMT (immiscible). Since the two nanocomposites have different chemical formulas 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 a previously reported aliphatic polyimide nanocomposite system, both FH and MMT nanocomposites were found to have the same increase in thermal stability (by TGA). The possibility exists that only the delaminated PS nanocomposites have reduced flammability; however, in a previous study we found that both epoxy and vinyl ester intercalated nanocomposites (with MMT) show reduced flammability. The lack of effectiveness for this intercalated PS-FH nanocomposite is in agreement with results reported by Showa-Denko on PBT, Nylon-6, and Nylon-6,6 nanocomposites using a similar layered silicate, fluorinated synthetic mica (FSM). Fluorinated synthetic mica has a high aspect ratio and chemical composition like FH. The flammability of Nylon-6-FSM 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 five or fewer layers for a V-2 or V-0 (self-extinguishing) rating to be obtained. Our view of the nanocomposite's flame retardant mechanism is that a high-performance carbonaceous–silicate char builds up on the surface during burning; this insulates the underlying material and slows the mass loss rate of decomposition products. This residue layer forms as the polymer burns away and the silicate layers reassemble into the multilayer char observed in the TEM. We have shown reduced flammability for both delaminated and intercalated MMT nanocomposites. However, it appears that the intercalated-FH nanocomposites are not effective. Possibly, the large aspect ratio of the FH interferes with this reassembly process. However, the potential difference in chemical reactivity of MMT versus FH cannot 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 2C18-MMT nanocomposite is prepared via melt blending in an extruder (at 170 °C, under \( \text{N}_2 \) or vacuum) or by solvent (toluene) blending, an intercalated–delaminated nanostructure results, which has reduced

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(32) Exhaustive visual inspection of 100 TEM images from PS-2C18-MMT was carried out to determine the number of the single, double, triple, or multiple layer particles present in the nanocomposite.
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 2C18-MMT extruded at 185 °C, shows. This may be due to degradation of the polymer during the extrusion, caused by thermal degradation of the organic treatment present on the clay.33,34 This degradation works in opposition to the flame retardancy mechanism of the clay, in that it lessens the protective effect that the clay layers provide the polymer nanocomposite. Indeed, the polydispersity (PDI, $M_w/M_n$ from GPC) of this sample is 2.40; this is a significant increase from the PDI of 1.8 for the immiscible PS–NaMMT sample, which was extruded under identical conditions. The fact that the organically treated MMT has a much larger change in PDI than the NaMMT sample, after extrusion at 185 °C in air, indicates that the organic treatment may play a role in the degradation reactions that broaden the PDI. The Hofmann degradation of tetraalkylammonium ions,35 which forms the less substituted olefin and the amine, could supply olefin at these temperatures that could combine with oxygen to give peroxoradicals. These radicals and other mechano-radicals would broaden the PDI through typical free radical processes. Additional studies of this type of degradation are underway in our laboratory.

**Summary**

All MMT-based nanocomposite systems reported so far show reduced flammability. Peak HRR is reduced by 50%–75% for Nylon-6, PS, and PPgMA nanocomposites. We have shown that the MMT must be nano-dispersed for it to affect the flammability. However, the clay need not be completely delaminated for it to affect the flammability of the nanocomposite. We have observed that an intercalated PS–fluorohectorite nanocomposite is ineffective at reducing the flammability of PS, possibly due to the large aspect ratio of fluorohectorite. However, the potential difference in chemical reactivity of fluorohectorite cannot be ruled out as a significant factor. We have evidence of an antagonistic interaction between high processing temperatures and the alkylammonium MMT, which causes an increase in the PDI in PS–MMT nanocomposites during processing. Our view of the general nanocomposite flame retardant mechanism is that a high-performance carbonaceous–silicate char builds up on the surface during burning; this insulates the underlying material and slows the mass loss rate of decomposition products.

Many issues are unresolved as to the mechanism of the property enhancements (flammability and physical) observed in polymer–layered-silicate nanocomposites. 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 in combination with other flame retardant additives. Indeed, several patents and publications have taken this latter approach to successfully improve both the flammability and the mechanical properties of many polymer systems.18–20

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(33) Krishnamorti, R. Personal communication.