



Flammability and thermal stability studies of polymer layered-silicate (clay) nanocomposites ¹

Jeffrey W. Gilman *

Materials Fire Research Group, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

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Abstract

In the pursuit of improved approaches to fire retarding polymers, a wide variety of concerns must be addressed in addition to the flammability issues. For commodity polymers, their low cost requires that the fire retardant (FR) approach also be of low cost. This limits solutions primarily to additive type approaches. These additives must be inexpensive and easily processed with the polymer. In addition, the additive must not excessively degrade the other performance properties of the polymer, and it must not create environmental problems when recycling or at the time of its final disposal. We have recently found that polymer layered-silicate (clay) nanocomposites have the unique combination of reduced flammability *and* improved physical properties. This paper is intended as an overview of the research to date, by our group and others, on the use of clays, dispersed at the nanometer level, in polymers for improving thermal stability and flammability. © 1999 Published by Elsevier Science B.V.

Keywords: montmorillonite; nanocomposites; flammability; polymers

1. Introduction

Layered (2:1) silicate minerals have been investigated for decades: to gain a better fundamental understanding of their unique properties, and to develop them in a variety of applications. Currently, hundreds of groups worldwide are involved in research on polymers intercalated into the gallery spaces of 2:1

* E-mail: jeffrey.gilman@nist.gov

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layered silicates due to the superior properties of these so-called polymer–clay nanocomposites as compared to those of conventional polymer–inorganic composites.

Polymer–clay nanocomposites were first reported in the literature as early as 1961, when Blumstein demonstrated polymerization of vinyl monomers intercalated into montmorillonite clay (Blumstein, 1961). The most recent methods to prepare polymer–clay nanocomposites have been developed by several groups. In general these methods achieve molecular level incorporation of the layered silicate (e.g., montmorillonite) into the polymer by addition of a modified silicate: either during the polymerization (in situ method) (Kojima et al., 1993; Usuki et al., 1993; Lan and Pinnavaia, 1994; Usuki et al., 1997), or to a solvent-swollen polymer, or to the polymer melt (Giannelis, 1996; Lee and Giannelis, 1997; Lee et al., 1997; Fisher et al., 1998).

Two terms (*intercalated* and *delaminated*) are used to describe the two general classes of nano-morphology that can be prepared. *Intercalated* structures are well ordered multi-layered structures where the extended polymer chains are inserted into the gallery space between the individual silicate layers (see Fig. 1). The *delaminated* (or *exfoliated*) structures result when the individual silicate layers are no longer close enough to interact with the adjacent layers' gallery cations (Lan and Pinnavaia, 1996). 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. X-ray diffraction measurements are used to characterize the nanostructures. Reflections in the low angle region indicate the d-spacing (basal spacing) of ordered intercalated and ordered delaminated

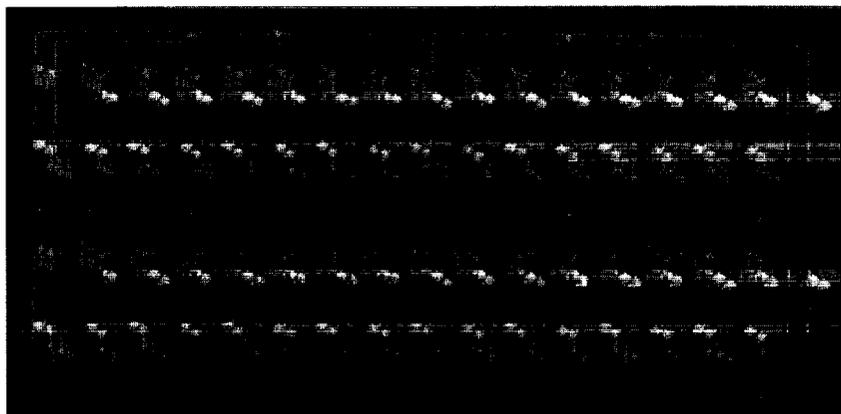


Fig. 1. Molecular representation of sodium montmorillonite, showing two aluminosilicate layers with the Na^+ cations in the interlayer gap or gallery.

nanocomposites; disordered delaminated nanocomposites show no peaks in this region due to the loss of structural registry of the layers and the large d-spacings (> 10 nm).

Polymer–clay nanocomposites have unique properties when compared to conventional filled polymers (Giannelis, 1996). 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% (Kojima et al., 1993, p. 1185). Decreased gas permeability, and increased solvent resistance also accompany the improved physical properties. Finally, nanocomposites often exhibit increased thermal stability: an important property for high temperature applications and improved flammability performance.

2. Thermal stability ²

Blumstein (1965) first reported the improved thermal stability of a polymer–clay nanocomposite that combined polymethylmethacrylate (PMMA) and montmorillonite clay. Although this clay-rich nanocomposite (mass fraction $\sim 10\%$ *intercalated* PMMA) would undoubtedly reflect 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, N₂, 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) shown in Fig. 2, reveals that both linear PMMA and crosslinked PMMA intercalated into Na montmorillonite have a 40°C to 50°C higher decomposition temperature (as measured at the point of 50% mass loss). Blumstein found that the thermal stability of the PMMA once it was extracted out of the nanocomposite was also better than the PMMA made from solution. He proposed that this may be due to a decrease in the relative amount of macromolecules terminated with double bonds for the PMMA polymerized in the confined environment inside the clay lamellae, as compared to the PMMA prepared in solution. This extracted

² 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.

