

PHENOLIC CYANATE ESTER CLAY NANOCOMPOSITES:
EFFECT OF AMMONIUM ION STRUCTURE ON
FLAMMABILITY AND NANO-DISPERSION.

Jeffrey W. Gilman^{*1}, Richard H. Harris, Jr.¹, Catheryn L. Jackson²,
Alexander B. Morgan¹, Lori D. Brassell¹ and Douglas L. Hunter³

¹Fire Science Division, ²Polymers Division
National Institute of Standards and Technology^ψ
Gaithersburg, MD 20899

³Southern Clay Products, Inc., Gonzales, TX 78629

Introduction. 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, many groups are involved in research on polymers intercalated into the gallery spaces of layered silicates, due to the superior properties of the polymer-clay nanocomposites (PCN). Several groups have developed the methods to achieve molecular level incorporation of the layered silicate (montmorillonite) into the polymer by addition of a modified, or pristine silicate: either prior to or during the polymerization,^{1,2,3,4,5} to a solvent-swollen polymer,⁶ or to the polymer melt.^{7,8}

We have recently found that PCNs have reduced flammability.⁹ This is particularly significant since reduced polymer flammability using additives is often done at the expense of physical properties. We report here on the use of montmorillonite (MMT) dispersed at the nanometer level, in phenolic cyanate ester (CE) resins for reduced flammability. We show that the use of alkyl ammonium-treated MMT reduces the peak heat release rate (HRR) by over 50%. We also show that the choice of ammonium treatment used to compatibilize the clay with the matrix can dramatically alter the nano-dispersion and the flammability properties. Specifically, we report on two methods used to "tether" the clay to the cured phenolic triazine matrix.

Experimental. Phenolic-based CE resin, Primaset PT-15 and PT-30, were obtained from LONZA Inc. Cobalt Nap-All™ (6% Co in mineral spirits, OMG America)¹⁰ was used as the cure catalyst in all cures. MMT clays were obtained from Southern Clay Products. All clays were dried at 150 °C for 1 h prior to use. The clays used include: methyl, tallow, bis-2-hydroxyethyl, ammonium MMT (OH-MMT), dimethyl, dihydrogenated-tallow ammonium MMT (A-MMT), and two different melamine-based ammonium MMT: MEL-MMT, prepared from melamine hydrochloride, MPP-MMT prepared from melamine pyrophosphate, and two mixed treatment clays: MEL-A-MMT and MPP-A-MMT, which combine the use of the different melamines with the quaternary alkyl ammonium.

Preparation of Nanocomposites. CE resins, MMT (10%) and catalyst were mixed at 60 °C to 65 °C for 15 min in a high-shear mixer (52.4 rad/s, 500 rpm). The samples were cured using a standard CE cure schedule.¹¹

Characterization. The CE cure was analyzed by FTIR on a Mattson IR-1000 (KBr pellets, doublet OCN stretch at ~2200 cm⁻¹ was monitored) and differential scanning calorimetry (DSC) (TA instruments Thermal Analysis 2000 system, N₂, 10 °C/min). To determine the extent to which the clay layers expanded to accommodate the CE resins, X-ray diffraction (XRD) measurements were taken and transmission electron microscopy (TEM) was performed. XRD data were collected on a Phillips diffractometer using Cu K α radiation, ($\alpha=0.1505945$ nm). Bright field TEM images of nanocomposites were obtained at 120 kV, under low dose conditions, with a Phillips 400T electron microscope. The samples were ultramicrotomed with a diamond knife at 20 °C, to give 70 nm thick sections. The sections were transferred from water to carbon-coated (type B) Cu grids of 200 mesh. No heavy metal staining of sections prior to imaging was required.

Flammability Testing. Evaluations of flammability were done using the Cone Calorimeter at an incident heat flux (35 kW/m²) typical of a small-fire scenario.¹² Peak heat release rate (HRR), at 35 kW/m², is reproducible to within $\pm 10\%$ (one σ). The uncertainties for the Cone Calorimeter are based on the statistics derived from 4 replicate runs of several representative composites. See error bars on plots.

Results and Discussion. Nanocomposite Synthesis. To prepare CE clay nanocomposites we surveyed intercalation of CE resin with: A-MMT, OH-MMT, and four different melamine-based ammonium MMTs: MEL-MMT, MPP-MMT, MEL-A-MMT and MPP-A-MMT.

