

## **CYANATE ESTER CLAY NANOCOMPOSITES: SYNTHESIS AND FLAMMABILITY STUDIES**

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### **ABSTRACT**

New goals outlined by the U. S. Federal Aviation Administration (FAA) Advanced Fire-Safe Aircraft Materials Research Program (1, 2) enumerate an order-of-magnitude improvement in aircraft cabin-material fire safety. In the pursuit of improved approaches to the design of ultra-fire-safe aircraft interior materials, a wide variety of concerns must be addressed in addition to flammability. For many polymers used in the interior of aircraft cost is a major concern for aircraft manufacturers. Therefore, an additive approach to improving the fire safety of polymers is attractive. The 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 improved flammability properties, and improved physical properties as well as recyclability. We report here on the use of a layered silicate, montmorillonite clay, dispersed at the nanometer level, in cyanate ester resins for improving flammability. We show that the use of melamine-treated montmorillonite in these resins yields *exfoliated* montmorillonite in the cured cyanate ester nanocomposites. This reduces the peak heat release rate by over 50%. We anticipate that this nanocomposite approach would be especially useful in improving toughened cyanate ester resins since the typical toughening agents used often increase the flammability and lower the modulus.

**KEY WORDS:** Nanocomposites, Phenolic-triazines, flammability.

## **1. INTRODUCTION**

**1.1. Polymer Layered Silicate (Clay) Nanocomposites** Layered silicate minerals (clays) have been investigated for decades to gain a better fundamental understanding of their unique properties, and to develop them for a variety of applications. Currently, hundreds of groups worldwide are involved in research on polymers intercalated into the gallery spaces of layered silicates, due to the superior properties of these so-called polymer-clay nanocomposites as

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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 (3). 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 prior to or during the polymerization (4, 5, 6, 7) (*in situ method*) to a solvent-swollen polymer (8) (*solution blending*), or to the polymer melt (9, 10).

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 Figure 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 (11). 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 be well ordered, as in an *intercalated* structure, or the layers may be more disordered<sup>†</sup>.

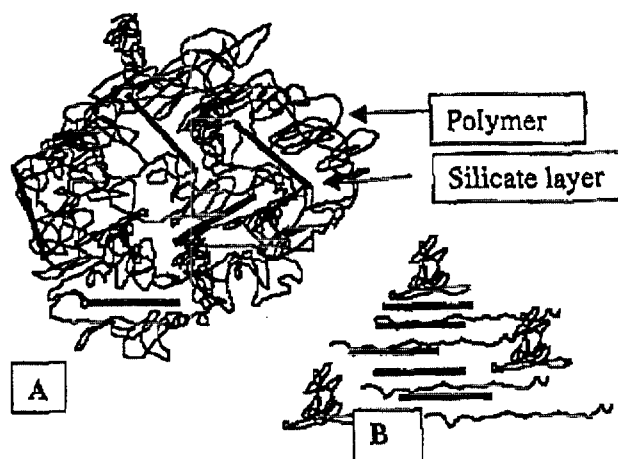


Figure 1. Drawing of disordered / exfoliated (A) and intercalated (B) polymer layered-silicate (clay) nanocomposite morphologies.

As stated above polymer-clay nanocomposites have unique properties when compared to conventional filled polymers. 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 % (5). 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.

Blumstein was the first to report on the improved thermal stability of a polymer-clay

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<sup>†</sup> 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 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).

nanocomposite: he studied nanocomposites that combined polymethylmethacrylate (PMMA) and sodium (Na) montmorillonite clay (3). Although this clay-rich nanocomposite (polymer mass fraction ~10 % as *intercalated* PMMA) would undoubtedly reflect properties dominated by the inorganic phase, the indications of enhanced polymer thermal properties were clear. Blumstein showed that PMMA inserted between the lamellae of montmorillonite clay resisted thermal degradation under conditions that would otherwise completely degrade pure PMMA (refluxing decane, 215 °C, N<sub>2</sub>, 48 h). These PMMA nanocomposites were prepared by free radical polymerization of methyl methacrylate (MMA) intercalated in the clay. X-ray analysis showed an increase of 0.76 nm in the basal spacing. Thermogravimetric analysis (TGA) revealed PMMA intercalated into Na-montmorillonite had a 40 °C to 50 °C higher decomposition temperature. Blumstein found that the inherent thermal stability of the PMMA once it was extracted out of the nanocomposite was better than the PMMA made from solution. He proposed that this was 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. Blumstein argued that the stability of the PMMA-nanocomposite is due both to its different structure, and to the restricted thermal motion of the PMMA in the gallery (3).

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 (12). However, not until more recent studies of improved thermal stability were reported, in both a polydimethylsiloxane (PDMS)-clay nanocomposite (13) and in a polyimide-clay nanocomposite (14), did the serious evaluation of the flammability properties of these materials begin.

In Burnside's studies on PDMS-clay nanocomposite (13) an improvement in thermal stability similar to that reported by Blumstein was observed; however, in this case the PDMS nanocomposite was not prepared by *in situ* polymerization, but by sonication of silanol-terminated PDMS with montmorillonite, which had been ion exchanged (dimethyl ditallow ammonium montmorillonite) and partially hydrated. In contrast to Blumstein's materials, this nanocomposite contained primarily polymer (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 (see Figure 1). In this case the nanostructure showed a 140 °C higher decomposition temperature than the pure PDMS. The increased thermal stability was attributed to hindered diffusion of volatile decomposition products from the nanocomposite, in view of the improved barrier properties observed for other polymer nanocomposites (13).

Giannelis' studies of aliphatic polyimide clay nanocomposites demonstrated four important issues associated with polymer-clay nanocomposites (14). First, that melt processing could be used to prepare both intercalated and delaminated polymer-clay nanocomposites (9). Second, the study found that an immiscible polyimide-clay mixture, which contained the same amount of silicate (mass fraction 10 %) as the intercalated and delaminated nanocomposites, showed no enhancement in thermal stability. This suggests that the nanostructure is critical to improved thermal stability. Third, the TGA data showed that the intercalated polyimide nanocomposite was more stable than the delaminated nanocomposite. Fourth, Giannelis describes self-extinguishing flammability behavior for the polyimide-clay nanocomposites.

**1.2. Cyanate Ester (CE) Resins** Our group and others have studied the flammability properties of CE resins and CE-fiber composites (15, 16). As VanKrevelen observed for phenolic resins the thermal stability and flammability of CE resins are closely related to their structure (17). Cost is a major concern for aircraft manufacturers considering use of cyanate

with Na-MMT, sonication for 10 minutes at 60 °C to 65 °C, was also used to aid dispersion of the clay (22). Without the sonication the Na-MMT did not disperse in the resin.

The samples were then cured by heating in a programmable, forced-air, convection oven. The cure heating schedule was as follows:

- 1) heat to 177 °C over 120 minutes, and then hold at 177 °C for 120 minutes.
- 2) cool to 30 °C over 60 minutes.

Post cure was accomplished according to the following:

- 3) heat to 100 °C over 15 minutes, and then hold at 100 °C for 30 minutes.
- 4) heat to 150 °C over 15 minutes, and then hold at 150 °C for 30 minutes.
- 5) heat to 200 °C over 15 minutes, and then hold at 200 °C for 60 minutes.
- 6) heat to 250 °C over 22 minutes, and then hold at 250 °C for 180 minutes.
- 7) cool to 30 °C over 60 minutes.

