

**FLAMMABILITY STUDIES OF POLYMER LAYERED  
SILICATE NANOCOMPOSITES**

by

**Jeffrey W. Gilman, Takashi Kashiwagi,  
James E.T. Brown, Sergei Lomakin  
Building and Fire Research Laboratory  
National Institute of Standards and Technology  
Gaithersburg, MD 20899, USA**

**Reprinted from the 43<sup>rd</sup> International SAMPE Symposium and Exhibition – Materials and Process Affordability Keys to the Future, May 31-June 4, 1998, Anaheim, CA. Proceedings. Volume 43, Book 1 of 2 Books. Edited by Howard S. Kliger, Benjamin M. Rasmussen, Louis A. Pilato and Tia Bension Tolle. Society for the Advancement of Material and Process Engineering (SAMPE), Covina, CA, 1053-1066 pp., 1998.**

**NOTE: This paper is a contribution of the National Institute of Standards and Technology and is not subjected to copyright.**

## FLAMMABILITY STUDIES OF POLYMER LAYERED SILICATE NANOCOMPOSITES

Jeffrey W. Gilman\*, Takashi Kashiwagi, James E. T. Brown, Sergei Lomakin<sup>†</sup>  
National Institute of Standards and Technology<sup>‡</sup>, Gaithersburg, MD

Emmanuel P. Giannelis, Evangelos Manias  
Cornell University  
Ithaca, NY

### ABSTRACT

Polymer layered silicate (PLS) nanocomposites are materials with unique properties when compared to conventional filled polymers (1). 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 (2). Previously, we reported on the flammability properties of *delaminated* nylon-6 layered silicate nanocomposites and *intercalated* polymer layered-silicate nanocomposites prepared from polystyrene, PS, and polypropylene-graft-maleic anhydride, PP-g-MA (3,4). Here, we will briefly review these results and report on our initial studies of the flammability of thermoset PLS nanocomposites; *intercalated* vinyl ester silicate and *intercalated* epoxy silicate nanocomposites.

### 1. INTRODUCTION

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 the low cost of these materials requires that the fire retardant (FR) approach also be of low cost. This limits solutions to the problem primarily to additive type approaches. These additives must be low cost and easily processed with the polymer. In addition, any additive must not excessively degrade the other performance properties of the polymer, and it must not create environmental problems in terms of recycling or disposal of the final product.

Polymer layered silicate (PLS) nanocomposites are hybrid organic polymer - inorganic materials with unique properties when compared to conventional filled polymers (1). In some cases increased thermal stability, an important property for improving flammability performance, is also accompanied by a doubling of tensile modulus and strength, as well as decreased gas permeability, increased solvent resistance, and higher heat distortion temperature. Methods to prepare PLS nanocomposites have been developed by several groups over the last decade (2, 5, 6, 7, 8, 9, 10).

**KEY WORDS:** Nanocomposite, Flammability, Silicate.

<sup>†</sup> NIST Guest Researcher from the Russian Academy of Sciences.

<sup>‡</sup> This work was carried out by the National Institute of Standards and Technology (NIST), an agency of the U. S. government, and by statute is not subject to copyright in the United States.

In general these methods achieve molecular level incorporation of layered silicate (e.g., montmorillonite) into the polymer by addition of a modified silicate; during the polymerization (*in situ*), or to a solvent swollen polymer, or to the polymer melt (1). Two terms (*intercalated* and *delaminated*) are used to describe the two general classes of nano-morphology that can be prepared. The *intercalated* structure, where the extended polymer chains are inserted into the gallery space between the individual silicate layers (see Figure 1). These are well ordered multi-layered structures. The *delaminated* (or *exfoliated*) structures result when the individual silicate layers are well dispersed in the organic polymer. The interlayer spacing (20 nm -200 nm) is on the order of the radius of gyration of the polymer. The silicate layers in a *delaminated* structure are not as well ordered as in a *intercalated* structure.

Nylon-6 and polycaprolactone silicate-nanocomposites have been prepared through *in situ* ring opening polymerization of monomers. This process requires some re-development of the polymer manufacturing process, and although nylon-6 silicate nanocomposite is commercially available, this approach may not be as attractive for other polymers. Melt intercalation of the polymer directly into the layered silicate was recently developed. In this process the appropriately modified layered silicate (cation exchanged montmorillonite) and the polymer are combined in the melt to form the nanocomposite (1). This process is of course most advantageous for thermoplastic polymers. For thermosetting resins the *in situ* polymerization method is still suitable, and the appearance of several publications (5, 10, 11) and patents (12, 13, 14) demonstrates that new thermoset silicate-nanocomposites with unique properties can be prepared. In the case of an unsaturated polyester thermoset resin, the *intercalated* nanocomposite was shown to have a higher Young's modulus than both the pure polymer and the *delaminated* nanocomposite (10).

