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Thermal Stability and Flame Retardancy of Poly(methyl methacrylate)-clay Nanocomposites

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Abstract

Three ammonium salts, hexadecylalldimethyl ammonium chloride (Allyl16), hexadecylvinylbenzylidimethyl ammonium chloride (VB16) and hexadecylvinylbenzylidimethyl ammonium chloride (Bz16) were synthesized and ion exchanged onto montmorillonite. Poly(methyl methacrylate)-clay nanocomposites of all three clays were

prepared by bulk polymerization and the resulting nanocomposites were characterized by X-ray diffraction and transmission electron microscopy. The clays which contain a pendant double bond are more likely to give an exfoliated material while that which contains no double bond is intercalated. The thermal stability and flame retardancy were measured by thermogravimetric analysis (TGA) and Cone Calorimetry respectively.

Keywords

Poly(methyl methacrylate), Nanocomposites, Cone calorimetry, TGA, TEM

1. Introduction

In recent years, a significant amount of work has been carried out on polymer–clay nanocomposites, because they show enhanced mechanical properties relative to the virgin polymer and to conventional inorganic-polymer composites [1, 2, 3]. In general, polymer–clay nanocomposites have been prepared by four techniques: exfoliation-adsorption [4, 5], in situ intercalative polymerization [3, 6], melt intercalation [7, 8, 9] and template synthesis [10]. PMMA–clay nanocomposite has been prepared by exfoliation-adsorption through emulsion polymerization [11, 12] or in situ intercalative polymerization [13]. By emulsion polymerization, an intercalated nanocomposite is obtained when the clay loading is more than 10% [11] and an exfoliated system is produced at about 5% clay [12]. The in situ polymerization produces only an intercalated structure [13].

In previous work from these laboratories, we have shown that the use of an ammonium-substitute clay which contains a styryl group produces an exfoliated structure, while only intercalated structures are produced when this double bond is absent [14]. In this study, three clays, two of which contain double bonds so that they may participate in the polymerization, and one which lacks this double bond, have been dispersed in methyl methacrylate and a bulk polymerization was performed. In addition to determining the nature of the nanocomposites, mechanical properties, thermal stability and flammability properties have been examined.

2. Experimental

2.1. Materials

The sodium-montmorillonite powder, with a cation exchange capacity of 91 Meq/100 g MMT, was provided by Southern Clay Product Inc. The majority of chemicals used in this study, including methyl methacrylate, 2,2'-azobis(isobutyronitrile) (AIBN), vinylbenzyl chloride, allyl chloride, benzyl chloride, ethyl acetate and inhibitor removal columns were purchased from Aldrich Chemical Company. TCI America supplied *N,N*-dimethyl-*n*-hexadecylamine.

2.2. Instrumentation

Infrared spectroscopy, FTIR, was performed on a Mattson Galaxy infrared spectrometer at 4 cm⁻¹ resolution. Thermogravimetric analysis, TGA, was performed on an Omnitherm 1000 unit under a flowing nitrogen atmosphere at a scan rate of 10 °C per min from 20 to 600 °C. Cone calorimetry was performed on an Atlas CONE -2 according to ASTM E 1354–92 at an incident flux of 50 kW/m² using a cone shaped heater. Exhaust flow was set at 0.023 m³/s and the spark was continuous until the sample ignited. Cone samples were prepared by compression molding 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. X-ray scattering (XRD) measurements were performed using a Rigaku powder diffractometer, with a Cu tube source ($\lambda=1.54 \text{ \AA}$) operated at 1 kW. Bright field transmission electron microscopy (TEM) images of the composites were obtained at 60 kV with a Zeiss 10c electron microscope. The samples were ultramicrotomed with a diamond knife on Riechert-Jung Ultra-Cut E microtome at room temperature to give ~70 nm thick sections. The sections were transferred from the knife-edge to 600

hexagonal mesh Cu grids. The contrast between the layered silicates and the polymer phase was sufficient for imaging, so no heavy metal staining of sections prior to imaging is required. The mechanical properties were measured on an Instron machine.

N,N-dimethyl-*n*-hexadecyl-(*p*-vinylbezl) ammonium chloride (VB16) was synthesized according to previous work [14] from *N,N*-dimethyl-*n*-hexadecylamine and *p*-vinylbenzyl chloride. *N,N*-dimethyl-*n*-hexadecylallyl ammonium chloride (Allyl16) and *N,N*-dimethyl-*n*-hexadecylbenzyl ammonium chloride (Bz16) were synthesized similarly, from *N,N*-dimethyl-*n*-hexadecylamine and allyl chloride or benzyl chloride, respectively. The ammonium-modified clays were prepared as previously described [14].