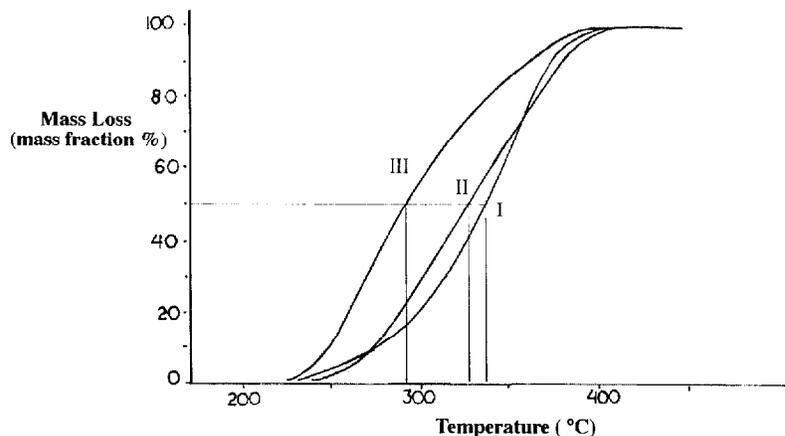


Fig. 2. TGA analysis of PMMA: (I) linear-PMMA *intercalated* clay nanocomposite (mass fraction $\sim 10\%$ *intercalated* PMMA), (II) crosslinked-PMMA *intercalated* clay nanocomposite (mass fraction $\sim 10\%$ *intercalated* PMMA), (III) pure PMMA (Blumstein, 1965). Lines were added to indicate 50% mass loss.

PMMA was not as stable as when intercalated in the nanocomposite. 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 Japanese patent application on nylon-6 clay nanocomposites (Fujiwara and Sakamoto, 1976). However, not until more recent studies of improved thermal stability were reported in both a polydimethylsiloxane-clay nanocomposite (Burnside and Giannelis, 1995) and in a polyimide-clay nanocomposite (Lee et al., 1997) did the serious evaluation of the flammability properties of these materials begin.

Fig. 3 shows TGA data for a polydimethylsiloxane (PDMS)-clay nanocomposite (Burnside and Giannelis, 1995). An improvement in thermal stability similar to that reported by Blumstein is apparent; however, in this case the PDMS nanocomposite was not prepared by in situ polymerization, but by sonication of silanol-terminated PDMS ($M_w = 18,000$) with montmorillonite, which had been ion exchanged (dimethyl ditallow ammonium montmorillonite) and partially hydrated. The PDMS was also crosslinked into an elastomer. 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 (as measured at the point of 50% mass loss). Burnside attributes the increased thermal stability to hindered diffusion of volatile decomposition

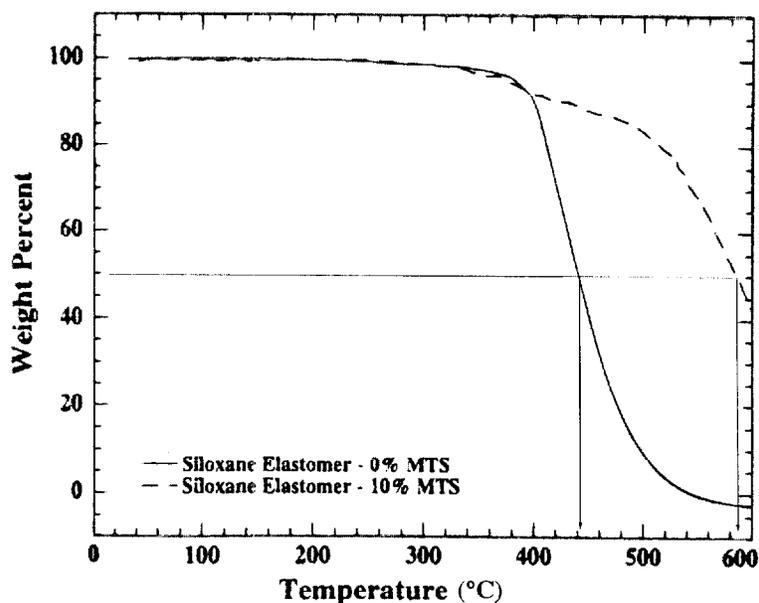


Fig. 3. TGA analysis of PDMS (solid line) and PDMS nanocomposite (dashed line) (mass fraction 10% mica-type-silicate, MTS) (Burnside and Giannelis, 1995). Lines were added to indicate 50% mass loss.

products from the nanocomposite, in view of the improved barrier properties observed for other polymer nanocomposites (Burnside and Giannelis, 1995, p. 1599).

Fig. 4 shows TGA analysis in nitrogen of several aliphatic polyimides, the pure aliphatic polyimide (PEI-10), the PEI-10 compounded with clay in the conventional filled fashion (immiscible sample), the intercalated PEI-10 nanocomposite and the delaminated PEI-10 nanocomposite. This work demonstrated four important issues associated with polymer–clay nanocomposites. First, melt processing can be used to prepare both intercalated and delaminated polymer–clay nanocomposites. This “melt intercalation” method has been extensively studied by the Giannelis group (Giannelis, 1996). Second, the immiscible PEI-clay sample, which contains the same amount of silicate (mass fraction 10%) as the intercalated and delaminated PEI nanocomposites, shows no enhancement in thermal properties. This suggests that the nanostructure is critical to improved thermal stability. Third, the TGA data shows that the intercalated PEI nanocomposite is more stable than the delaminated PEI nanocomposite. A somewhat surprising result since both samples contain the same mass fraction of clay (10%). Fourth, Giannelis actually describes self-extinguishing flammability behavior for the PEI-clay nanocomposites (Lee et al., 1997, p. 516). Intercalated PEI nanocomposites were made using two different alkylammonium exchanged layered silicates: montmorillonite and fluorohec-

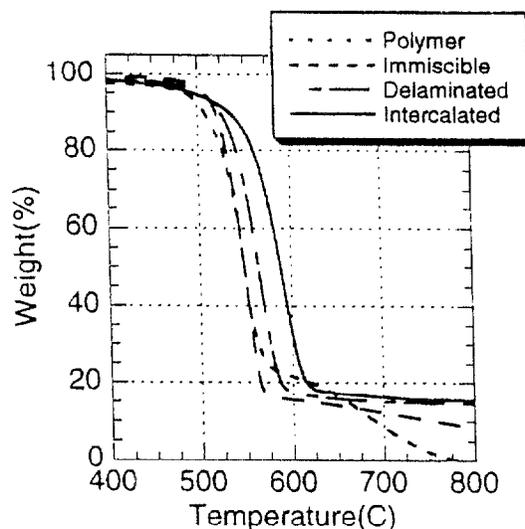


Fig. 4. TGA analysis of PEI and PEI clay mixture, intercalated PEI-nanocomposite, and delaminated PEI-nanocomposite in nitrogen (mass fraction $\sim 10\%$ clay) (Lee et al., 1997).

torite; however, no differences in thermal properties were observed for these two silicates, which differ in aspect ratio (1000 to 1, and 1500 to 1, respectively) and cation exchange capacity (0.8 meq/g and 1.3 meq/g, respectively).

