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# Polystyrene Nanocomposites Based on An Oligomerically-Modified Clay Containing Maleic Anhydride

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## Abstract

An oligomerically-modified clay containing maleic anhydride was used to prepare polystyrene-clay nanocomposites by melt blending and the effect of this modified clay on the thermal stability and fire performance was studied. These nanocomposites were characterized by X-ray diffraction, transmission electron microscopy, thermogravimetric analysis and cone calorimetry. The results show a mixed

immiscible/intercalated/delaminated morphology. The maleic anhydride modified clay improved the compatibility between the clay and the polystyrene.

## Keywords

Nanocomposites, Polystyrene, Fire retardancy, Maleic anhydride, Clays

## 1. Introduction

Polymer clay nanocomposites exhibit improved properties, including barrier, fire and mechanical, at very low clay loading (3%, for example) and this has been an active research field in polymer chemistry and material science for the past decade. The most commonly used clay is montmorillonite, while hectorite is less commonly used. Hectorite is a magnesium–lithium trioctahedral smectite that occurs in the Mojave Desert near Hector, California; its chemical composition is  $[(Mg_{5.33}Li_{0.60})(Si_{7.98}Al_{0.02})O_{20}(OH)_4]Na_{0.76}$  [1]. The interlayer of hectorite is the most expandable of all smectite clays and it is an excellent adsorbing agent for polar organic molecules. The hydrophilicity of smectites arises from the negative charge on the clay layers and from the presence of exchangeable cations in the interlayer space [2].

The preparation of a nanocomposite may be accomplished either by an in-situ polymerisation or by blending, with melt blending the preferred industrial process. Nanocomposites are described according to the dispersion of the clay in the polymer. In order to form a nanocomposite, the clay must be uniformly distributed, if this uniform distribution is not achieved, the material is best described as a microcomposite or as an immiscible nanocomposite. In an immiscible nanocomposite the clay is not well-dispersed and it is acting as a conventional filler and not as a nano-dimensional material. When the clay is well-dispersed, two different types of nanocomposites may be obtained. If the registry between the clay layers is maintained, intercalated nanocomposites are obtained. If this registry between the clay layers is lost, the nanocomposite is described as delaminated, also known as exfoliated. It is generally accepted that delamination is required for enhanced permeability and mechanical properties while the type of the nanocomposite, intercalated or delaminated, does not seem to be important for thermal properties and fire retardancy of polymer materials [3], [4].

It can be difficult to achieve true nano-dispersion of the clay in the polymer matrix, because the majority of polymers are hydrophobic while the clays are hydrophilic. Many methods have been used to improve the compatibility between the clay and the polymer; the commonly used method is to ion exchange an organic 'onium' ion for the inorganic cation in the gallery space of the clay. The addition of monomeric modified clays can improve the interfacial adhesion [5], [6]. Attachment of polymer to the silicate layers has been shown to be akin to polymer brushes at the clay surface and promotes compatibility [7]. The direct use of compatibilisers can promote the compatibility of the clay and polymer and, sometimes, more than one method has been used to obtain good nano-dispersion.

Maleic anhydride (MA) or polymer-grafted-MA has been used as a compatibiliser to enhance the compatibility between the polymer and the pristine or organically-modified clay. Much work has been done with polyolefin-graft-MA as compatibiliser to enhance the possibility of intercalation of polymer between the clay layers while less work has been done with polystyrene-graft-MA. Wang and Wilkie [8] prepared polystyrene- (PS-) and polypropylene- (PP-) clay nanocomposites by in situ reactive