2.3. Preparation of PMMA-clay nanocomposites

The nanocomposites were prepared according to the following procedure. In a 200 ml beaker were placed 3 g of organically modified clay, 1 g AIBN as radical initiator, and 100 g of monomeric methyl methacrylate (MMA). This mixture was stirred at room temperature under flowing nitrogen gas until it was homogeneous, then it was heated to 80 °C for a few minutes to prepolymerize. After cooling to room temperature, the sample was polymerized at 60 °C for 24 h, then at 80 °C for another 24 h under nitrogen atmosphere. Finally the nanocomposite was dried under vacuum for 6 h at 100 °C. This is the identical procedure that was used for the preparation of polystyrene-clay nanocomposites [3]. The full time was required for the polymerization of styrene, however methyl methacrylate polymerizes much more rapidly. For instance, when styrene is polymerized, after a few minutes at 80 °C, and before the bulk polymerization at 60 °C, a viscous solution, but not a gel, is observed. In the case of methyl methacrylate, the formation of a glass is observed before polymerization proceeds at 60 °C.

3. Results and discussion

The structures of ammonium salts used to exchange the sodium ion of the clay are shown in Fig. 1. VB16 and Allyl16 contain a vinyl group on the ammonium salts and it is expected that some of the polymerization will occur on this cation while Bz16 can show no polymerization onto the cation.

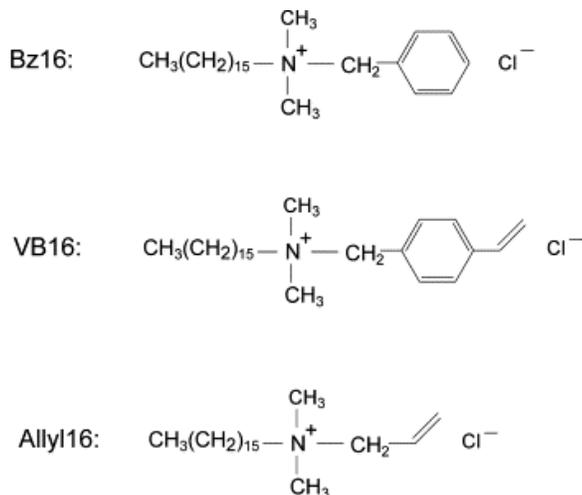


Fig. 1. The structures of ammonium salts used to modify clay.

Nanocomposites are described as either intercalated, if registry is maintained between the clay layers, or exfoliated (also called delaminated), if this registry is lost. In an intercalated structure one finds well-ordered multi-layered structures in which the polymer chains are inserted between the galleries of the clay, increasing the gallery spacing. On the other hand, in an exfoliated structure the spacing between galleries becomes so large that the silicate layers are no longer able to interact with the cations. Determination of the structures in a

nanocomposite requires the measurement of both the d -spacing from X-ray diffraction, XRD, and transmission electron microscopy, TEM. In an immiscible mixture, the d -spacing should be virtually identical with that of the original clay while, if a nanocomposite is formed, the d -spacing must increase. For an exfoliated nanocomposite, no peak is usually seen; the absence of an XRD peak is not sufficient to identify a material as exfoliated. Frequently a mixture of intercalated and exfoliated structures are obtained and this requires TEM for characterization.

The XRD data for all of the nanocomposites described herein, and the starting clay, are shown in [Table 1](#). All of the organically-modified clays have larger d -spacing than the sodium clay due to the larger volume of organic cations and all of nanocomposites show larger d -spacing than the starting clays. This indicates the formation of intercalated structures. Although the vinyl-containing clay, VB16 and Allyl16, show peaks in the XRD, the intensity of these peaks is smaller than that of Bz16 which contains no vinyl group and thus is expected to be only intercalated. This suggests that the vinyl-containing clays may show some mixture of intercalated and exfoliated structures.