## 2. BACKGROUND

Thermal analysis (TGA) of several different PLS nanocomposite resin systems has revealed the intriguing result that *intercalated* nanocomposites are more thermally stable than the *delaminated* nanocomposites (4, 9, 10). Molecular dynamics simulations of the thermal degradation of a series of polypropylene (PP)/graphite nanocomposites recently found that the most pronounced stabilization of the polymer occurred where the graphite layers were separated by 3 nm; that is, had an *intercalated* structure (15). Previously, we reported on the flammability properties of several thermoplastic polymer nanocomposites; *delaminated* nylon-6 layered silicate nanocomposites and *intercalated* polymer layered-silicate nanocomposites prepared from polystyrene, PS, and polypropylene-graft-maleic anhydride, PP-g-MA (3, 4, 9). The flammability data for nylon-6, PS and PP-g-MA, and new data on nylon-12 is shown in Table 1. The data shows that both the peak and average heat release rates (HRR) were reduced significantly for *intercalated* and *delaminated* PLS nanocomposites with low mass fraction (2 % to 5 %) of silicate. The HRR plots for nylon-6 and nylon-6 silicate-nanocomposite (mass fraction 5 %) at 35 kW/m<sup>2</sup> heat flux are shown in Figure 2, and are typical of those found for all the PLS nanocomposites in Table 1. The nylon-6 nanocomposite has a 63 % lower HRR than the pure nylon-6. Furthermore, for the PS silicate nanocomposite the magnitude of improvement in flammability performance is comparable to that found for PS flame retarded using a total mass fraction of 30 % of decabromodiphenyl oxide, DBDPO, and antimony trioxide, Sb<sub>2</sub>O<sub>3</sub>, (see Table 1). This is accomplished without as much of an increase in the soot (SEA) or CO yields. The data also indicates that the rate of mass loss during combustion of the PLS nanocomposite is significantly reduced from the values observed for the pure polymers (see Figure 3). Since the heat of combustion, SEA 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.



Figure 1. Molecular representation of sodium montmorillonite, showing two aluminosilicate layers with the Na<sup>+</sup> cations in the interlayer gap or gallery (1.14 nm layer-to-layer spacing).

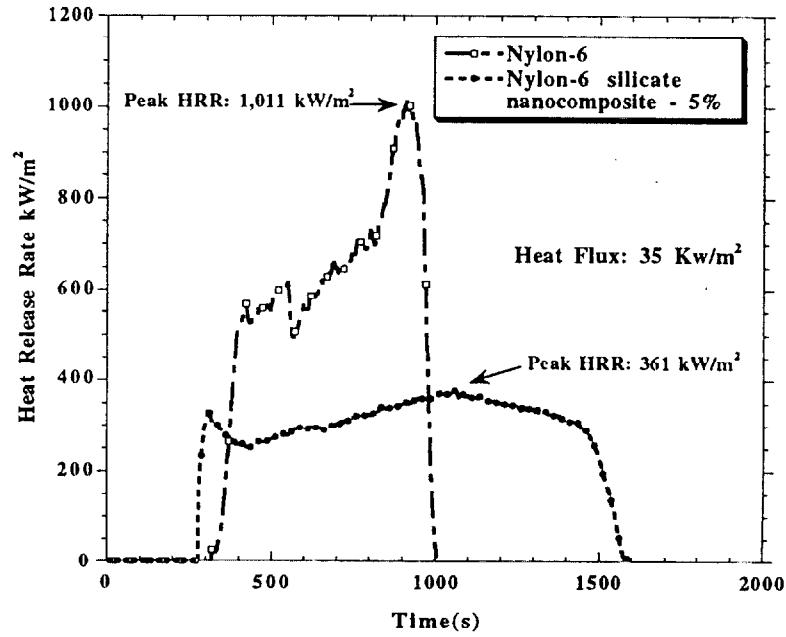


Figure 2. Comparison of the Heat Release Rate (HRR) plot for nylon-6, nylon-6 silicate-nanocomposite (mass fraction 5 %) at 35 kW/m<sup>2</sup> heat flux, showing a 63 % reduction in HRR for the nanocomposite.

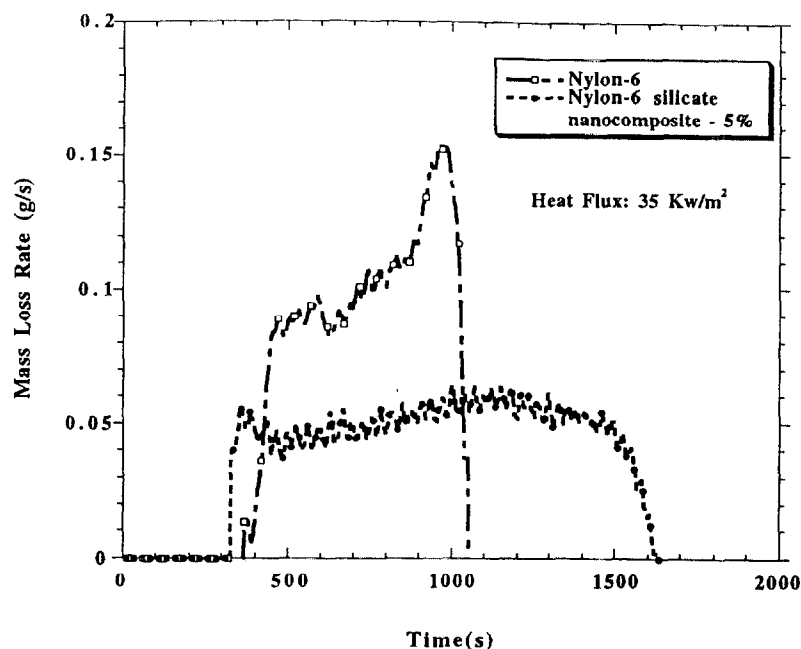


Figure 3. The mass loss rate data for nylon-6, nylon-6 silicate-nanocomposites (5%). The curves closely resemble the HRR curves (Figure 2), indicating that the reduction in HRR for the nanocomposites is primarily due to the reduced mass loss rate and the resulting lower fuel feed rate to the gas phase.