Analysis of the effect of the various additives on the cure was done by FTIR. The FTIR spectra taken following post-cure (Figure 2) show that the degree of cure is essentially the same for the pure cyanate esters as for the cyanate esters with the additives. Specifically, the doublet OCN stretch at  $\sim 2200\text{ cm}^{-1}$  is almost completely gone in the spectra for all 4 samples. The cured pure PT-15 actually has the most residual OCN.

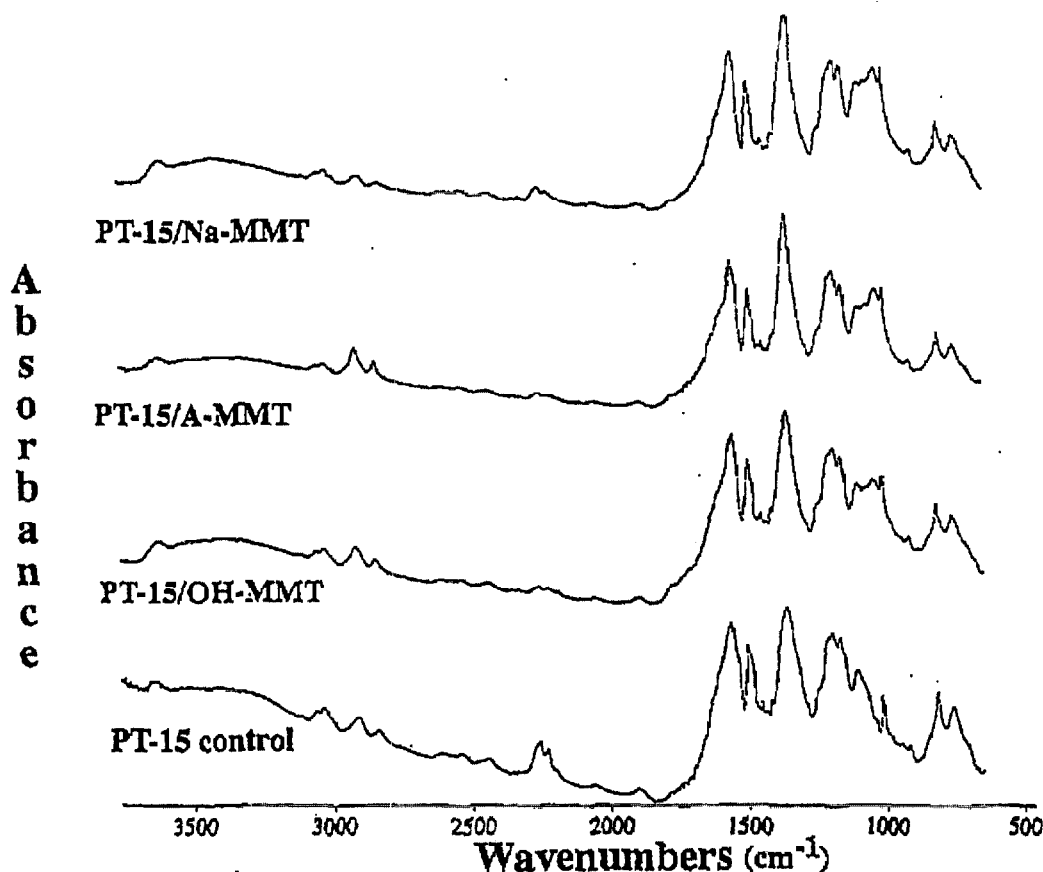


Figure 2. FT-IR of PT-15 cyanate ester, PT-15 w/ Na-MMT, PT-15 w/ A-MMT, and PT-15w/ OH-MMT, after post cure.

To determine the extent to which the clay layers expanded to accommodate the cyanate ester resins, X-ray diffraction (XRD) measurements were taken. X-ray diffraction data 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-clay monoliths were typically 14 mm by 14 mm with a 2 mm thickness.

ester resins in the interior of the aircraft. Therefore, an additive approach to improving the fire safety of these polymers is attractive. However, the 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. Recently, ultra-low flammability CE resins have been developed (18); however, while these materials are being developed, a need exists for reducing the flammability of more low cost, widely available, CE resins such as those based on bis-phenol-A and phenolic precursors. Considerable work has been done on cyanate esters evaluating conventional additive-type flame retardants such as brominated epoxies, phosphorus compounds, and sulfur linkages to name a few. A number of drawbacks have been identified with some of these approaches, while others show promise (19, 20, 21). To date, no cyanate ester clay nanocomposites have been reported in the literature.

We have prepared both intercalated and exfoliated CE clay nanocomposites, and we have characterized their flammability properties.

## 2. EXPERIMENTAL<sup>‡</sup>

**2.1. Materials** Phenolic-based cyanate ester resins were used throughout this study. Primaset PT-30 (PT-30) and Primaset PT-15 (PT-15), were obtained from LONZA Inc. The layered silicates (clays) used to prepare the nanocomposites were all montmorillonite-based clays, which we obtained from Southern Clay Products. The clays used include, purified sodium montmorillonite (Na-MMT), methyl, tallow, bis-2-hydroxyethyl, ammonium montmorillonite (OH-MMT), dimethyl, ditallow ammonium montmorillonite (A-MMT), and two different melamine-based ammonium montmorillonites: MEL-MMT, prepared from melamine hydrochloride, and MPP-MMT prepared from melamine pyrophosphate. Two additional treated clays were also prepared, which are similar to MEL-MMT and MPP-MMT except that some of the melamine salts were substituted by a non-polar ammonium salt. They are designated MEL-A-MMT and MPP-A-MMT.

TGA, in air, of the alkyl ammonium treated clays, OH-MMT and A-MMT, reveals that they contain a mass fraction of 30 %, and 40 %, alkyl ammonium, respectively. TGA of the melamine-treated clays, MEL-MMT and MPP-MMT, shows that they contain a mass fraction of 20 % melamine (or melamine and alkyl ammonium for MEL-A-MMT and MPP-A-MMT). This takes into account water loss, but assumes that the ammonium treatments completely volatilize.

**2.2. Procedure for Synthesis of Cyanate Ester Clay Nanocomposites** The cyanate ester resins (PT-15 or PT-30) contained in 125 mL polypropylene beakers were placed in a water bath maintained at 60 °C to 65 °C. A high-shear mixing blade was placed into the resin, and stirring at 52.4 rad/s (500 rpm) with minimal vortex was started. The additives were slowly added and mixed for fifteen minutes. All additives were dried at 150 °C for 1 h prior to use. Sixty gram samples were prepared each time. The mass fraction of additive was usually 10 % or 20 %. While still hot, the 60 g sample was divided into 2-23 g portions contained in Al dishes fashioned from heavy duty aluminum foil. These Cone Calorimetry samples measured 7.6 cm in diameter and 5 mm thick. Another sample (5 g) contained in a 5 cm diameter Al weighing dish was also prepared for FTIR, DSC, TGA and XRD analysis. Some tests were done in which a mass fraction of 0.02 % Co catalyst (based on the weight of cyanate ester resin) was added to decrease the gel time. In these tests, the catalyst was added after the 15 minutes of stirring with the additives and stirred for an additional 3 minutes. For resin mixed

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<sup>‡</sup> Certain commercial equipment, instruments, materials, services or companies are identified in this paper in order to specify adequately the experimental procedure. This in no way implies endorsement or recommendation by NIST.