3. Flammability properties

Characterization of the flammability properties of a variety of polymer–clay nanocomposites, under fire-like conditions, using the Cone Calorimeter (Gilman et al., 1997, 1998a,b) has revealed improved flammability properties for many different types of polymer–clay nanocomposites. 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 other. Heat release rate, in particular *peak* HRR has been found to be the most important parameter to evaluate fire safety (Babrauskas and Peacock, 1992). Using the Cone Calorimeter we have shown an improvement in flammability properties for several *thermoplastic* polymer–clay nanocomposites; *delaminated* nylon-6 and nylon-12 clay nanocomposites, and *intercalated* PS and PP clay nanocomposites (Gilman et al., 1998a, p. 203). The cone calorimetry flammability data for a variety of polymer–clay nanocomposites is shown in Table 1. The cone calorimetry data shows that both the peak and average HRR were reduced significantly for *intercalated* and *delaminated* nanocomposites with low silicate

Table 1

Cone calorimeter data. Heat flux: 35 kW/m², H_c : heat of combustion, peak heat release rate, mass loss rate and specific extinction area (SEA) data, measured at 35 kW/m², are reproducible to within $\pm 10\%$. The carbon monoxide and heat of combustion data are reproducible to within $\pm 15\%$

Sample (<i>structure</i>)	Residue yield (%) ± 0.5	Peak HRR ($\Delta\%$) (kW/m ²)	Mean HRR ($\Delta\%$) (kW/m ²)	Mean H_c (MJ/kg)	Mean SEA (m ² /kg)	Mean CO yield (kg/kg)
Nylon-6	1	1010	603	27	197	0.01
Nylon-6 silicate-nanocomposite 2% delaminated	3	686 (32%)	390 (35%)	27	271	0.01
Nylon-6 silicate-nanocomposite 5% delaminated	6	378 (63%)	304 (50%)	27	296	0.02
Nylon-12	0	1710	846	40	387	0.02
Nylon-12 silicate-nanocomposite 2% delaminated	2	1060 (38%)	719 (15%)	40	435	0.02
PS	0	1120	703	29	1460	0.09
PS silicate-mix 3% immiscible	3	1080	715	29	1840	0.09
PS silicate-nanocomposite 3% intercalated	4	567 (48%)	444 (38%)	27	1730	0.08
PS w/ DBDPO/ Sb ₂ O ₃ 30%	3	491 (56%)	318 (54%)	11	2580	0.14
PP	0	1525	536	39	704	0.02
PP silicate nanocomposite 2% intercalated	5	450 (70%)	322 (40%)	44	1028	0.02

mass fraction (2% to 5%). Similar results were also obtained for *thermoset* polymer nanocomposites made from vinyl esters and epoxies (Gilman et al., 1998a,b).

The heat release rate (HRR) plots for nylon-6 and nylon-6 silicate-nanocomposite (mass fraction 5%) at 35 kW/m² heat flux are shown in Fig. 5, and are typical of those found for all the nanocomposites in Table 1. The nylon-6 nanocomposite has a 63% lower HRR than the pure nylon-6. Comparison of the Cone Calorimeter data in Table 1, for the nylon-6, nylon-12, PS, and PP³ nanocomposites, reveals that the heat of combustion (H_c), specific extinction area (SEA, a measure of smoke yield) and carbon monoxide yields are un-

³ An explanation of the increased H_c for PP-nanocomposite is offered later in the paper.

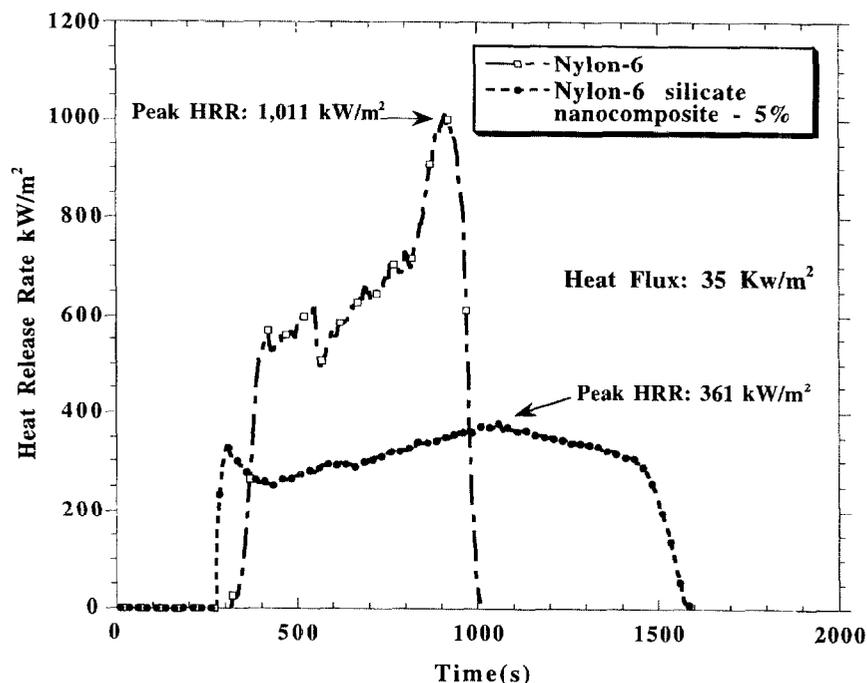


Fig. 5. Comparison of the Heat Release Rate (HRR) plot for nylon-6, nylon-6 silicate-nanocomposite (mass fraction 5%) at 35 kW/m² heat flux, showing a 63% reduction in HRR for the nanocomposite.