A-MMT is a quaternary alkyl ammonium treated MMT useful for intercalating many polymers. The OH-MMT and MEL-MMT provide the opportunity to form an ionic bond (tether) between the cured phenolic triazine matrix and the MMT. This intragallery reaction might also provide a driving force to facilitate intercalation, by locating cure sites inside the clay galleries.¹³ It could also improve the thermal stability,¹⁴ and the toughness of the nanocomposite. The OH-MMT will react with CE to form an unstable iminocarbonate, which then reacts with two moles of CE to give an ether linkage to the triazine, and a disubstituted-phenol. This effectively increases the molecular weight between crosslinks in the matrix (see Figure 1). The melamine treated MMTs may also form a tether between the matrix and the MMT, but through a different reaction: the reaction of the melamine NH₂ with the CE. This forms the stable isourea linkage (see Figure 2). This treatment combines the approach used to intercalate pure phenolic resins, i.e., the use of a primary alkyl ammonium,¹⁵ with the use of a structure very similar to the triazine. Melamine also has known flame retardant properties,¹⁶ and has been used to obtain UL94 V-0 flammability ratings in thermoplastic nanocomposites.¹⁷

DSC data of the CE cure, in the presence of the various organo-clays, shows that the potential for success for the OH-MMT and A-MMT is better than that for the melamine treated clays. Specifically, OH-MMT and A-MMT have lower exotherm maxima cure temperatures ($T_{c,max}$) than that for PT-15, either with, or without, Co catalyst, whereas with catalyst present the melamine treated MMTs have higher $T_{c,max}$ than PT-15 (see Figure 3). Therefore, intragallery cure will occur before cure in the bulk for A-MMT and OH-MMT, but the opposite may occur for the melamine treated MMT. The XRD characterization of PT-15/A-MMT and PT-15/OH-MMT establishes that they are indeed ordered-intercalated nanocomposites with 3.6 nm and 3.8 nm d-spacings, respectively. For PT-15/A-MMT this corresponds to a 0.4 nm expansion of the clay layers. However, for PT-15/OH-MMT a 2.0 nm expansion is observed. The greater layer expansion for OH-MMT versus A-MMT may be due to different intragallery reactions, or to different compatibility. TEM (not shown) of these samples shows intact tactoids (similar to Figure 4 left). So, it appears that the OH-MMT did react with the CE in the gallery and facilitate intercalation, but not exfoliation. The A-MMT also caused the CE to cure, as DSC shows a larger reduction in $T_{c,max}$ for the PT-15/A-MMT than for PT-15/OH-MMT (Figure 3), and since XRD and TEM (Figure 4) show it has an intercalated structure. Furthermore, FTIR analysis for the PT-15 w/ A-MMT and PT-15 w/ OH-MMT shows a greater degree of cure compared to the pure PT-15. As stated above, the $T_{c,max}$ for the PT-15/MEL-MMT (with catalyst) occurs at a higher temperature than the $T_{c,max}$ for PT-15 control (with catalyst) (see Figure 3). Therefore, the cure in the bulk resin is faster than intragallery cure via melamine-CE reactions. The XRD of the PT-15/MEL-MMT and PT-15/MPP-MMT samples indicates that they are disordered, due to the absence of low angle peaks. TEM analysis (Figure 4) of these materials shows the samples still contain large MMT tactoids. With no peaks in the XRD they are either disordered-immiscible or disordered-intercalated. The polymerization reaction may encapsulate the clay tactoids, defeat the driving force to facilitate intercalation, and prevent nano-dispersion. However, another possibility is that some reaction and intercalation occurs, but only in a heterogeneous fashion, and to a limited extent: just enough to disorder the clay. Indeed, the results for the mixed treatment clays, PT-15/MEL-A-MMT and PT-15/MPP-A-MMT, tend to support the second theory. Following cure of these samples, XRD showed no change in the low angle peak ($2\theta = 6.0^\circ$, 1.47 nm) indicating ordered-immiscible mixtures. If the cure caused disordering these samples would show no peaks either.

Nanocomposite Flammability Properties. The HRR results for the intercalated nanocomposites, PT-15/A-MMT and PT-15/OH-MMT, are shown in Figure 5. PT-15/A-MMT has a 54% lower peak HRR than the PT-15. However, PT-15/OH-MMT has very different flammability properties. Instead of reducing the flammability the OH-MMT increases the HRR of the PT-15. To realize the magnitude of this effect compare the PT-15/A-MMT to the PT-15/OH-MMT. The effective influence of the OH-MMT is to increase

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the peak HRR from 515 kW/m² to 1340 kW/m². A possible reason for this loss in effectiveness may be due to the phenol functionality formed (Figure 1). The origin of this de-stabilizing effect is under investigation. We have also seen this effect in polybenzoxazines /OH-MMT nanocomposites.¹⁸