Evaluations of flammability were done using the Cone Calorimeter (23). 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 (24). 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  $\pm 10\%$  ( $\sigma$ ). The carbon monoxide and heat of combustion data are reproducible to within  $\pm 10\%$  ( $\sigma$ ). The uncertainties for the Cone Calorimeter are based on the statistics derived from 4 replicate runs of several representative composites. The heat release rate data plots on all samples are based on the average of 2 to 4 replicates.

### 3. RESULTS AND DISCUSSION

**3.1. Nanocomposite Synthesis** In a previous publication (25) we showed that a nanomorphology is absolutely required to obtain improved flammability properties. Simply mixing the clay into the polymer to give dispersion of the inorganic in the polymer, at the agglomerate or the primary particle scale, to prepare a micro-composite does not reduce the flammability. Others have demonstrated the same for the other physical property improvements associated with polymer-clay nanocomposites. The intercalation of polymers or monomers into the gallery space between the clay layers is controlled by the compatibility of the polymer or monomer with the environment in the gallery. Organic materials that can interact strongly with the cations in the gallery will intercalate. Polar polymers such as polyethylene oxide, PEO, and monomers like methylmethacrylate will intercalate directly into sodium montmorillonite. However, most other organic materials require that the sodium present in the galleries of the clay be ion exchanged for a more organophilic cation like a quaternary alkyl ammonium (9). Precise matching of the gallery environment and the material to be inserted is needed to facilitate intercalation and ultimately exfoliation. Attempts have been made to model this process and to determine what the important factors are, so as to be able to predict the best approach for treating the clay for a given monomer or polymer (26, 27).

To prepare cyanate ester clay nanocomposites we needed to find an effective organic treatment for montmorillonite. We decided to use melamine salts to treat the montmorillonite. This treatment combines the approach used to intercalate pure novolac phenolic resins, namely the use of a primary alkyl ammonium (28), with the use of a structure very similar to the triazine. We felt a triazine-type structure would offer compatibility for the triazine crosslink functionality as it formed during the polymerization of the cyanate ester (Figure 3).

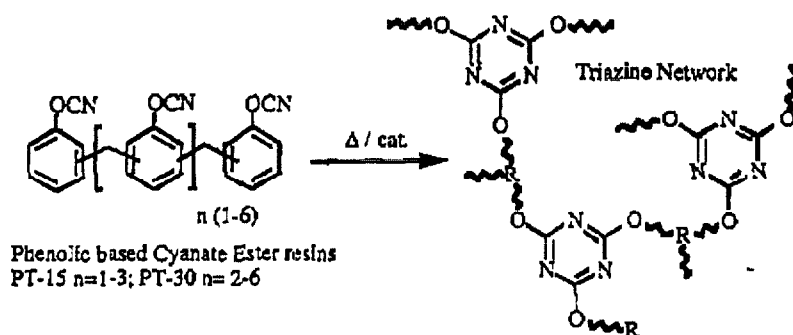


Figure 3. Phenolic based Cyanate Ester resin structure and Triazine structure.

In addition, melamine has known flame retardant properties (29), and has been used to obtain UL94 V-0 flammability rating in Nylon-6, polybutylene terephthalate, polyoxymethylene and polyphenylene sulfide clay nanocomposites, using the synthetic silicate fluorohectorite (30).

We also surveyed several other treatments, which might allow intercalation of phenolic-based

cyanate esters. We attempted melt intercalation of the two cyanate ester resins, PT-15 and PT-30, into: pristine sodium montmorillonite (Na-MMT), methyl, tallow, bis-2-hydroxyethyl, ammonium montmorillonite (OH-MMT), dimethyl, ditallow ammonium montmorillonite (A-MMT), melamine hydrochloride exchanged montmorillonite (MEL-MMT), melamine pyrophosphate exchanged montmorillonite (MPP-MMT); and two treated clays similar to MEL-MMT and MPP-MMT. These are designated MEL-A-MMT and MPP-A-MMT, and are prepared by substituting a less polar ammonium salt for some of the melamine salt.

The XRD characterization of the melamine-treated clays, and the cured PT-15 cyanate ester clay composites are shown in Figure 4. The XRD data reveals the expansion of the layer spacing from treatment of the Na-montmorillonite clay with the organic ammonium salts. The d-spacings increase from 1.2 nm for Na-MMT ( $2\theta$  of  $7.5^\circ$ ), to a d-spacing of 1.3 nm ( $2\theta$  of  $6.8^\circ$ ) for MEL-MMT and MPP-MMT, and to a d-spacing of 1.5 nm ( $2\theta$  of  $6.0^\circ$ ) for both MEL-A-MMT and MPP-A-MMT. The lack of an XRD peak in the low angle region for the PT-15/MEL-MMT and PT-15/MPP-MMT composites indicates the formation of a disordered, delaminated, nanocomposite structure (31). However, XRD peaks in the PT-15/MEL-A-MMT and PT-15/MPP-A-MMT samples remain unchanged, suggesting no intercalation. Only an immiscible mixture formed using the latter two clays. It appears the compatibility of the PT-15 resin with the melamine-treated clays is better than with the clays that contain melamine and quaternary ammonium cations.