changed; 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 a gas phase flame retardant, PS flame retarded with decabromo diphenyl oxide (DBDPO) and Sb₂O₃ are shown in Table 1. These data show the primarily gas phase effect of bromine. The resulting incomplete combustion is reflected in a lower specific heat of combustion (H_c) and higher CO yield. The primary parameter responsible for the lower HRR of the nanocomposites is the mass loss rate (MLR) during combustion. The MLR of the nanocomposites is significantly reduced from those values observed for the pure polymers. Fig. 6 shows the MLR for nylon-6 nanocomposite compared to that for pure nylon-6. These two sets of data essentially mirror the HRR data.

Each of the thermoplastic nanocomposite systems we have examined shows the same behavior as the nylon-6-clay nanocomposites. Furthermore, comparison of the residue yields (taken after combustion in the Cone Calorimeter) for the each of the nanocomposites in Table 1, reveals little improvement in the carbonaceous char yields, once the presence of the silicate in the residue is accounted for. These data indicate that the mechanism of flame retardancy may

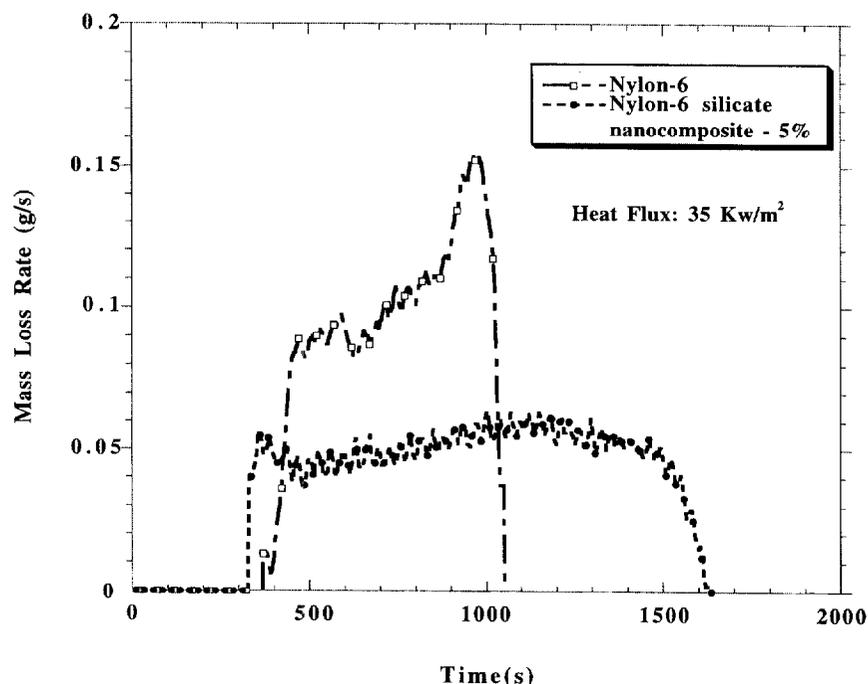


Fig. 6. The mass loss rate data for nylon-6, nylon-6 silicate-nanocomposites (5%). The curves closely resemble the HRR curves (Fig. 5), indicating that the reduction in HRR for the nanocomposites is primarily due to the reduced mass loss rate and the resulting lower fuel feed rate to the gas phase (Gilman et al., 1997).

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. This is in contrast to other studies of the pyrolysis reactions of organic compounds in layered-silicate intercalates. These studies reported formation of carbonaceous-silicate residues and other condensation and crosslinking-type reaction products (Thomas, 1982).

To study the condensed phase decomposition processes of the nanocomposites we conducted pyrolysis experiments in our radiative gasification apparatus (see Fig. 7). The gasification apparatus allows visual observation, and study of mass and heat transfer processes during pyrolysis, in a nitrogen atmosphere, of samples identical to those used in the Cone Calorimeter. This is done without complications from gas phase combustion, such as heat feedback and obscuration of the sample surface from the flame.

The mass loss rate (MLR) data and bottom-surface thermocouple data for nylon-6 and nylon-6 clay nanocomposite, gathered in the N_2 gasification apparatus, are shown in Fig. 8. Digitized video images from the pyrolysis experiments are shown in Fig. 9. They show that at 180 s, when the MLR for

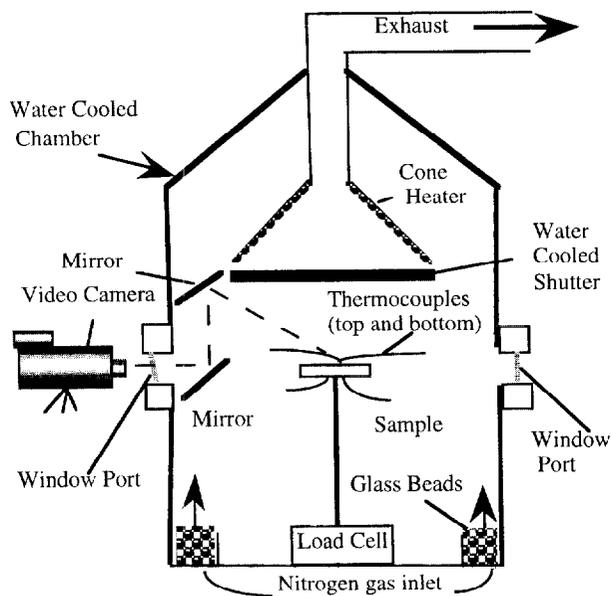


Fig. 7. A schematic of the radiative gasification apparatus (1 m diameter, 2 m height). The gasification apparatus allows pyrolysis, in a nitrogen atmosphere, of samples identical to those used in the Cone Calorimeter.

the nylon-6 silicate nanocomposite slows compared to the pure nylon-6, the surface of the nanocomposite is over 50% covered by char. The bottom-surface thermocouple data shows the insulating effect of the char layer for the nanocomposite sample. It is important to note that until the char layer forms, the MLR of both samples is the same indicating that the nylon-6-clay nanocomposite does not have greater inherent thermal stability than the pure nylon-6. These experiments show that it is the char formation that controls the MLR and therefore the flammability. This is in agreement with TGA data for nylon-6-clay nanocomposite which shows no increase in thermal stability (Gilman et al., 1997).