### 3. EXPERIMENTAL

Evaluations of flammability were done using the Cone Calorimeter (16). The tests were done at an incident heat flux of 35 kW/m<sup>2</sup> using the cone heater. A heat flux of 35 kW/m<sup>2</sup> represents a typical small-fire scenario (17). 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 the thousands of samples combusted to date. The cone data reported here is the average of two or three replicated experiments. Cone samples for thermoplastic polymers were prepared by compression molding the samples (25g - 55 g) into 75 mm diameter disks, 10 mm-15 mm thick, using a press with a heated mold.

The vinyl ester (18) samples were prepared at room temperature (25 °C) by mixing the resin (modified bisphenol-A epoxy based vinyl ester, a combination of a nitrile rubber and bisphenol-A epoxy based vinyl ester, mass fraction of 58 % in styrene - Derakane 8084, and bis-A/novolac epoxy based vinyl ester, a combination of bisphenol-A epoxy based vinyl ester and novolac epoxy based vinyl ester, mass fraction of 67 % in styrene - Derakane 441, both from Dow Chemical Co., see Figure 6) with the initiator (2-butanone peroxide, mass fraction of 1.25 %) the cobalt catalyst (mass fraction of 0.3 %, Cobalt naphthenate, mass fraction of 6 % in mineral spirits, OMG Americas Inc.) and an organically modified silicate (OMS), dimethyl ditallow ammonium montmorillonite, Closite-15A, Southern Clay Products, Inc.) using an overhead mechanical stirrer for 5 minutes. The mixtures were poured into aluminum sample dishes (75 mm diameter x 15 mm depth) and cured at room temperature for 12 h and then post-cured at 70° C for 8 h.

The epoxy samples of diglycidyl ether bisphenol-A based epoxy (DGEBA, DER 331, Dow Chemical Co.) were prepared using a previously published procedure (11). The mixtures were poured into aluminum sample dishes (75 mm diameter x 15 mm depth) and cured at room temperature for 18 h and then post-cured at 100° C for 3 h. Methylenedianiline (MDA) and

benzyltrimethylammonium chloride (BDMA) were used as curing agents. The OMS used was dimethyl ditallow ammonium montmorillonite.

Nylon-6 and nylon-6 silicate nanocomposites (silicate mass fraction of 2 % and 5 %) nylon-12 and nylon-12 silicate nanocomposites (silicate mass fraction of 2 % ) were obtained from UBE industries and were used as received.

Preparation of PS- silicate -nanocomposite (silicate mass fraction of 3 %) was accomplished by melt blending PS (Styron 6127, Dow Chemical Co.) with dimethyl dioctadecyl ammonium-exchanged montmorillonite (1). This yields a nanocomposite with the *intercalated* structure. The intergallery spacing, by X-ray diffraction, XRD, is 3.1 nm ( $2\theta = 2.6^\circ$ ). The *immiscible* PS-silicate mix, where the silicate is only mixed in at the primary-particle size scale ( $\sim 5 \mu\text{m}$ ), is prepared under the same melt blending conditions except the alkyl ammonium used to compatibilize the montmorillonite has only one octadecyl R group instead of two. This renders the ion exchanged montmorillonite slightly less organophilic and intercalation does not occur.

Preparation of PP-g-MA- silicate -nanocomposite (silicate mass fraction of 5 %) by melt blending was accomplished by pressing the PP-g-MA (mixed with the dimethyl ditallow ammonium-exchanged montmorillonite, Cloisite 15A, at  $160^\circ\text{C}$  for 30 minutes using a Carver press, followed by heating in a vacuum oven for several hours at  $160^\circ\text{C}$ . This yields a nanocomposite with the *intercalated* structure. The intergallery spacing, by XRD analysis, is 3.6 nm. PP-g-MA (m.p.  $152^\circ\text{C}$ ) was purchased from Aldrich and contains a mass fraction of 0.6 % maleic anhydride. It has a melt index of 115 g / 600 s and a Mw of  $\sim 10\text{K}$ , Mn  $\sim 5\text{K}$ .

X-ray diffraction (XRD) spectra were collected on a Phillips diffractometer using Cu K $\alpha$  radiation, ( $\lambda = 0.1505945 \text{ nm}$ ). Powder samples were ground to a particle size of less than  $40 \mu\text{m}$ . Solid polymer-silicate monoliths were typically 14 mm by 14 mm with a 2 mm thickness.

For the transmission electron microscopy (TEM), the char was broken into small pieces, embedded in an epoxy resin (Epofix), and cured overnight at room temperature. Ultra-thin sections were prepared with a  $45^\circ$  diamond knife at room temperature using a DuPont-Sorvall 6000 ultramicrotome. Thin sections (nominally 50 nm-70 nm) were floated onto water and mounted on 200-mesh carbon-coated copper grids. Bright-field TEM images were obtained with a Philips 400T microscope operating at 120 kV, utilizing low-dose techniques.