blending with both the organically-modified clays and the pristine inorganic clay in the presence of maleic anhydride. The presence of maleic anhydride increases the possibility of nanocomposite formation for polystyrene but this does not appear to help with polypropylene; it is a challenge to make polypropylene nanocomposites if one uses virgin polypropylene rather than the graft copolymer with maleic anhydride. Hasegawa and Usuki [9] reported that polyolefins grafted with 0.09–4.5% MA groups intercalate into the stearyl ammonium organically-modified clay. Molten MA-modified polypropylene continuously intercalates into the clay galleries and the silicate layers delaminate spontaneously without shear. When shear is applied, the silicate layers homogeneously disperse into MA-modified polypropylene. Nam et al. [10] combined polypropylene (PP)-*g*-MA and an organically modified clay to prepare polypropylene/clay nanocomposites by melt extrusion and obtained intercalated nanocomposites with an increased modulus, compared with the PP matrix in the absence of clay. Kim et al. [11] prepared a polymer clay nanocomposite by melt blending PP, PP-*g*-MA and organically modified clay and found that this had enhanced thermal stability, compared with the PP and PP-*g*-MA matrix. Wang et al. [3] reported polypropylene/clay nanocomposites modified with various levels of maleic anhydride grafted polypropylene compatibiliser using a twin-screw extruder. They found that there is an optimum level of compatibiliser, which yields the greatest improvement of composite properties. Though PP-*g*-MA with low molecular weight and high MA content could lead to good clay dispersion, it resulted in less improvement in both the mechanical and thermal properties of polypropylene/clay nanocomposites.

In this work, an oligomerically-modified clay, prepared by ion-exchange with the oligomer prepared from maleic anhydride (MA), styrene (ST) and vinylbenzyltrimethylammonium chloride (VBTACl) terpolymer, herein called MAST, was used to prepare polystyrene–clay nanocomposites by melt blending.

## 2. Experimental

### 2.1. Materials

The majority of chemicals used in this study, including (ar-)vinylbenzyltrimethylammonium chloride (VBTACl), maleic anhydride (MA), styrene, 2,2'-azobisisobutyronitrile (AIBN), inhibitor removal reagents, polystyrene (PS) (melt flow index 200 °C/5 kg, 7.5 g/10 min,  $M_w = 230,000$ ), were acquired from the Aldrich Chemical Co. Pristine hectorite clay was provided by Elementis Specialties, Inc.

### 2.2. Instrumentation

X-ray diffraction (XRD) patterns were obtained using a Rigaku Geiger Flex, 2-circle powder diffractometer equipped with Cu-K $\alpha$  generator ( $\lambda = 1.5404 \text{ \AA}$ ); generator tension is 50 kV and generator current is 20 mA. All the samples were compression moulded at 170–180 °C into 20 mm  $\times$  15 mm  $\times$  1 mm plaques for XRD measurements. Thermogravimetric analysis (TGA) was performed on a Cahn TG131 unit under a 30 ml/min flowing nitrogen atmosphere at a scan rate of 10 °C/min from 20 °C to 600 °C. Bright field transmission electron microscopy (TEM) image was obtained at 120 kV, under low-dose conditions, with a Phillips 400T electron microscopy. The sample was ultramicrotomed with a diamond knife on a Leica Ultracur UCT microtome at room temperature to give 70-nm-thick section. The section was transferred from water to 200 mesh carbon-coated Cu grids. The contrast between the layered silicate and the polymer phase was sufficient for imaging, so no

heavy metal staining of sections prior to imaging was required. Cone calorimetry was performed using an Atlas Cone 2 instrument according ASTM E 1354 at an incident flux of 35 kW/m<sup>2</sup> or 50 kW/m<sup>2</sup>. Exhaust flow was set at 24 L/s and the spark was continuous until the sample gets ignited. Cone samples were prepared by compression moulding the sample (20–50 g) into square plaques using a heated press. Typical results from Cone calorimetry are reproducible to within about ±10%; these uncertainties are based on many runs in which thousands of samples have been combusted [12], [13].