Additional support for a common fire retardant mechanism comes from transmission electron microscopy (TEM) analysis of the combustion char from nylon-6-clay nanocomposite, and X-ray diffraction (XRD) analysis of chars from a variety of nanocomposites. TEM of a section of the combustion char from the nylon-6 silicate-nanocomposite (5%) is shown in Fig. 10. A multilayered silicate structure is seen after combustion, with the darker, 1 nm thick, silicate sheets forming a large array of fairly even layers. This was the primary morphology seen in the TEM of the char, however, some voids were also present. The delaminated hybrid structure 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 char layer, just as the nanostructure enhances the properties of the polymer. This multi-

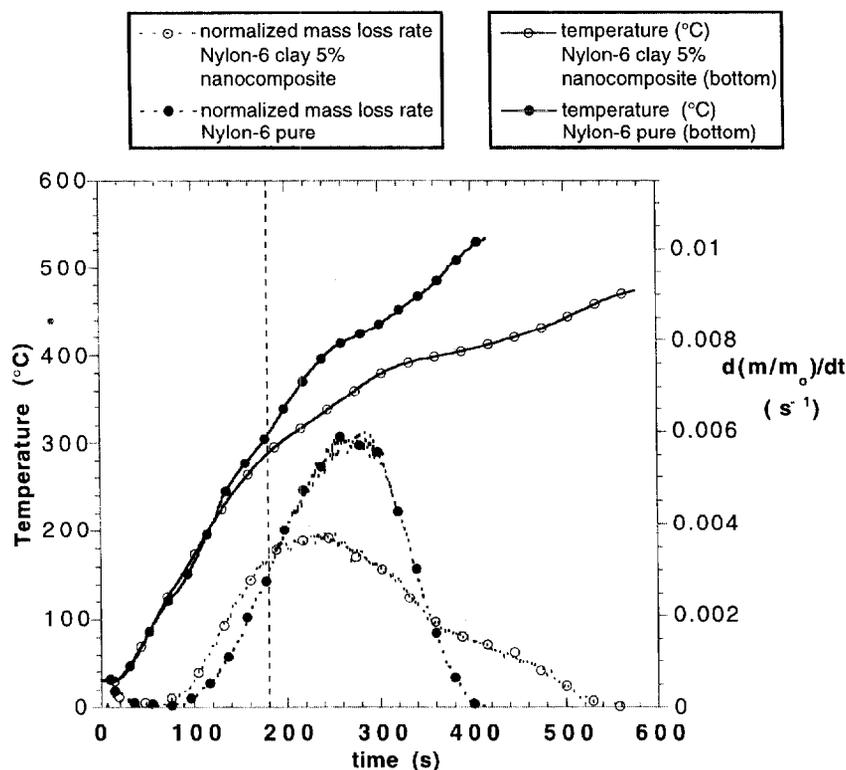


Fig. 8. Normalized mass loss rate (MLR) and temperature versus time plots for the gasification experiments for nylon-6 and nylon-6 silicate (5%) nanocomposite in a N_2 atmosphere. All samples were exposed to a flux of 40 kW/m^2 in a N_2 atmosphere. The mass loss rate curves begin to differ at 180 s when the surface of the nanocomposite sample is partially covered by char. The insulating effect of the char can be seen in the bottom-surface thermocouple data for the nanocomposite (Gilman et al., 1998a).

layered silicate structure may act as an excellent insulator and mass transport barrier, slowing the escape of the volatile products generated as the nylon-6 decomposes (Gilman et al., 1998a,b). 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, in agreement with the interlayer spacing measured in the TEM. This result is independent of the chemical structure (*thermoplastic polyamide*, *thermosetting aromatic amine cured epoxy* or *tertiary amine cured epoxy*), or nano-structure (*delaminated* or *intercalate*) of the original nanocomposite (Gilman et al., 1998b, p. 1053).

We stated above that the H_c for nylon-6-clay nanocomposite was the same as that for pure nylon-6. However, a somewhat different result was found for PS and PP in terms of H_c . The HRR plots for the PS system are shown in Fig. 11. In the PS system both the intercalated PS nanocomposite and the immiscible PS