#### 4. RESULTS AND DISCUSSION

Epoxy and vinyl ester resin systems represent a large fraction of the commercial thermoset polymer, coating, and composite markets (19, 20). A reduction in the flammability of these inherently highly flammable materials should increase their use. For the purpose of determining the flammability properties of thermoset PLS nanocomposites, especially the *intercalated* type, we have prepared and studied two *intercalated* vinyl ester nanocomposites and two *intercalated* epoxy nanocomposites.

**4.1. Characterization of Nanocomposites by XRD.** The microstructure of the epoxy and vinyl ester nanocomposites was characterized using XRD. The XRD patterns which reveal the *intercalated* structure of the modified-bisphenol-A (MBA) vinyl ester silicate nanocomposite and the bis-A/novolac (BAN) vinyl ester silicate nanocomposite are shown in Figure 4. The interlayer spacing for the MBA nanocomposite is 4.8 nm which represents a 1.5 nm expansion of the interlayer spacing of the silicate layers present in the original organically modified montmorillonite. The interlayer spacing for the BAN nanocomposite is 6.2 nm which represents a 2.9 nm expansion of the interlayer spacing of the silicate layers. The different degree of *intercalation* for these two vinyl ester systems is most likely due to the different structures of the components of the formulations, shown in Figure 6, and the resulting polarity and conformational mobility differences.

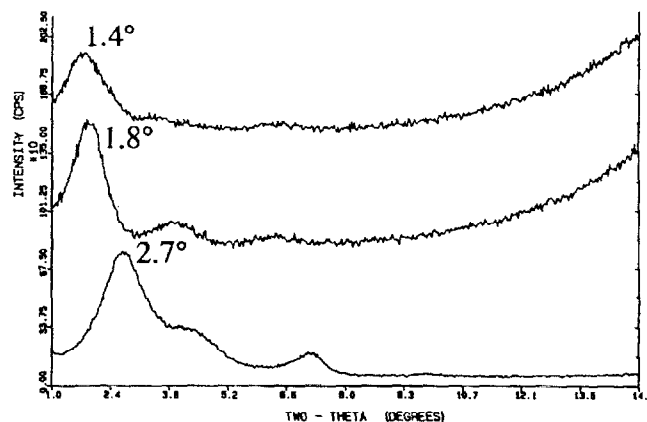


Figure 4. XRD patterns of: pure OMS, dimethyl ditallow ammonium- montmorillonite (bottom,  $2\theta = 2.7^\circ$ , layer spacing 3.3 nm); cured modified-bisphenol-A epoxy based vinyl ester silicate nanocomposite (middle, 6 % silicate,  $2\theta = 1.8^\circ$ , layer spacing 4.8 nm) and cured bis-A/novolac epoxy based vinyl ester silicate nanocomposite (top, 6 % silicate,  $2\theta = 1.4^\circ$ , layer spacing 6.2 nm).

The XRD characterization of the DGEBA epoxy silicate nanocomposites, cured with either MDA or BDMA, shown in Figure 5, confirms *intercalated* structures, with interlayer spacings of 3.5 nm and 4.3 nm, respectively. These results parallel previously published work where MDA/DGEBA epoxy silicate nanocomposite exhibited less expansion of the silicate spacing than the BDMA/DGEBA epoxy silicate nanocomposite (11). It was proposed that the MDA, a diamine, could bridge the silicate layers and thereby prevent complete delamination. The BDMA, a monoamine, would not have this limitation. In the previous system however, the BDMA/DGEBA nanocomposite was fully *delaminated* whereas it is only *intercalated* here. The reason for this difference lies in the different alkyl ammonium montmorillonites used. In the previous study where the BDMA/DGEBA nanocomposite *delaminated*, the OMS used was bis(hydroxyethyl) methyl tallow montmorillonite. The hydroxyethyl groups in this OMS react with the oxirane rings of the DGEBA aiding in the dispersion of the silicate in the resin. The resulting epoxy network contains chemical bonds to the alkyl ammonium cation and therefore an ionic tether to the silicate (11). The strength of this ionic tether between the polymer and the silicate was found to have a direct relationship to the tensile strength of the nylon-6 nanocomposites (21). We used an OMS without reactive functionality (dimethyl ditallow ammonium montmorillonite). This results in a cured DGEBA nanocomposites without an ionic ether to the silicate for both the MDA and BDMA cured epoxies. It should be noted that since the MDA contains four active N-H hydrogens it can react directly as a crosslinking agent with DGEBA. The BDMA contains no active N-H, and it acts only as a catalyst for the homopolymerization of DGEBA. This results in formation of a purely polyether network for the BDMA/DGEBA epoxies (11, 19).