### 2.3. Preparation of terpolymer MAST modified clay (Fig. 1)

In a 500 ml three-necked round bottom flask were placed 25 g (0.25 mol) maleic anhydride (MA), 23 g (0.22 mol) of inhibitor-free styrene, 2.0 g (0.010 mol) of 4-vinylbenzyltrimethylammonium chloride (VBTACl), 5 g of 2,2'-azobisisobutyronitrile (AIBN), and 300 ml solvent (CHCl<sub>3</sub>/2-butanone = 1/1). The contents of the flask were stirred until all had dissolved at room temperature under a nitrogen flow, then it was heated with stirring to 60 °C using an oil bath. After 1 h, a light yellow solution appeared. The contents of the flask were heated for an additional 2 h, then the mixture was cooled to room temperature and the solvent was evaporated. The resulting solid was dissolved in acetone, then precipitated by the addition of methanol; 43 g of a white solid, MAST, was recovered and its molecular weight was in the range of 5200 ± 1000, based on the relative viscosity of standard polystyrene-*co*-maleic anhydride. <sup>13</sup>C NMR (75 MHz, acetone-*d*<sub>6</sub>, δ, ppm) 19.70, 22.99, 28.67, 34.48, 39.71, 42.69, 51.63, 53.22, 129.64, 138.50, 172.78 (anhydride C=O). Major IR peaks, (KBr, cm<sup>-1</sup>) 3415, 3031, 2900, 1856 (asymmetric stretch of anhydride C=O), 1779 (symmetric stretch of anhydride C=O), 1636, 1495, 1455, 1226, 1080, 956 (anhydride C–O–C), 926 (anhydride C–O–C), 757, 705.

A 15.8 g portion of clay in 1000 ml distilled water and 500 ml acetone was stirred at room temperature for 5 h. A 94 g portion of the MAST oligomer, dissolved in 1000 ml of acetone in a 3000 ml round bottom flask, was added drop-wise to the dispersed clay; a precipitate formed immediately and the slurry was stirred at room temperature for 12 h. After the stirring was stopped, the supernatant liquid was poured off and a fresh mixture of H<sub>2</sub>O/acetone (40/60) was added and the slurry was stirred again for additional 12 h at room temperature. The slurry was filtered and the precipitate was air-dried for 1 day and then in a vacuum oven at 40 °C for 48 h and 98 g of clay was obtained. Infrared, (KBr, cm<sup>-1</sup>): 1845, 1778 (anhydride), 1717 (ester/acid). This material is referred to as MAST hectorite clay in this paper.

### 2.4. Preparation of polymer–clay nanocomposites by melt blending

All the nanocomposites in this study were prepared by melt blending in a Brabender Plasticorder at high speed (60 rpm) at 190 °C for 15 min. The composition of each nanocomposite is calculated from the amount of pristine clay (derived from TGA data) and polymer charged to the Brabender.

### 2.5. Measurement of molecular weight

The molecular weights were determined by relative viscosity measurements using standard polystyrene-*co*-maleic anhydride. The viscosity average molecular weight was 5200 ± 1000.

## 3. Results and discussion

In order to prepare polymer clay nanocomposites, the gallery space must be large and sufficiently organophilic to permit the entry of the organic polymer. The usual treatment is to replace the

inorganic ions of clay by an ammonium ion that contains at least one long alkyl chain. The identity of the cation can be critical to the formation of the nanocomposite. The method of preparation to be used also affects the choice of the organically-modified clay. For instance, clay that contains one long alkyl chain and three methyl groups can be used in the in-situ polymerisation of polystyrene but two long alkyl chains are required for the preparation by melt blending [11], [14]. In addition, the nature of the polymer also affects the formation of the nanocomposite. For example, it is normally necessary to combine polypropylene-graft-MA and an organically-modified clay with polypropylene to prepare polypropylene/clay nanocomposites. In recent work from these laboratories, it has been shown that an oligomerically-modified clay (COPS clay) can be used directly to prepare delaminated and intercalated nanocomposites of PS, HIPS, ABS, PE, PP and PMMA by melt blending [15], [16]. In this work, another oligomerically-modified clay, known as MAST clay, is used to prepare nanocomposites; the synthetic route for the formation of this oligomeric salt is shown in Fig. 1. According to the molecular weight (5200), molar reaction ratio and reactivity ratios [17] every 50 styrene and maleic anhydride units will contain one ammonium cation and this modified clay is expected to exhibit good compatibility between the clay and polystyrene. The reactivity ratios for styrene and maleic anhydride,  $r_1 = 0.02 \pm 0.03$ ,  $r_2 = 0.02 \pm 0.02$  [17], suggest that an alternating polymer should be formed. The figure below simply shows the composition of the terpolymer and does not reflect its arrangement or the relative amounts. It is clear from infrared spectroscopy that the copolymer which was prepared does contain both maleic anhydride and styrene while some of the anhydride units have been converted to an ester/acid combination in the process of producing the oligomerically-modified clay. It is also obvious from the spectrum that some of this material is still in the form of the anhydride.