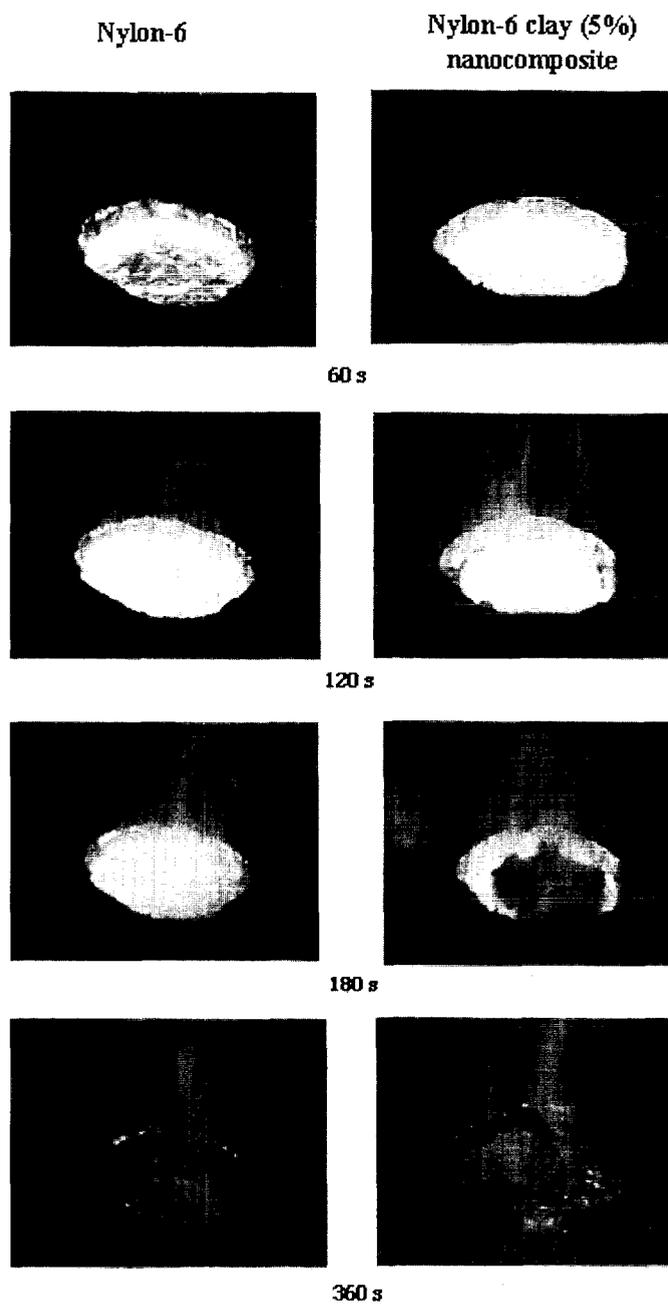


Fig. 9. Digitized video images from radiative gasification experiments performed on nylon-6 and nylon-6-clay nanocomposite in N_2 at a heat flux of 40 kW/m^2 . Initial char formation is visible at 120 s for the nylon-6-clay nanocomposite sample (right set of images). Most of the surface is covered by char at 180 s (Gilman et al., 1998a).



Fig. 10. TEM of a section of the combustion char from the nylon-6 silicate-nanocomposite (5%) showing the carbon-silicate (1 nm thick, dark bands) multilayered structure. This layer may act as an insulator and a mass transport barrier (Gilman et al., 1997).

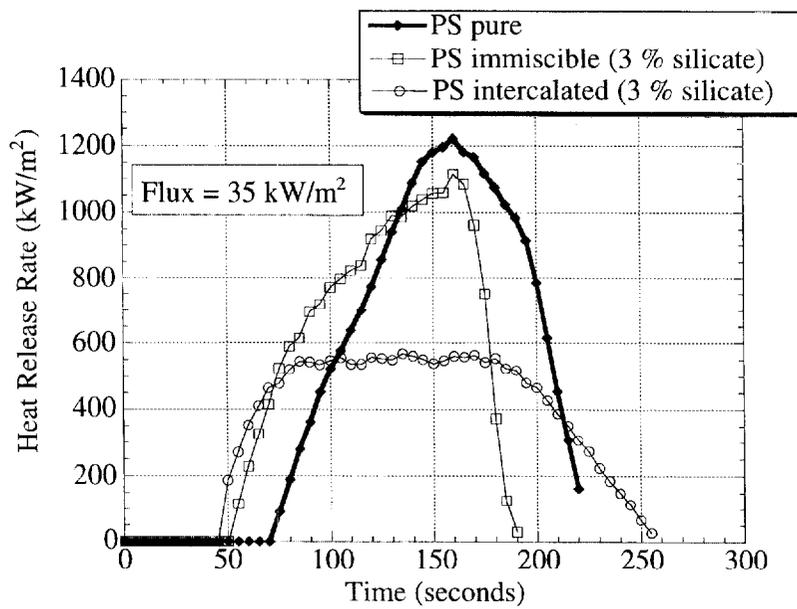


Fig. 11. Comparison of the Heat Release Rate (HRR) plots for PS, PS-silicate (clay) nanocomposite, and for PS-silicate (clay) immiscible-composite, at 35 kW/m² heat flux, showing a 48% reduction in peak HRR for the nanocomposite with only a mass fraction 3% clay (Gilman et al., 1998a).

composite-mixture show higher HRR initially as compared to pure PS. This is due to the earlier ignition of these two samples, which in turn may be from a more rapid evolution of decomposition products as the samples heat up. However, there appears to be an additional factor; a higher H_c from 50 s to 170 s during the burning of these samples as compared to the H_c for pure PS (see Fig. 12). This increased H_c indicates that the fuel that is generated by sample decomposition during this part of the burn has a different structure than that produced later. Later, after 170 s the H_c of the three samples are comparable, within the 15% uncertainty of H_c . This effect can also be observed in the HRR and H_c plots for the PP system shown in Figs. 13 and 14, respectively. An understanding of the reasons for the higher Heat of combustion for nanocomposites is very important since it works in opposition to reducing the mass loss rate and overall flammability.