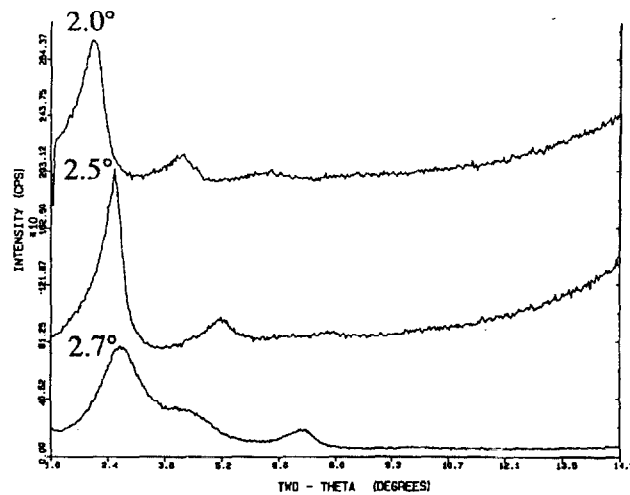


Figure 5. XRD patterns of: pure organic modified silicate, dimethyl ditallow ammonium-montmorillonite (**bottom**,  $2\theta = 2.7^\circ$ , layer spacing 3.3 nm); MDA cured epoxy silicate nanocomposite (**middle**, 6 % silicate,  $2\theta = 2.5^\circ$ , layer spacing 3.5 nm) and BDMA cured epoxy silicate nanocomposite (**top**, 6 % silicate,  $2\theta = 2.0^\circ$ , layer spacing 4.3 nm).

**4.2. Epoxy and Vinyl Ester Flammability Properties.** The results of combustion of the vinyl esters and their respective nanocomposite versions in the Cone calorimeter are shown in Table 2. Just as with the thermoplastic PLS nanocomposites both the peak and average heat release rates (HRR) were significantly improved for these *intercalated* vinyl ester nanocomposites with low mass fraction (6 %) of silicate. Furthermore, the primary difference (aside from HRR) between the flammability properties of the pure vinyl esters and the nanocomposites is the mass loss rates (MLR). The heat of combustion ( $H_c$ ), soot (SEA) and carbon monoxide yields are unchanged.

The results of combustion of the MDA/DGEBA and BDMA/DGEBA epoxies and their respective nanocomposite versions in the Cone calorimeter are shown in Table 3. The data shows essentially the same behavior as for the vinyl ester nanocomposites, about a 40 % reduction in peak HRR, average HRR, and average MLR. The heat of combustion ( $H_c$ ), soot (SEA) and carbon monoxide yields are unchanged. The HRR plots for DGEBA/MDA and the DGEBA/MDA silicate nanocomposite (6%) are shown in Figure 7. This plot is representative of the HRR behavior for both the epoxies and vinyl esters. Although ignition times in the cone calorimeter are accompanied by somewhat large uncertainties ( $\pm 25\%$ ) shorter ignition times are generally observed for the PLS nanocomposites. This may be caused by the low thermal stability of the quaternary alkyl ammonium cation contained in the organic modified montmorillonite used to prepare the PLS nanocomposites.



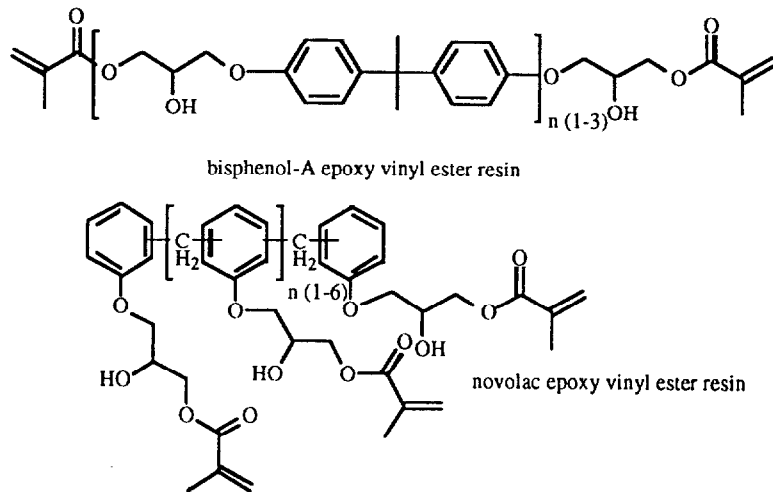


Figure 6. Vinyl ester resin chemical structures.

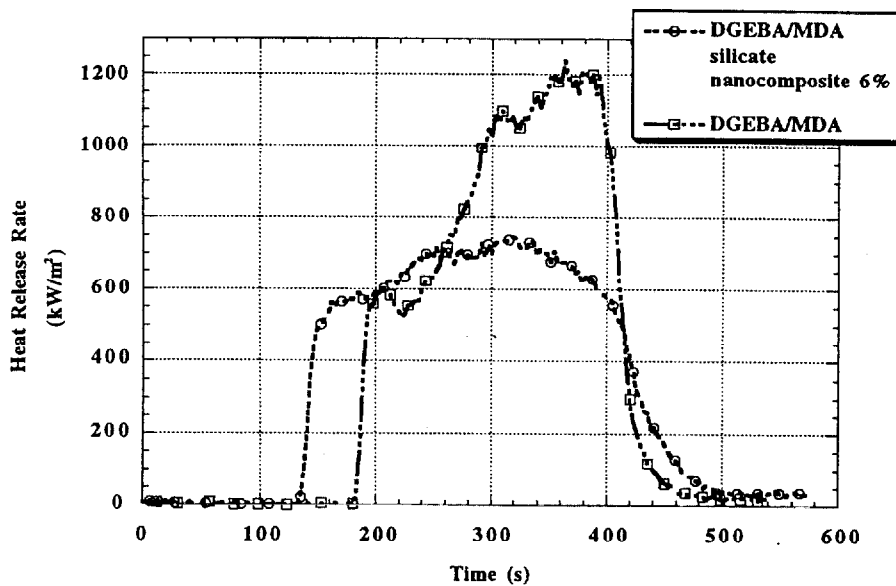


Figure 7. Comparison of the Heat Release Rate (HRR) plots for DGEBA/MDA and DGEBA/MDA silicate nanocomposite (mass fraction 6 %) at 35 kW/m<sup>2</sup> heat flux, showing a 40 % reduction in the peak HRR for the nanocomposite.