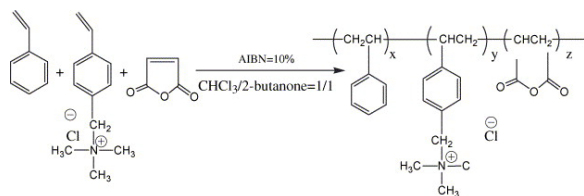


Fig. 1. The synthetic route for the formation of the terpolymer MAST.

### 3.1. X-ray diffraction (XRD) characterization of nanocomposites

X-ray diffraction, XRD, provides information on the changes of the inter-layer spacing of the clay upon the formation of a nanocomposite. The formation of an intercalated structure should result in a decrease in  $2\theta$ , indicating an increase in the d-spacing; the formation of a delaminated structure usually results in the complete loss of registry between the clay layers and no peak can be seen in the XRD trace. In some cases, a disordered immiscible system is obtained and this also shows no peaks, so the absence of an XRD peak cannot be taken as definitive evidence for the formation of a delaminated nanocomposite and additional evidence, usually transmission electron microscopy, is required. Fig. 2 presents the XRD data for the MAST clay and its PS nanocomposites. A small diffuse peak near  $1.8^\circ$  (d-spacing = 4.9 nm) suggests that a mixed intercalated/delaminated structure for the MAST modified clay while no peaks are observed for all of the PS MAST nanocomposites, which could mean either that a delaminated or an immiscible nanocomposite has been formed.

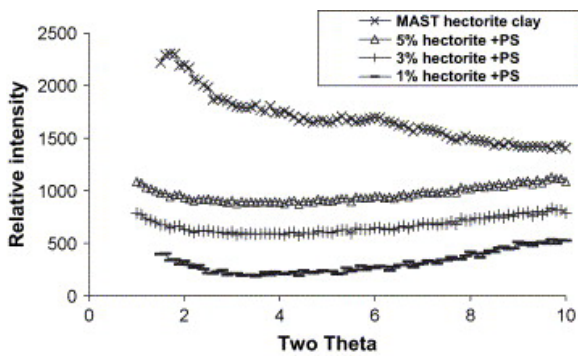


Fig. 2. XRD traces for MAST hectorite clay and its nanocomposites. The numbers in the legend refer to the amount of inorganic clay that is present.

### 3.2. TEM characterization of nanocomposites

Transmission electron microscopy, TEM, provides an actual image of the clay layers to permit the identification of the morphology of the nanocomposite. Usually both low magnification images, to show if the clay is well-dispersed or not, and high magnification images, to provide an identification of the morphology, are necessary. TEM is complementary to XRD, especially when peaks are not observed in XRD. Fig. 3 shows the TEM images for the PS MAST nanocomposite. The image on the left at low magnification shows both the presence of tactoids and, from the colour variation, that some of the clay is well-dispersed. At high magnification (on the right), one can see individual clay layers; some of these are in registry with other clay layers (with a d-spacing larger than 10 nm) while others do not show this registry. It is reasonable to describe this material as a mixed immiscible/intercalated/delaminated nanocomposite, i.e., this system contains clay which is acting as a filler and is not well-dispersed, the immiscible portion, and clay which is well-dispersed and this is present in both intercalated and delaminated forms.