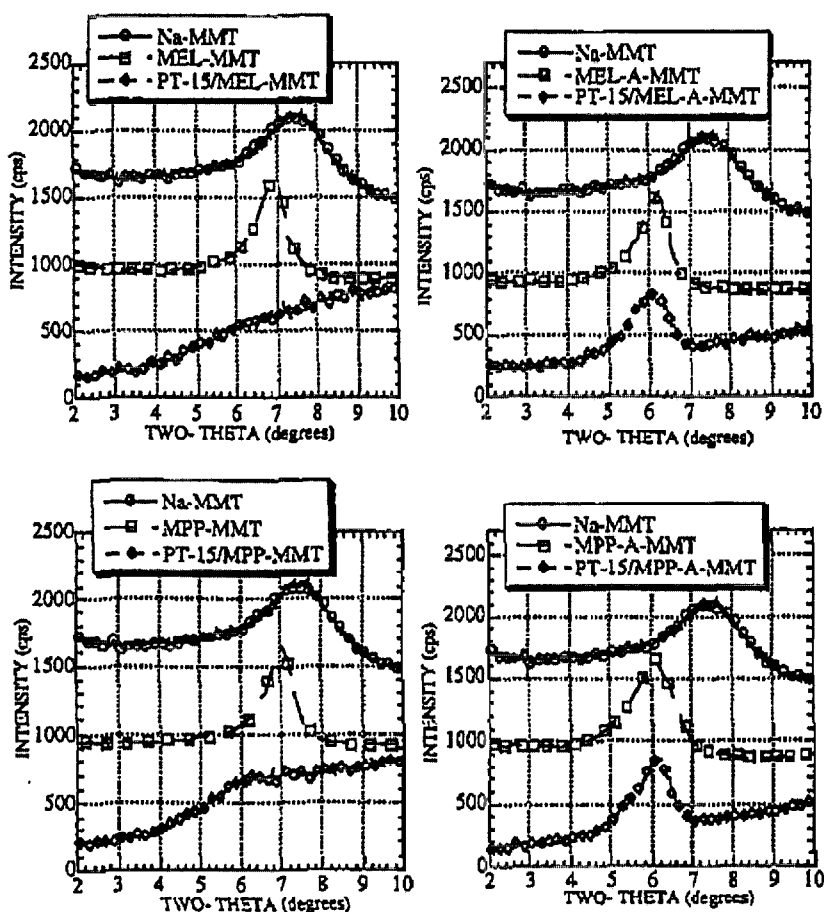


Figure 4. X-ray diffraction data for pristine sodium montmorillonite (Na-MMT), and cyanate ester resin PT-15 with either, MEL-MMT, MPP-MMT, MEL-A-MMT or MPP-A-MMT. In each case, the mass fraction of additive is 10 %. This data indicates the formation of a disordered delaminated nanocomposite (31) structure for the PT-15/MEL-MMT and PT-15/MPP-MMT nanocomposites. However, XRD peaks in the PT-15/MEL-A-MMT and PT-15/MPP-A-MMT samples remain unchanged suggesting no intercalation.

The XRD characterization of PT-15 cyanate ester resin with: dimethyl, ditallow ammonium montmorillonite (A-MMT); methyl, tallow, bis-2-hydroxyethyl, ammonium montmorillonite (OH-MMT), or pristine sodium montmorillonite (Na-MMT) is shown in Figure 5. This data establishes that PT-15 w/ 10 % A-MMT and PT-15 w/ 10 % OH-MMT are intercalated nanocomposites with 3.6 nm and 3.8 nm d-spacings respectively. For PT-15 w/ 10 % A-MMT this corresponds to a 0.4 nm expansion of the clay layers. For PT-15 w/ 10 % OH-MMT a 2 nm expansion is observed. In addition, the data for PT-15 w/ 5 % Na-MMT indicates it is a disordered, delaminated, nanocomposite (31).

The XRD data for PT-30 cyanate ester resin with: OH-MMT, and Na-MMT is shown in Figure 6. This data indicates that PT-30 w/ 10 % OH-MMT is an intercalated nanocomposite with a 4.0 nm d-spacing. In addition, the data for PT-15 w/ 5 % Na-MMT indicates it is a disordered, delaminated, nanocomposite (31).

The XRD data for PT-30 cyanate ester resin with A-MMT is shown in Figure 7. Although, both samples have the same main (001) peak ( $2\Theta = 2.7^\circ$  (d-spacing of  $\sim 3.2$  nm)), the loss of the shoulder in the XRD of A-MMT at  $2\Theta = 4.4^\circ$ , and the loss of the peak at  $2\Theta = 7.2^\circ$ , coupled with the appearance of a new peak at  $2\Theta = 5.5^\circ$  provides evidence that the PT-30 with A-MMT is an intercalated nanocomposite. However, comparison of the XRD data (d-spacings) for PT-15 and PT-30 (Figure 5 versus Figure 7) shows, that when combined with A-MMT, the lower molecular weight PT-15 intercalated more resin in the galleries than the PT-30. This is consistent with Giannelis' results on polymer melt intercalation kinetics, which show the molecular weight dependence for polymer intercalation to be similar to self-diffusion in the bulk, i.e., apparent diffusivity ( $D$ )  $\sim M_w^{-2}$  (32).

As stated above we evaluated a variety of clay treatments to determine which treatments would render the clay compatible with the cyanate ester and the triazine functionality. The melamine-treated clays were investigated because of melamine's similar triazine structure, and it's known flame retardant properties. However, an additional benefit was envisioned for both the melamine-treated clays (MEL-MMT, MPP-MMT) and the bis (hydroxyethyl) substituted ammonium treated clay (OH-MMT). Since, both these clay treatments have active-hydrogen functional groups, they can react with the cyanate esters. The reaction of the amine on melamine with the cyanate ester resin is shown in Figure 8. This reaction should result in formation of a stable isourea linkage between the triazine network and the melamine. This attaches the network to the surface of the silicate layer through the ammonium-silicate ionic bond. A strong interaction, or bond, between polymer and the silicate has been shown to improve both the thermal stability (33) and mechanical properties of nanocomposites (5). In addition, it has been shown, that when the catalyst or reactive cite for polymerization resides in the gallery, the system is driven to complete *exfoliation* by the driving force of the polymerization reaction (34, 35).



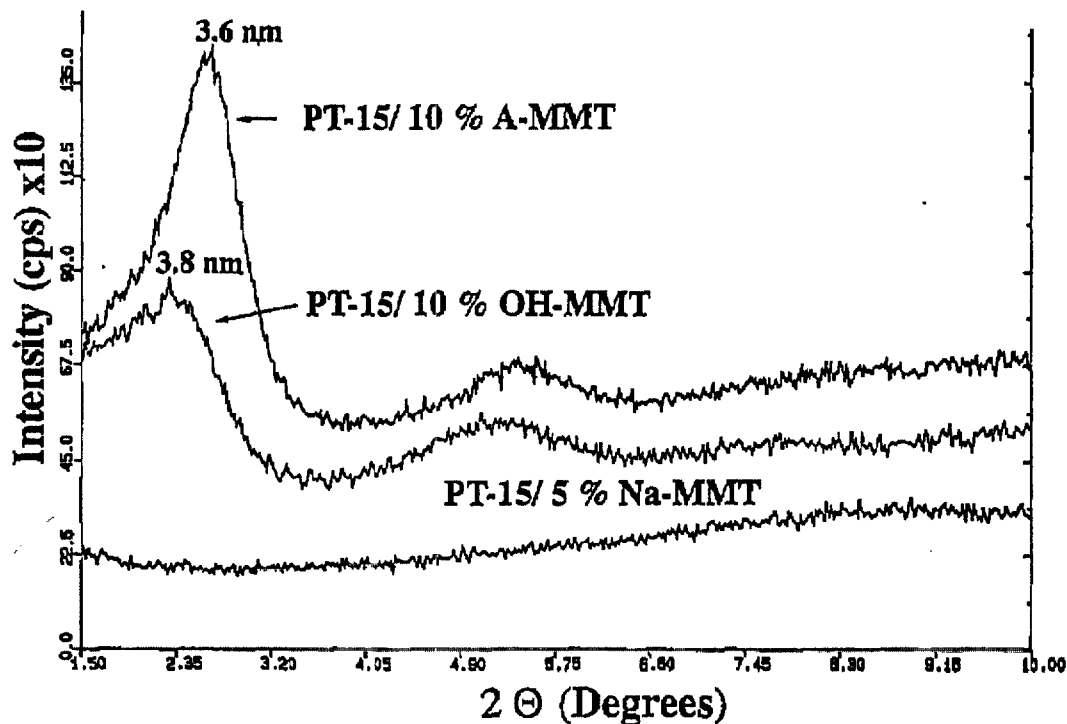


Figure 5. X-ray diffraction data for PT-15 with: A-MMT, OH-MMT, or Na-MMT. This data indicates that the PT-15 w/ 10 % A-MMT is an intercalated nanocomposite with a 3.6 nm d-spacing. This is a 0.4 nm expansion of the initial 3.2 nm d-spacing for A-MMT. The same interpretation holds for PT-15 w/ 10 % OH-MMT. Here the 3.8 nm d-spacing of the nanocomposite represents a 1.8 nm expansion of the initial 1.8 nm d-spacing for OH-MMT. In addition, the data for PT-15 w/ 5 % Na-MMT indicates it is a disordered delaminated nanocomposite (31).