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)
<b>Nylon-6</b>	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
<b>Nylon-12</b>	0	1710	846	40	387	0.02
Nylon-12 silicate- nanocomposite 2% <i>delaminated</i>	2	1060 (38%)	719 (15%)	40	435	0.02
<b>PS</b>	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</i>	4	567 (48%)	444 (38%)	27	1,730	0.08
<b>PS</b> w/ DBDPO/Sb <sub>2</sub> O <sub>3</sub> 30%	3	491 (56%)	318 (54%)	11	2,580	0.14
<b>PP-g-MA</b>	0	2,030	861	38	756	0.04
PP-g-MA silicate nanocomposite 5% <i>intercalated</i>	8	922 (54%)	651 (24%)	37	994	0.05

Heat flux : 35 kW/m<sup>2</sup>, H<sub>c</sub> : Heat of combustion, SEA : Specific Extinction Area

Table 2. Cone calorimeter data for MBA and BAN vinyl esters

Sample	Residue Yield (%) $\pm 0.5$	Peak HRR ( $\Delta\%$ ) (kW/m <sup>2</sup> )	Mean HRR ( $\Delta\%$ ) (kW/m <sup>2</sup> )	Mean MLR (g/s m <sup>2</sup> )	Mean H <sub>c</sub> (MJ/kg)	Mean SEA (m <sup>2</sup> /kg)	Mean CO yield (kg/kg)
<b>Mod-Bis-A Vinyl Ester</b>	0	879	598	26	23	1360	0.06
Mod-Bis-A Vinyl Ester**	8	656 (25%)	365 (39%)	18 (30%)	20	1300	0.06
<b>Bis-A /Novolac Vinyl Ester</b>	2	977	628	29	21	1380	0.06
Bis-A /Novolac Vinyl Ester **	9	596 (39%)	352 (44%)	18 (39%)	20	1400	0.06

Heat flux : 35 kW/m<sup>2</sup>, H<sub>c</sub> : Heat of combustion, SEA : Specific Extinction Area, MLR : Mass Loss Rate

\*\* : 6 % silicate *intercalated* nanocomposite

Table 3. Cone calorimeter data for DGEBA/MDA and DGEBA/BDMA epoxies.

Sample	Residue Yield (%) $\pm 0.5$	Peak HRR ( $\Delta\%$ ) (kW/m <sup>2</sup> )	Mean HRR ( $\Delta\%$ ) (kW/m <sup>2</sup> )	Mean MLR (g/s m <sup>2</sup> )	Mean H <sub>c</sub> (MJ/kg)	Mean SEA (m <sup>2</sup> /kg)	Mean CO yield (kg/kg)
<b>Epoxy resin DGEBA/MDA</b>	11	1296	767	36	26	1340	0.07
Epoxy resin DGEBA/MDA**	19	773 (40%)	540 (29%)	24 (33%)	26	1480	0.06
<b>Epoxy resin DGEBA/BDMA</b>	3	1336	775	34	28	1260	0.06
Epoxy resin DGEBA/BDMA**	10	769 (42%)	509 (35%)	21 (38%)	30	1330	0.06

Heat flux : 35 kW/m<sup>2</sup>, H<sub>c</sub> : Heat of combustion, SEA : Specific Extinction Area, MLR : Mass Loss Rate

\*\* : 6 % silicate *intercalated* nanocomposite

The data 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. As stated above these flammability properties are characteristic of both the thermoplastic and thermoset PLS nanocomposites.

**4.2. Char Formation and Characterization.** Comparison of the residue yields for thermoplastics and thermosets reveals little improvement in the carbonaceous char yields, once the presence of the silicate in the residue is accounted for. This was somewhat surprising since other studies of the thermal reactions in layered organic-silicate intercalates, at 400 °C, reported formation of carbonaceous-silicate residues and other condensation and crosslinking type reaction products (22). These data indicate that, although the mechanism of flame retardancy may be very similar for each of the systems studied, it is not via retention of a large fraction of carbonaceous char in the condensed phase. A recent study in our laboratory of the nylon-6

silicate nanocomposite pyrolysis process, in a nitrogen atmosphere, using a radiative gasification apparatus (shown in Figure 8) revealed that the reduction in MLR does not occur until the sample surface is partially covered with char (4). The MLR data for these  $N_2$  gasification experiments are shown in Figure 9. Visual observation of the pyrolysis shows that at 180 s when the MLR for the nylon-6 silicate nanocomposite slows, compared to the pure nylon-6, the surface of the nanocomposite is over 50 % covered by char.