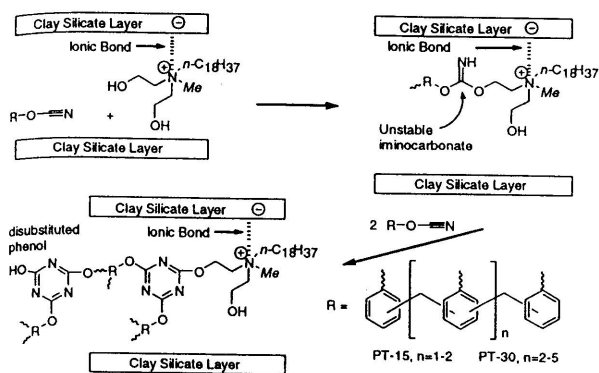


Figure 1. The reaction of OH-MMT with PT-15.

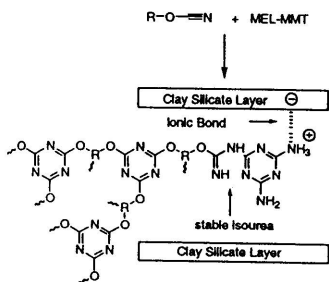


Figure 2. The reaction of melamine with the PT-15.

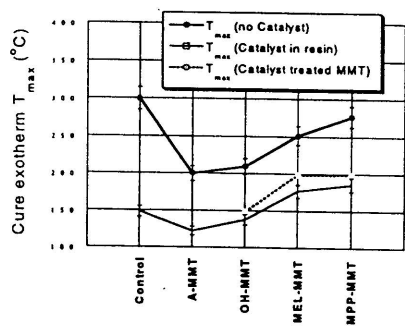


Figure 3. Cure-exotherm temperatures (T_{c,max}) for PT-15 and PT-15 /MMTs.

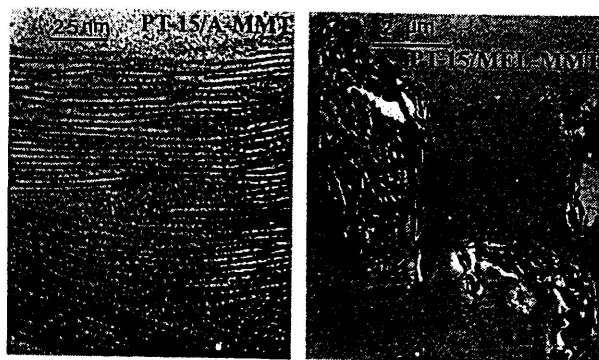


Figure 4. TEM of PT-15/A-MMT (left) and PT-15/MEL-MMT (right).

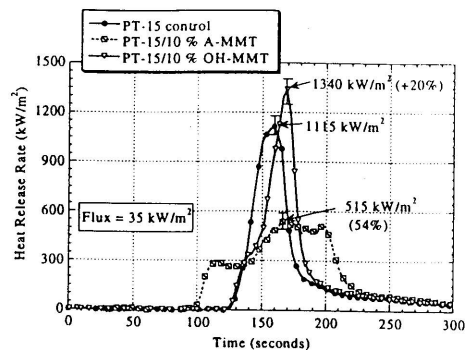


Figure 5. HRR data for PT-15, PT-15/A-MMT and PT-15/OH-MMT.

The HRR data (not shown) for the melamine MMTs reveals that the MPP-MMT reduces the peak HRR by 27 %, while the MEL-MMT reduces the peak HRR by 46 %. The mixed treatment clays MEL-A-MMT and MPP-A-MMT had no effect on HRR. For comparison, the conventional flame retardants (CFR) melamine pyrophosphate (MPP) and melamine cyanurate (MCY) in PT-30 (10 % additive) have a peak HRR of 700 kW/m², and 500 kW/m², respectively. These peak HRRs are comparable to the results found here for the clay-nanocomposites. The MEL-MMT and MPP-MMT have similar fraction of melamine compared to the CFR formulations, and produce no improvement in FR effect, i.e., not even the simple sum of the FR effect of melamine and the typical FR effect from the nanocomposites is observed. However, the intercalated nanocomposite, PT-15/A-MMT, has a 54 % lower HRR without CFR, and it may also have improved mechanical properties.^{13c} compared to the conventional flame retarded CE.

Conclusions. We have shown that the ammonium treatment used to compatibilize the MMT with the polymer can dramatically alter nano-dispersion and flammability properties. For intercalated PT-15/MMT, nanocomposites this reduces the peak HRR by over 50 %.

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