One possible explanation for the different behavior of the PS and PP systems relative to the nylon-6 system lies in the different organic treatments for the clays used to prepare each system. The nylon-6-clay nanocomposites are made via a ring-opening polymerization, which is initiated by the long chain α , ω amino acids used to treat the clay. This organic treatment becomes part of the polymer. In contrast the organic modification of the clay used to prepare the PP

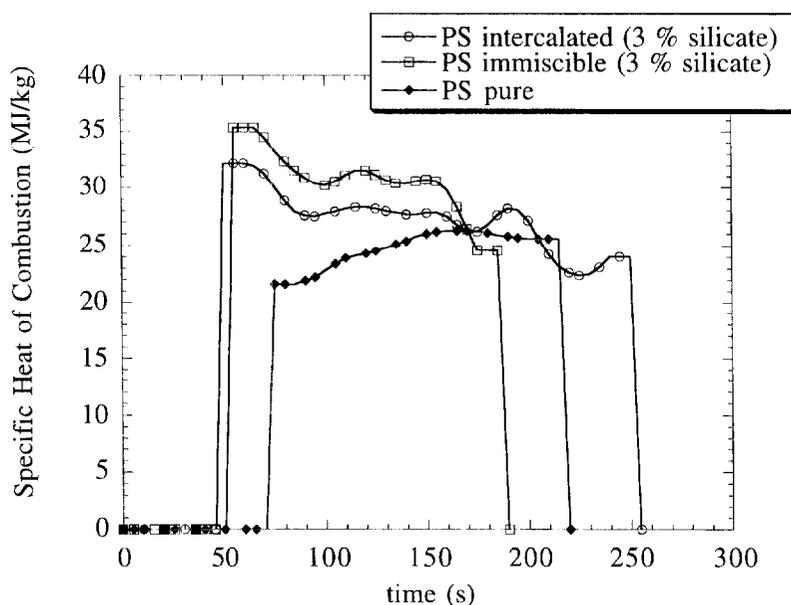


Fig. 12. Comparison of the Specific Heat of Combustion (H_c) plots for PS, PS-silicate (clay) nanocomposite, and for PS-silicate (clay) immiscible-composite, at 35 kW/m² heat flux. This data shows an increase in H_c from 50 s to 150 s for the PS-silicate (clay) nanocomposite and for PS-silicate (clay) immiscible-composite (Gilman et al., 1998a).

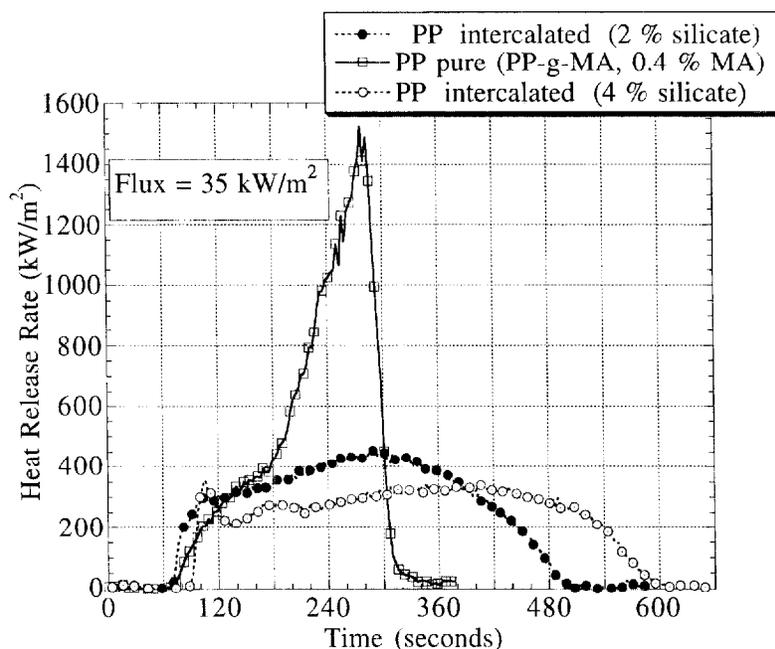


Fig. 13. Comparison of the Heat Release Rate (HRR) plots for PP, and two PP-silicate (clay) nanocomposites, at 35 kW/m^2 heat flux, showing a 70% to 80% reduction in peak HRR for the nanocomposites with only a mass fraction of 2% or 4% clay, respectively.

and PS nanocomposites (and the immiscible PS composite mixture) are long chain (18 carbons) quaternary alkylammonium compounds. These compounds render the clay organophilic so melt blending yields the nanocomposites. However, the quaternary alkylammonium compounds do not get bonded to the polymer. TGA shows that the alkylammonium treated clays contain a mass fraction of between 40% and 50% organic from the alkylammonium, and that they begin to degrade at 250°C , presumably from decomposition of the quaternary alkylammonium compounds, into volatile alkenes and amines. This rather poor thermal stability compared to the host polymers, PS or PP, may supply the volatiles which yield the higher H_c mentioned above. Preliminary TGA-FTIR analysis of the PS samples indicates a higher concentration of aliphatic hydrocarbons in the PS-clay samples, in the initial stages of the pyrolysis, compared to the pure PS sample. PS decomposes primarily to styrene monomer, which burns incompletely producing soot and CO. The H_c is therefore lower than a comparable eight carbon aliphatic-hydrocarbon which burns nearly completely. In a similar crosslinked-PS system Giannelis has found that by bonding the organic-clay treatment to the PS matrix the thermal stability of the resulting nanocomposite is radically improved (Giannelis, 1998). This explanation may not be the only factor responsible for the higher H_c ; especially in the PP

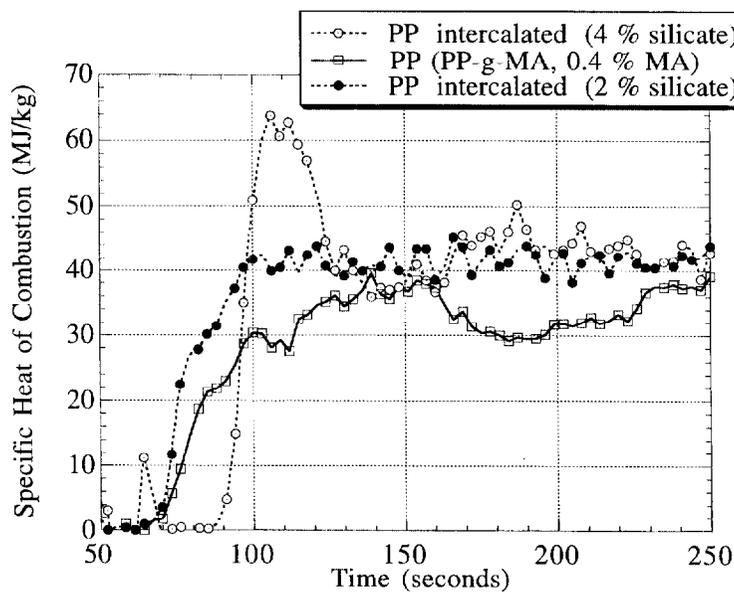


Fig. 14. Comparison of the Specific Heat of Combustion (H_c) plots for PP, and two PP-silicate (clay) nanocomposites (clay mass fraction 2% or 4%). Similar to the H_c data for PS, this data shows an increase in H_c from just following ignition to 130 s, and from 170 s to 220 s for both PP-silicate (clay) nanocomposites.

nanocomposites since we see higher H_c in the middle of the combustion process from 170 s to 220 s.