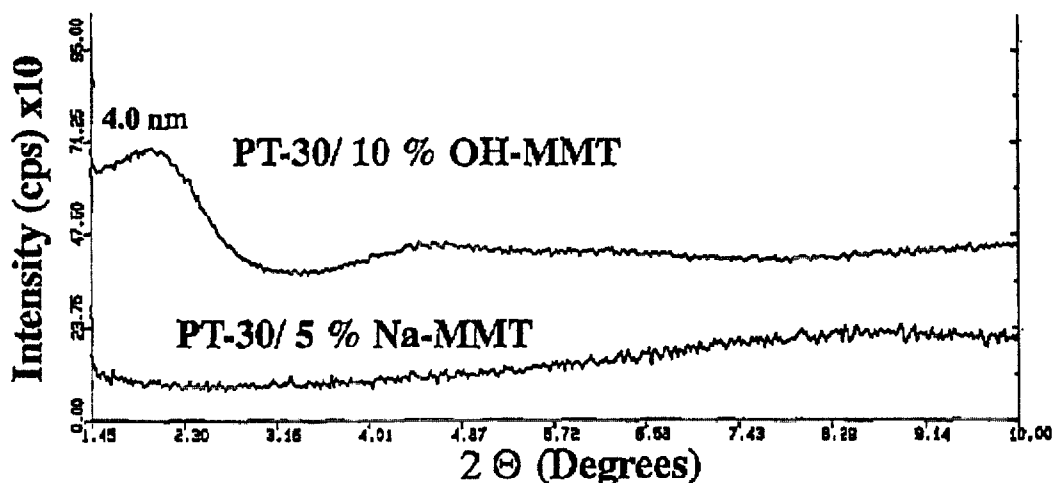


Figure 6. X-ray diffraction data for PT-30 cyanate ester resin with: OH-MMT or Na-MMT. This data indicates that PT-30 w/ 10 % OH-MMT is an intercalated nanocomposite with a 4.0 nm d-spacing. The 4.0 nm d-spacing represents a 2 nm expansion of the initial 1.8 nm d-spacing for OH-MMT. In addition, the data for PT-30 w/ 5 % Na-MMT indicates it is a disordered, delaminated, nanocomposite (31).

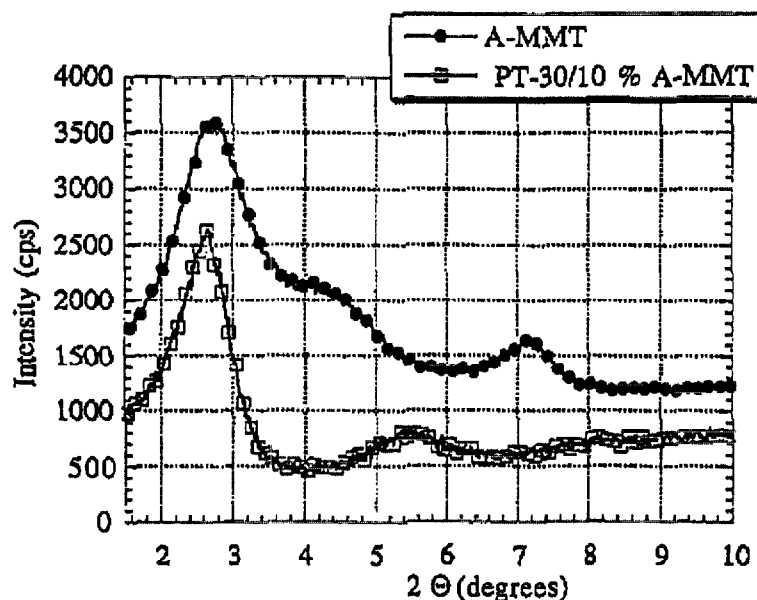


Figure 7. X-ray diffraction data for A-MMT, and PT-30 with A-MMT.

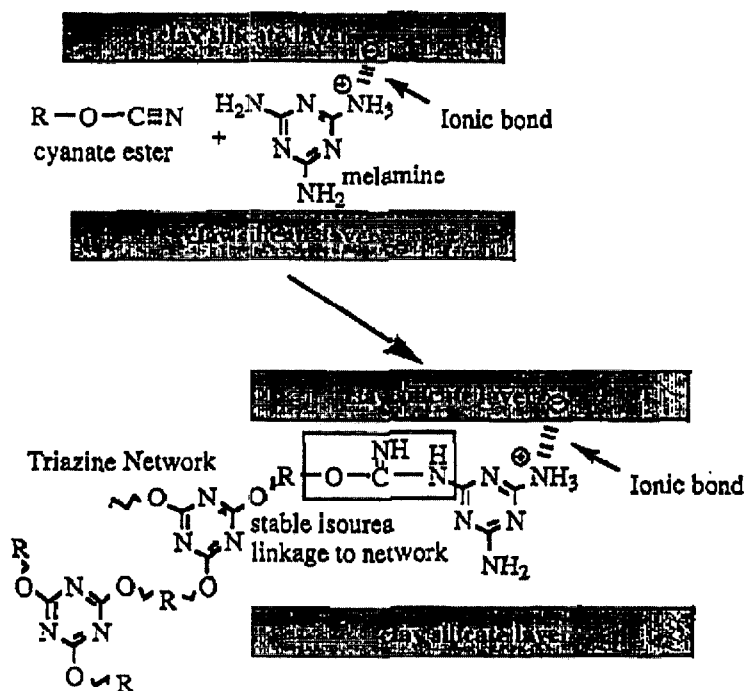


Figure 8. The reaction of the amine on melamine with the cyanate ester resin to form the isourea linkage between the triazine network and the melamine. This presumably occurs at more than one of the amines and tethers the network to the silicate layer without creating dangling-chains in the matrix.

Therefore, the reaction of the melamine-treated clays, and the OH-MMT, with the cyanate esters should assist in dispersing the clays in the resin. However, as Figure 9 shows, the reaction of the alcohol group from OH-MMT is not as straightforward as the melamine reaction. The alcohol first reacts with one mole of cyanate ester to form an iminocarbonate, which then reacts with 2 moles of cyanate ester to form the triazine plus another mole of alcohol. The alcohol produced is a dangling chain-end in the network. This may lower the mechanical properties of the network slightly. Based on the mole ratio of alcohol to cyanate ester (1 to 60 for a nanocomposite with a mass fraction of 10 % OH-MMT) one out of 60

cyanate ester groups in the matrix will be attached to the ammonium, and hence attached to the silicate layer, and one out of 60 cyanate ester groups will become a dangling chain-end in the matrix. These two effects may work in opposition to each other. Indeed, Pinnavaia has recently shown, in a polyurethane-montmorillonite nanocomposite, that dangling-chains formed in the polyurethane network, by reaction of isocyanate and primary alkylammonium, may serve to increase the elasticity of the matrix (36). In addition, he found in an epoxy-magadite nanocomposite that the dangling-chains weaken the matrix and thus counteract the reinforcing effect of the silicate layer (37). In contrast, since the melamine-treated clays are multi-functional they should not generate dangling-chains, and therefore should perform better, in terms of both thermal stability and mechanical properties.