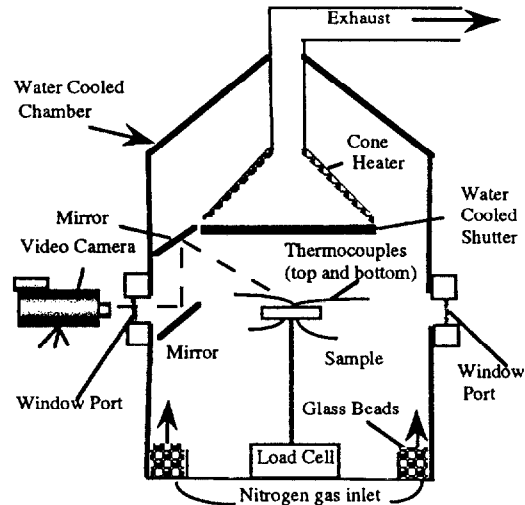


Figure 8. A schematic of the radiative gasification apparatus (1 m diameter, 2 m height). The gasification apparatus allows pyrolysis, in a nitrogen atmosphere, of samples identical to those used in the Cone calorimeter.

TEM of a section of the combustion char from the nylon-6 silicate-nanocomposite (5 %) is shown in Figure 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. This multilayered 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 (4). XRD analysis of chars from combustion of nylon-6, and the two DGEBA nanocomposites (Figure 11) shows that the interlayer spacing of the chars is the same, 1.3 nm, independent of the chemical structure (thermoplastic polyamide, thermoset aromatic diamine cured epoxy or thermoset homopolymerized epoxy) or nano-structure (*delaminated* or *intercalate*) of the nanocomposite.

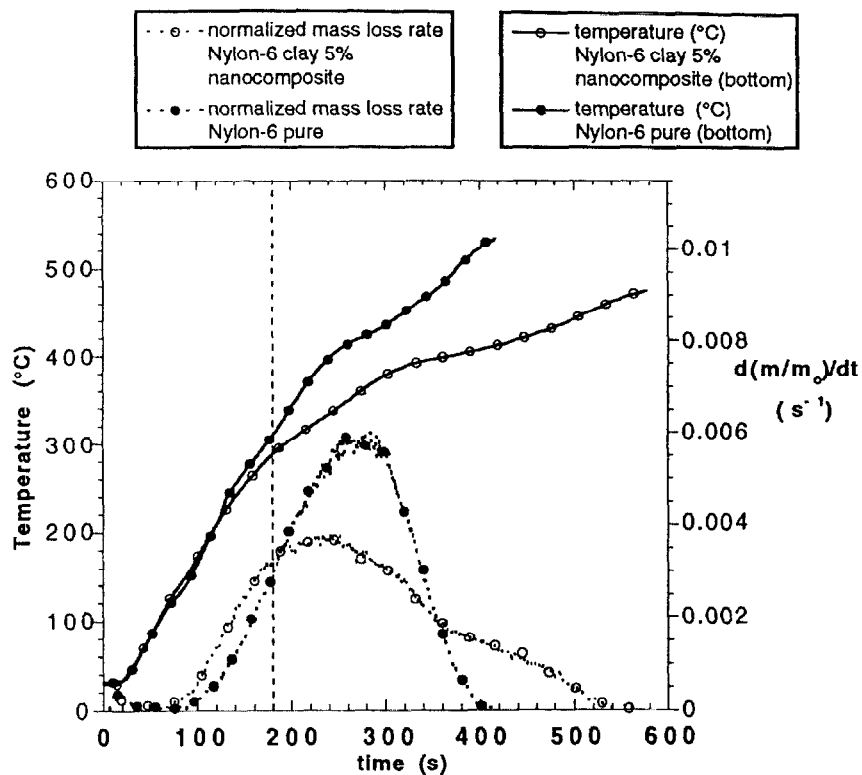


Figure 9. Normalized Mass loss rate and temperature versus time plots for the gasification experiments for nylon-6 and nylon-6 silicate (5%) nanocomposite in a  $N_2$  atmosphere. All samples were exposed to a flux of  $40 \text{ kW/m}^2$  in a  $N_2$  atmosphere. The mass loss rate curves begin to differ at 180 seconds 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.

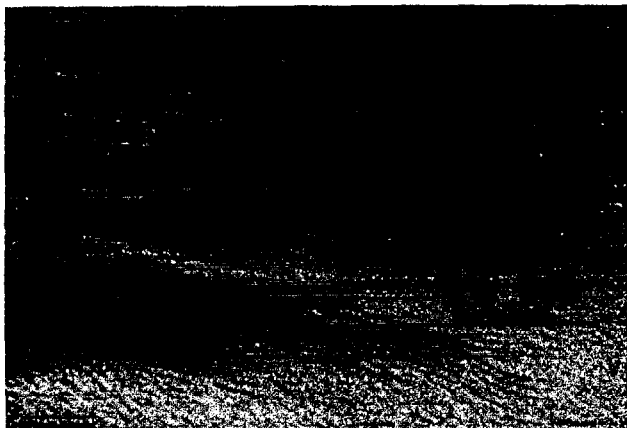


Figure 10. TEM of a section of the combustion char from the nylon-6 silicate-nanocomposite (5%) showing the carbon-silicate (1 nm thick, dark bands) multilayered structure. This layer may act as an insulator and a mass transport barrier.

## 5. FUTURE WORK

The future focus of this project will be on the continued development of a fundamental understanding of the fire retardant mechanism of polymer layered silicate nanocomposites. The effect of nano-structure on the flammability properties of a given nanocomposite system will be investigated. This work will be done within the Flammability of Nanocomposites Consortium.