4. Nanocomposites and conventional flame retardants

The following two uses of polymer–clay nanocomposites combine them with commercial flame retardant products. Bourbigot has substituted nylon-6-clay nanocomposite for pentaerythritol in an intumescent flame retardant formulation with ammonium polyphosphate (APP). Bourbigot demonstrated measurable improvement in the mechanical and flammability properties of an ethylene vinyl acetate (EVA) formulation using this approach (Bourbigot et al., 1998). The HRR plot is shown in Fig. 15. The mechanical properties data is shown in Fig. 16.

A recent patent by Inoue and Hosokawa reports the use of silicate-triazine intercalation compounds in fire resistant polymeric composites (Inoue and Hosokawa, 1998). By combining the known FR properties of melamine and those of polymer–clay nanocomposites the inventors produced V-0 ratings in the UL-94 flammability test, while increasing both the bending modulus and the heat distortion temperature. Nylon-6, polybutylene terephthalate (PBT), poly-

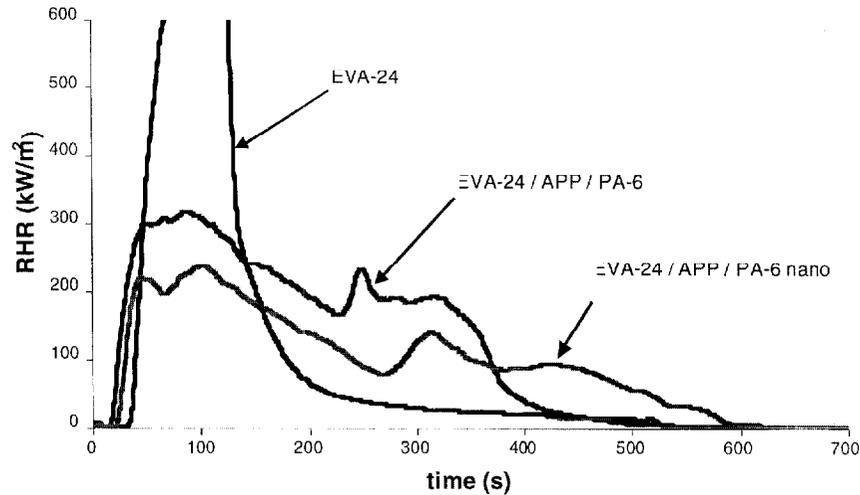


Fig. 15. Rate of Heat Release (RHR or HRR) values versus time plots for: EVA (mass fraction 8% VA), EVA24-APP/PA-6 and EVA24-APP/PA-6nano (Bourbigot et al., 1998).

oxymethylene (POM) and polyphenylene sulfide (PPS) were prepared as silicate-triazine nanocomposites using the synthetic silicate, fluorohectorite. Various melamine salts were pre-intercalated into the clay, 10% to 15% total mass fraction of additives was used. Inoue and Hosokawa characterized the spacing between the clay layers using TEM; they found that without a uniform dispersion of the clay layers in the polymer only a HB rating (self extinguishing in a horizontal burn) was obtained in the UL 94 test.

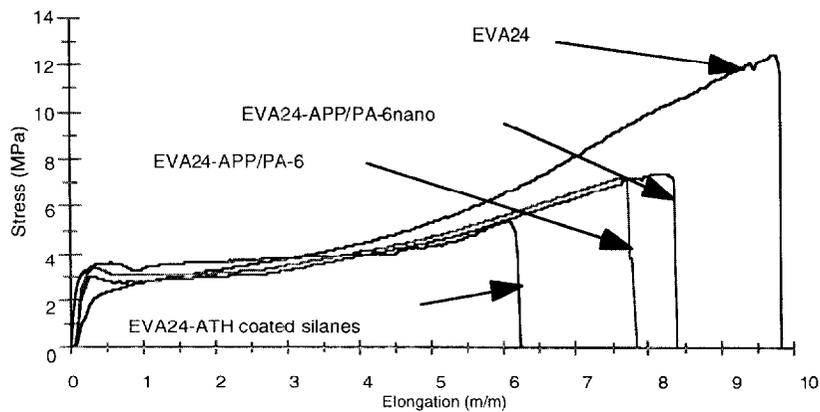


Fig. 16. Mechanical property (stress-strain) data for EVA (mass fraction 8% VA), EVA24-APP/PA-6 and EVA24-APP/PA-6nano (Bourbigot et al., 1998).

5. Summary

Polymer–clay nanocomposites are materials that in many of the cases studied have improved thermal properties. Furthermore, all the nanocomposite systems reported so far also show improved flammability properties. The delaminated versions of nanocomposites also offer measurable improvements in a variety of physical properties. The intercalated versions also offer the above benefits, but with less improvement in physical properties. Many issues are unresolved as to the mechanism of these property enhancements. For example, in terms of flammability properties: how important is inherent thermal stability relative to the effect of layered-carbonaceous char formation? Which nanostructure, intercalated or delaminated, gives the best flammability properties? Hopefully the high level of research and development activity focused on polymer–clay nanocomposites will continue so that these issues may be resolved. When they are, 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.

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