**3.2. Nanocomposite Flammability Properties** We evaluated the flammability properties of the cyanate ester clay nanocomposites using the Cone Calorimeter. The results are shown in Figure 10, Figure 11, and Figure 12. The heat release rate (HRR) data shown in Figure 10 reveals that the two melamine-treated clays, MEL-MMT and MPP-MMT, give different results for PT-15. MEL-MMT is more effective than MPP-MMT at reducing the peak HRR. This may be due to the different sources of melamine used to prepare MEL-MMT and MPP-MMT. MEL-MMT was prepared from melamine hydrochloride, and MPP-MMT was prepared from melamine pyrophosphate.

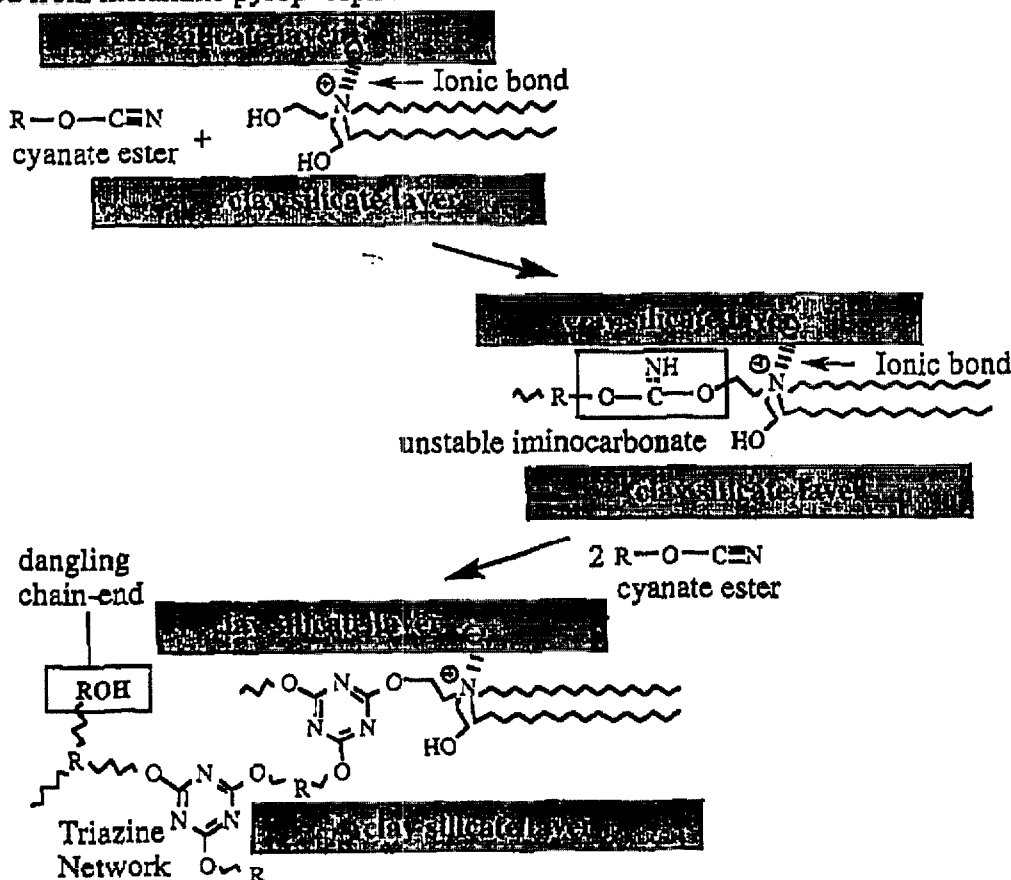


Figure 9. The reaction of the alcohol group from OH-MMT with one moles of cyanate ester to form an iminocarbonate, which then reacts with 2 moles of cyanate ester to form the triazine plus a mole of alcohol (a dangling-chain end).

In the ion exchange process the sodium salt of each melamine salt is generated as the melamine-clay is formed. The NaCl will not react with the clay, but the Na pyrophosphate (or the polyphosphoric acid formed in the aqueous-HCl) can react with the OH functionality in the clay. This may modify the chemical properties of the treated clay and may effect the thermal stability of the nanocomposite. Another possible reason for the different effectiveness

for the two melamine-treated clays is that the degree of distribution of the clay in each nanocomposite may be different. Figure 10 also shows that the immiscible composite, PT-15 with MPP-A-MMT, has the same flammability as the pure resin. This data confirms that the clay must be dispersed at the nano-scale to reduce the flammability. PT-15 with MEL-A-MMT gave the same result.

In addition to the HRR behavior, the Cone Calorimeter also allows characterization of: mass loss rate (MLR), specific extinction area (SEA, a measure of smoke density), carbon monoxide (CO) yield, and heat of combustion ( $H_c$ ). This yields information about how an additive, or change in polymer structure, affects the flammability. If the gas phase combustion processes change the  $H_c$ , SEA, and CO yield will be affected significantly. However, if the condensed phase processes are modified then these quantities will not change significantly, but the MLR will change. In all of the cyanate ester clay nanocomposites we evaluated we found that, aside from the HRR, the primary parameter influenced by the nano-dispersed clay was the MLR. None of the other measureands were affected. We have observed the same results for most other clay nanocomposites (15, 25).