## 6. CONCLUSIONS

The flammability properties of thermoplastic and thermoset polymer layered silicate nanocomposites are reported. The peak and average heat release rate (HRR) are reduced by 40 % to 60% in *delaminated* and *intercalated* nanocomposites containing a silicate mass fraction of only 2 % to 6 %. Not only is this a very promising new method for flame retarding polymers, but it does not have the usual drawbacks associated with other additives. That is, the physical properties are not degraded by the additive (silicate); instead they are greatly improved. Furthermore, this system does not increase the carbon monoxide or soot produced during the combustion. The nanocomposite structure of the char appears to enhance the performance of the char layer. This layer may act as an insulator and a mass transport barrier slowing the escape of the volatile products generated as the polymer decomposes.

## 7. ACKNOWLEDGMENTS

The authors would like to thank Dr. R. Lyon and the Federal Aviation Administration for partial funding of this work, through Interagency Agreement DTFA0003-92-Z-0018. We would also like to thank Mr. Michael Smith for Cone Calorimeter analysis, Ms. Lori Brassel for preparation of vinyl ester and epoxy samples, Dr. Catheryn Jackson and Dr. Henri Chanzy for TEM analysis of the char samples, Dr. M. Nyden for the montmorillonite structure, and Dr. James Cline for use of XRD facilities.

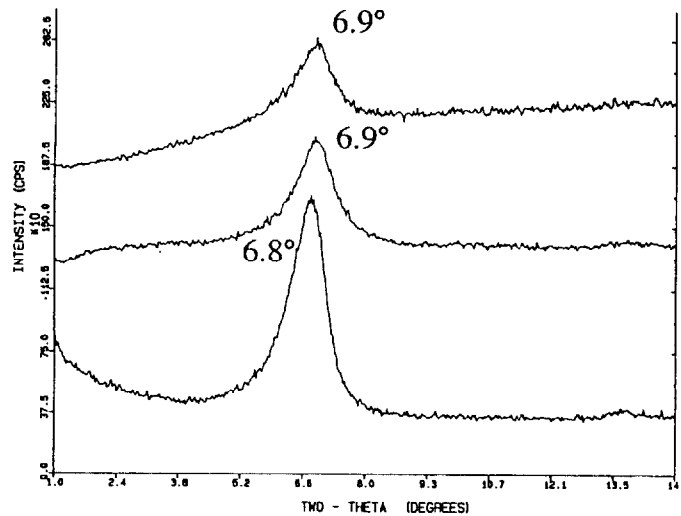


Figure 11. Char XRD patterns of silicate nanocomposites: nylon-6 (bottom), DGEBA/BDMA (middle), and DGEBA/MDA (top). All chars have a interlayer spacing of ~1.3 nm, which is confirmed by TEM.

## 8. REFERENCES

1. E. P. Giannelis, *Advanced Materials*, **8**, (1) 29 (1996).
2. Y. Kojima, A. Usuki, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi, and O. Kamigaito, *J. Mater. Res.* **8**, 1185 (1993).

3. J. W. Gilman, T. Kashiwagi, J. D. Lichtenhan, *SAMPE Journal*, **33**, no. 4, 40 (1997)
4. J. W. Gilman, T. Kashiwagi, S. Lomakin, E. P. Giannelis, E. Manias, J. D. Lichtenhan, P. Jones in *Fire Retardancy of Polymers : the Use of Intumescence*, G. Camino, M. Le B S. Bourbigot & R. DeLobel eds., The Royal Society of Chemistry, Cambridge (1998) in press
5. M.S. Wang, T. J. Pinnavaia, *Chem. Mater.* **6**, 468 (1994).
6. A. Usuki, A. Okada, T. Kurauchi, *J. App. Poly. Sci.* **63**, 137 (1997).
7. A. Usuki, Y. Kojima, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi, and Kamigaito, *J. Mater. Res.* **8**, 1179 (1993).
8. Y. Kojima, A. Usuki, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi, and Kamigaito, *J. Mater. Res.* **8**, 1185 (1993).
9. J. Lee, T. Takekoshi and E. Giannelis, *Mat. Res. Soc. Symp. Proc.* vol 457, p. 513, (1997)
10. J. Lee and E. Giannelis, *Polymer Preprints*, vol. 38, p. 688, (1997).
11. P.B. Messersmith, E. P. Giannelis, *Chem. Mater.* **6**, 1719 (1994).
12. S. Miyanaga, Y. Tsunoda, Japanese Patent JP 09,255,747, 1996.
13. A. Usuki, et.al., US Patent 4,889,885, 1989.
14. E. N. Kresge, D. J. Lohse, US patent 5,665,183, 1997.
15. M. Nyden, J. W. Gilman, *Comp. and Theor. Polym. Sci.* in press (1998).
16. V. Babrauskas, R. Peacock, *Fire Safety Journal*, **18**, 255 (1992).
17. V. Babrauskas, *Fire and Materials*, **19**, 243 (1995).
18. 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.
19. R. S. Bauer, ed. *Epoxy Resin Chemistry II*, ACS Symposium Series 221, American Chemical Society, Washington, D.C. 1983.
20. C. D. Dudgeon in *Composites: Engineered Materials Handbook*, vol 1, sec. 2, ASM International, Metals Park, OH, 1987.
21. A. Usuki et. al., *J. Appl. Poly. Sci.*, **55**, 119 (1995).
22. J. M. Thomas, "Intercalation Chemistry", Chapter 3, p. 55, Academic Press, Inc., London, 1982.