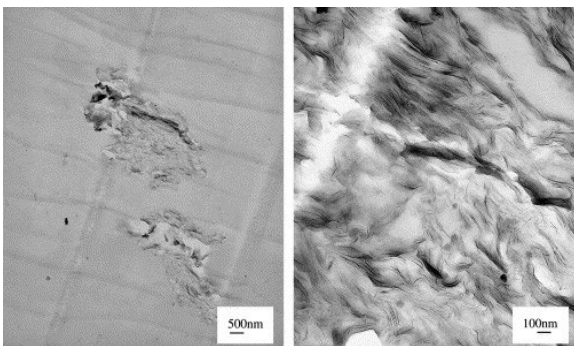


Fig. 3. TEM image at low (left) and high (right) magnification for PS melt blended with MAST clay (3% inorganic clay).

### 3.3. Thermogravimetric analysis (TGA) characterization of nanocomposites

Table 1 and Fig. 4 provide TGA data and curves for the polystyrene/MAST clay nanocomposites. The data includes the temperature at which 10% degradation occurs ( $T_{0.1}$ ), a measure of the onset temperature of the degradation, the temperature at which 50% degradation occurs ( $T_{0.5}$ ), the mid-point of the degradation process, and the fraction of materials which does not volatilise at 600 °C, denoted as char. One can see from these data that all the nanocomposites exhibit an increase in the

onset and mid-point temperature of degradation relative to virgin polystyrene, which indicates that PS MAST nanocomposites have enhanced thermal stability. The entry MAST hectorite clay in this, and other, tables, indicates the oligomerically-modified clay whose preparation was described in Section 2 while the entries 1% hectorite is the mass % of this oligomerically-modified clay that was combined with the polymer. It is normally observed for polystyrene nanocomposites that the onset temperature of the degradation does increase [14]. As the amount of clay increases, the onset temperature of the degradation is observed to decrease, probably because the MAST clay has a lower thermal stability than PS. In previous work, another oligomerically-modified clay, called COPS clay [15], [16], has been described. COPS clay is an oligomeric material which contains styrene and a small amount of vinylbenzyl chloride, which permits the formation of an ammonium salt and subsequent ion-exchange onto the clay. At the same clay loading, MAST clay shows 10–12% more char formation than does COPS clay, which suggests that the presence of the MA unit promotes char formation of polystyrene.

Table 1. TGA data of MAST clay and its nanocomposites

Sample	$T_{0.1}$ (°C)	$T_{0.5}$ (°C)	Char %
PS	381	421	0
MAST hectorite clay	257	411	36
1% MAST-hectorite + PS	407	438	2
3% MAST-hectorite + PS	400	441	5
5% MAST-hectorite + PS	386	440	8

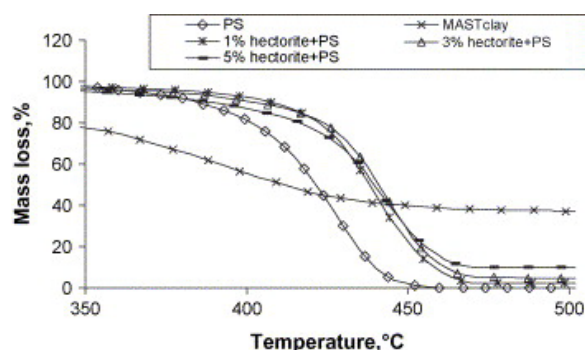


Fig. 4. TGA curve for MAST hectorite clay and its PS nanocomposite.