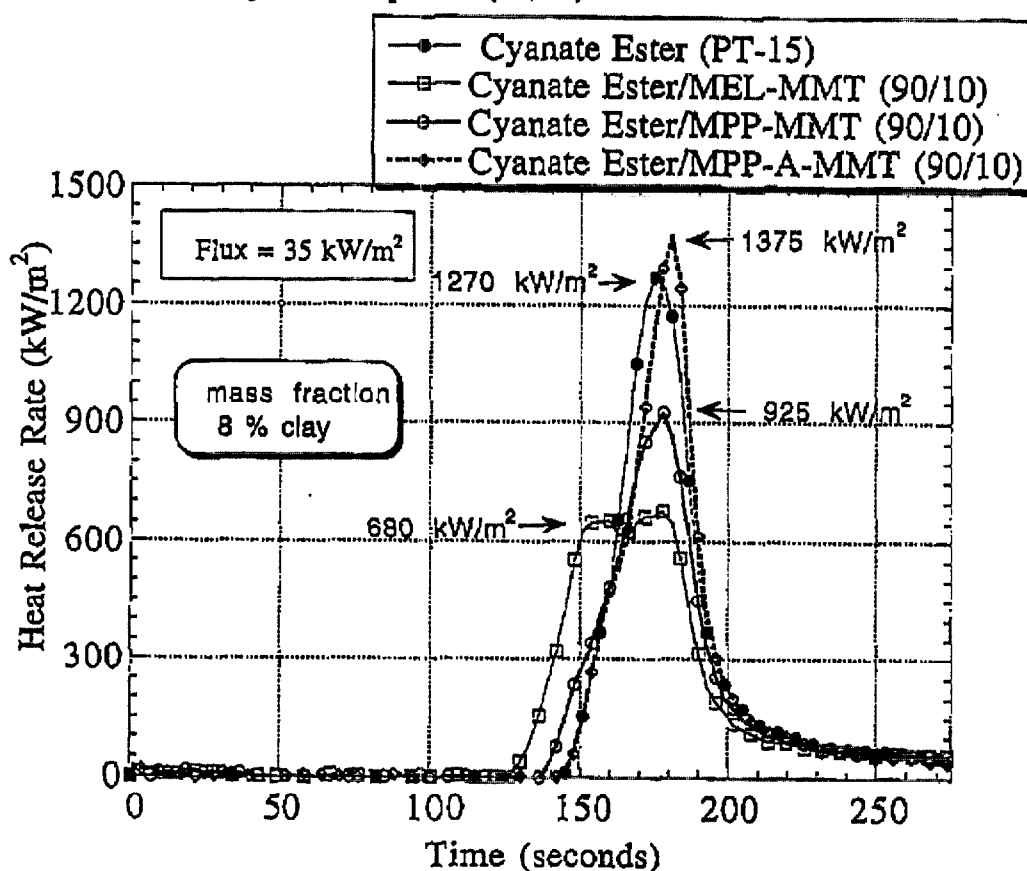


Figure 10. Heat release rate (HRR) data for cyanate ester resin PT-15, and PT-15 with: melamine hydrochloride exchanged montmorillonite (MEL-MMT), or melamine pyrophosphate exchanged montmorillonite (MPP-MMT) and melamine pyrophosphate / non-polar ammonium hydrochloride exchanged montmorillonite (MPP-A-MMT). A mass fraction of 10 % treated clay was used in each case.

The Cone Calorimeter data in Figure 11 shows the effectiveness of the MEL-MMT and MPP-MMT in the PT-30 resin. However, in these samples a mass fraction of 16 % clay is used. Surprisingly, the MPP-MMT reduces the peak HRR by 66 % while the MEL-MMT reduces the peak HRR by 54 %. The reasons stated above may explain the different degrees of effectiveness for the two melamine-clays, but the reasons for the reversal in relative effectiveness are unclear.

For purposes of comparison we also evaluated the flammability properties of PT-30 with a variety of commercial flame retardants based on melamine. We evaluated melamine pyrophosphate (MPP) and melamine cyanurate (MCY). In each case a mass fraction of 10 % additive was used. We also evaluated melamine diborate (MDB). In this case a mass fraction of 20 % additive was used. The PT-30/MPP had a peak HRR of 700 kW/m<sup>2</sup>, the PT-30/MCY had a peak HRR of 500 kW/m<sup>2</sup>, and the PT-30/MDB had a peak HRR of 460 kW/m<sup>2</sup>. The peak HRR for each of these systems is comparable to the results found here for the clay-nanocomposites.

The HRR data shown in Figure 12 reveals that the disordered nanocomposite, where no treatment is used on the clay, PT-15 with Na-MMT, has a 31 % lower peak HRR than the pure PT-15. Furthermore, we see that the two intercalated nanocomposites: PT-15 with A-MMT and PT-15 with OH-MMT have very different flammability properties. Recall that the PT-15 with OH-MMT has the reactive hydroxyethyl functionality, and that the reaction of the hydroxyethyl is expected to proceed as shown in Figure 9. Using OH-MMT we envisioned a significant reduction in HRR, just as we observed for the nanocomposites made from the reactive melamine-treated clays, MEL-MMT and MPP-MMT. However, instead the OH-MMT increases the flammability of the PT-15. To realize the magnitude of this effect the most appropriate comparison is to compare the PT-15/A-MMT to the PT-15/OH-MMT, since they are both intercalated nanocomposites.

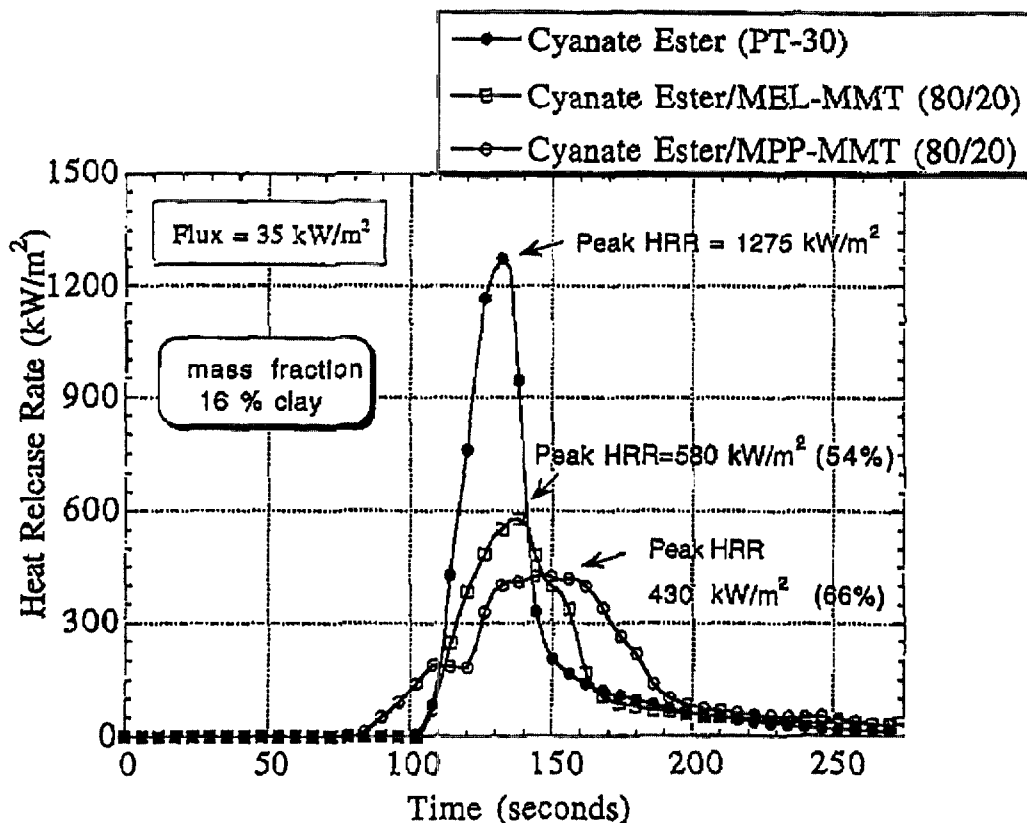


Figure 11. Heat release rate (HRR) data for cyanate ester resin PT-30 and PT-30 with either, melamine hydrochloride exchanged montmorillonite (MEL-MMT), or melamine pyrophosphate exchanged montmorillonite (MPP-MMT). A mass fraction of 20 % treated clay was used in each case.

The influence of the OH-MMT is to increase the peak HRR from 515 kW/m<sup>2</sup> to 1340 kW/m<sup>2</sup>. A possible reason for this loss in effectiveness may be due to the fact that the hydroxyl groups react with the PT-15 to form not only a direct linkage to the triazine network, but also to form another hydroxyl (a phenol), which is a dead-end or dangling end in the network (see Figure

9). Indeed, TGA shows that the PT-15 / OH-MMT nanocomposite has a 25 °C lower thermal stability than the PT-15 / A-MMT nanocomposite. Possibly, at high temperature the phenol catalyzes the triazine degradation. In contrast the PT-30/MEL-MMT and the PT-30/MPP-MMT, have 75 °C to 100 °C greater thermal stability than any of the other PT-30 clay nanocomposites (Na-MMT or OH-MMT or A-MMT). There are several differences between PT-30 melamine treated clay nanocomposites and the other nanocomposites. Therefore, it is difficult to comment on whether the improved thermal stability is due to the delaminated versus intercalated structure, or to the nature of the reaction of melamine with the cyanate ester, or to the inherent better thermal stability of the melamine treated clays. Additional investigations into these issues continue.

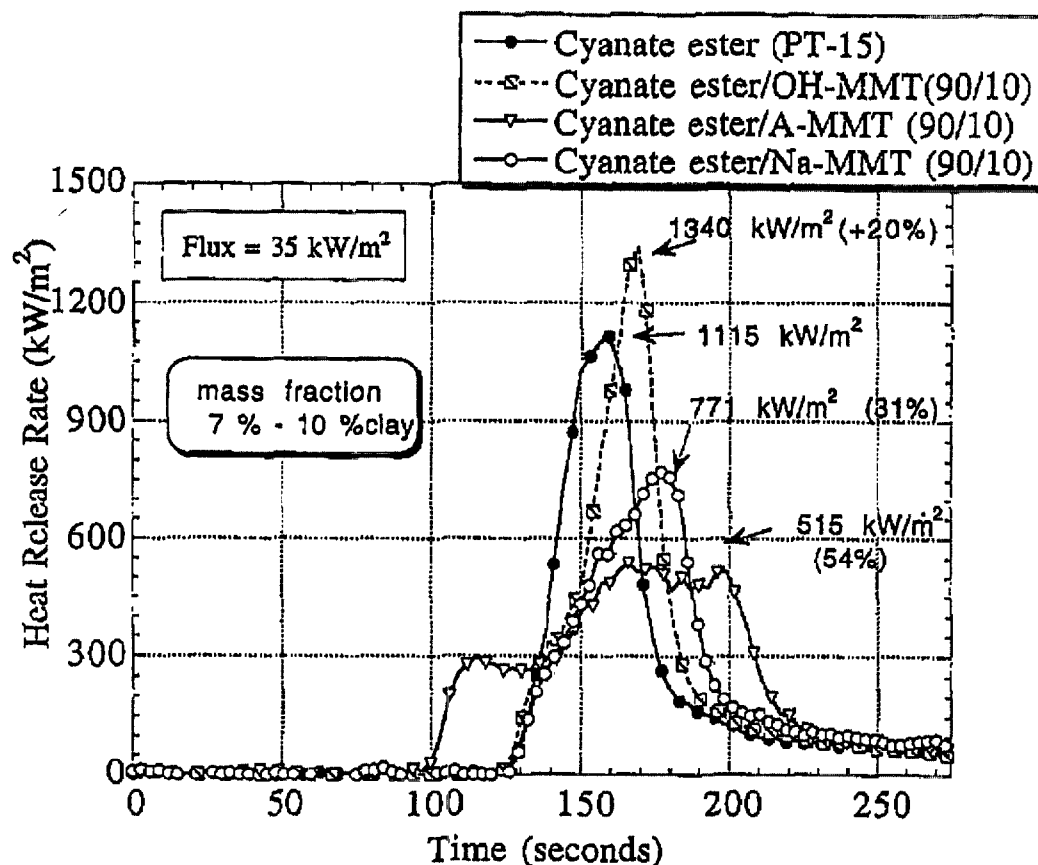


Figure 12. Heat release rate (HRR) data for cyanate ester resin PT-15 and PT-15 with: pristine sodium montmorillonite (Na-MMT), methyl, tallow, bis-2-hydroxyethyl, ammonium montmorillonite (OH-MMT), dimethyl, ditallow ammonium montmorillonite (A-MMT). A mass fraction of 10 % treated clay was used in each case.

**3.3. Char formation** The phenolic-based cyanate ester resins have unique flammability properties. They are a very high char yield system, but they are relatively flammable if not flame retarded. The large amount of char (60 % to 70 %) appears to form too slowly to prevent the violent degradation and rapid mass loss characteristic of these materials. During combustion we observed, as others have (16), that the char cracks under the pressure from rapid volatilization. The combustion samples burn in a characteristic and unusual manner. As the resin heats up some char forms, however, it appears to crack and many gas "jets" form on the surface of the sample. These "jets" ignite and burn violently much like small blow-torches. This results in a 30 % mass loss in only 1-2 minutes. However, the flammability behavior of the cyanate ester nanocomposites is different. The char which forms during combustion appears to crack less, and the number and intensity of the gas/flame "jets" is reduced, hence the lower HRR.

In other nanocomposite systems we have found, using XRD and TEM, that a common

carbonaceous-silicate nanocomposite char forms during combustion. The d-spacing of this multi-layer carbonaceous-silicate char is 1.3 nm for chars derived from nylon-6 clay nanocomposite and epoxy clay nanocomposites (15). We see the same type of char here. Furthermore, as we found before, the presence of the clay does not affect the char yield. Therefore, the flammability is not reduced by an increase in the amount of carbon (in the form of char) retained in the condensed phase. For several of the cyanate ester clay nanocomposites, e. g., PT-15 / A-MMT and PT-30 / A-MMT, the ordered multi-layered carbonaceous-silicate char structure observed by XRD has a d-spacing of 2.1 nm. This corresponds to a factor of 2 or 3 times as much carbonaceous material sandwiched between the silicate layers as we found in previous nanocomposite chars. In contrast, chars from combustion of another set of cyanate ester clay nanocomposites (PT-30 / Na-MMT, PT-30 / MEL-MMT, etc.) show no peaks in the low angle region of the XRD. This indicates a disordered carbonaceous-silicate char. Nanocomposites that yield chars with this later structure are equally effective at reducing flammability.

We will be using TEM and other techniques to further study the mechanism of flammability improvement in polymer clay nanocomposites. We will also evaluate the mechanical properties of the cyanate ester clay nanocomposites, to determine the optimum clay treatment for both flammability improvement and mechanical properties improvements.

#### 4. CONCLUSIONS

We have shown that the use of treated montmorillonite clay in cyanate ester resins yields *exfoliated and intercalated* montmorillonite in cured cyanate ester nanocomposites. This reduces the peak heat release rate by over 50%. We propose that improvements, such as better barrier properties and mechanical properties, induced in the polymer by the nano-dispersed clay, are also found in the char formed from combustion. It is these improvements in the quality of the char that result in reduced flammability.

#### 5. ACKNOWLEDGMENTS

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