### 3.4. Cone calorimetric characterization of nanocomposites

The fire properties of the nanocomposites were assessed by cone calorimetry and the results are shown in Table 2 and Fig. 5. The major parameters that may be obtained from the cone calorimeter include: the time to ignition; the heat release rate and especially its peak value, PHRR; the time to PHRR; the specific extinction area, SEA, a measure of smoke; and the mass loss rate, MLR, which normally tracks very well with changes in the peak heat release rate. In previous work from NIST and these laboratories, it has been shown that the rate of heat release is significantly decreased for nanocomposites and the same reduction is seen, whether intercalated or delaminated nanocomposites are produced, while a microcomposite does not show a reduction in the peak heat release rate [11], [18]. It is generally considered in this laboratory that a reduction in PHRR must exceed 15% to be significant and indicate that the system has some amount of nano-dispersion. From



the data, one can see there is a substantial reduction in the peak heat release. As expected the mass loss rate drops and the amount of smoke is slightly increased. Compared with the previous study [16], COPS clay nanocomposites and MAST clay nanocomposites show the same reduction in the peak heat release (in both cases 32% reduction) and neither of these is close to 50–60% reduction, which is typically observed for well-dispersed PS nanocomposites [3]. This is an indication that very good nano-dispersion throughout the polymer matrix has not been obtained, in agreement with the XRD and TEM data, which indicate that a mixed immiscible/intercalated/delaminated structure has been obtained. XRD and TEM sample only a very small portion of the sample and cannot give information on the bulk while the cone calorimeter samples the bulk sample and can provide similar information.

Table 2. Cone calorimetric data of MAST modified hectorite clay blended with PS at 35 kW/m<sup>2</sup>

Sample	Time to ignition (s)	PHRR <sup>a</sup> (kW/m <sup>2</sup> ) (% reduction) <sup>b</sup>	Time to PHRR (s)	Total heat released (MJ/m <sup>2</sup> )	ASEA <sup>c</sup> (M <sup>2</sup> /kg)	MLR <sup>d</sup> (g/s m <sup>2</sup> )
PS	65 ± 2	1230 ± 56	142 ± 12	93 ± 5	1315 ± 81	30 ± 1
1% MAST-hectorite	38 ± 1	1011 ± 62 (18)	138 ± 10	88 ± 6	1336 ± 13	26 ± 1
3% MAST-hectorite	34 ± 2	894 ± 4 (32)	131 ± 17	85 ± 4	1323 ± 30	24 ± 1
5% MAST-hectorite	33 ± 2	728 ± 20 (41)	101 ± 25	75 ± 5	1327 ± 10	22 ± 1

<sup>a</sup>PHRR peak heat release rate.

<sup>b</sup>% Reduce = [PHRR(virgin polymer) – PHRR(nanocomposite)]/PHRR (virgin polymer).

<sup>c</sup>ASEA: Average specific extinction area.

<sup>d</sup>AMLR: Average mass loss rate.

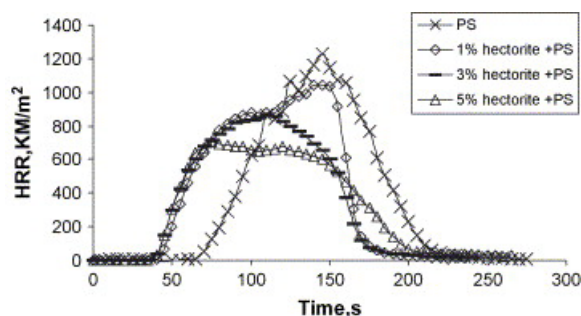


Fig. 5. Heat release rate curves for PS MAST clay nanocomposites.

## 4. Conclusions

Polystyrene–clay nanocomposites can be prepared by melt blending polystyrene with an oligomerically-modified MAST clay which contains maleic anhydride, styrene, and vinylbenzyltrimethylammonium chloride. The XRD and TEM reveal that the MAST clay nanocomposite has both some regions where tactoids are observed but, at the same time, there are also regions of good nano-dispersion. The results from cone calorimetry confirm these results and indicate that there is some fraction which is immiscible, since the reduction in the peak heat release rate does not approach the maximum value that has been observed with other organically-modified clays.

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