Table 1. XRD data of PMMA nanocomposites

Clay	d_{001} (nm)	d_{001} of Composites (nm) [Intensity, (cps)]	Difference of d_{001} (nm)
Na-clay	1.20		
Bz16	1.80	3.27 (5327)	1.47
VB16	2.52	4.65 (1821)	2.13
Allyl16	2.08	3.40 (1620)	1.32

TEM ([Fig. 2](#), [Fig. 3](#), [Fig. 4](#)) provides confirmation of the intercalated nature of the Bz16 nanocomposite and the mixed intercalated-exfoliated nature of both allyl16 and VB16. When polystyrene nanocomposites of VB16 were produced, a completely exfoliated material was obtained. A possible reason is the high polymerization rate for PMMA, due to the high rate of propagation and the pronounced gel effect. The gel effect is most important because it causes a sharp decrease in the termination rate and leads to an increase in the overall polymerization rate and in molecular weight [\[15\]](#). Because of the higher polymerization rate, the PMMA quickly becomes a glassy polymer, with the result that it is more difficult for monomers to insert into the clay gallery space. Thus there are insufficient monomers present within the clay and expansion of the d -spacing does not continue to reach the fully exfoliated structure. This confirms the concept of Pinnavaia et al. in the case of the clay epoxy system. They pointed out that the key to achieving an exfoliated clay composite structure in an epoxy matrix is competition between the intragallery polymerization rate and the extragallery polymerization rate [\[16\]](#).

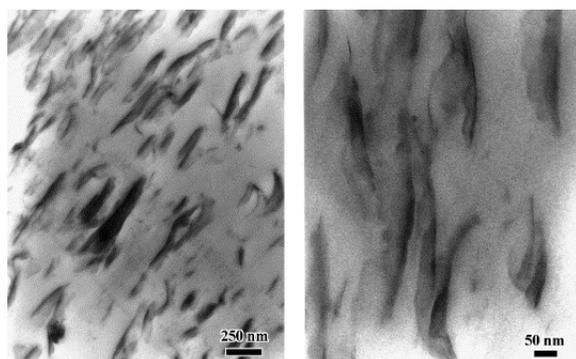


Fig. 2. TEM of the poly(methyl methacrylate)-Bz16 nanocomposite.

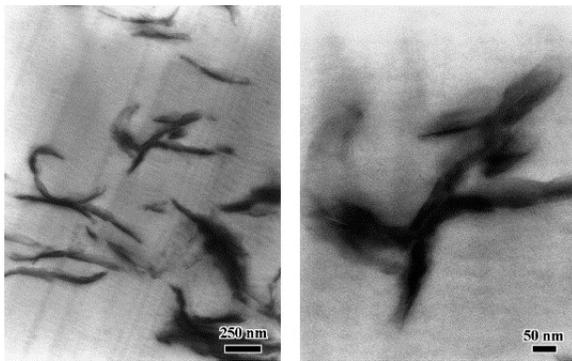


Fig. 3. TEM of the poly(methyl methacrylate)-allyl16 nanocomposite.

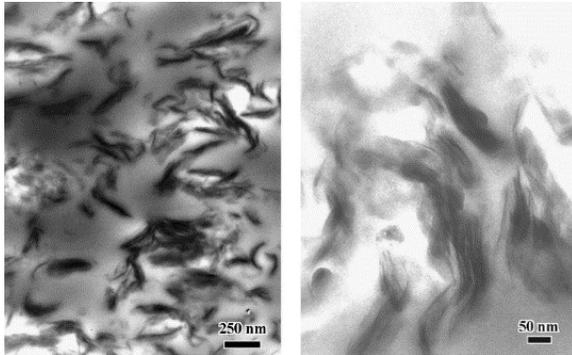


Fig. 4. TEM of poly(methyl methacrylate)-VB16 nanocomposite.

The first indication of enhanced thermal stability in nanocomposites appears in the reports of Blumstein [17], [18], [19], [20], [21], [22], [23], [24], [25], who studied the thermal stability of PMMA intercalated within clay. He proposed that the enhanced thermal stability of the PMMA-based nanocomposites was due to both the difference of chemical structure and restricted thermal motion of polymer chains in the silicate interlayers.

The thermal stability of these nanocomposites is higher than that of pure PMMA; the TGA data showing the temperature at which 10% degradation occurs, $T_{0.1}$, the temperature at which 50% degradation occurs, $T_{0.5}$, and the amount of material which is not volatile at 600 °C, char, is shown in Table 2. The temperature at which 10% degradation occurs is a measure of the onset temperature of the degradation and this is lower for Bz16 but is increased for both allyl16 and VB16. Likewise the temperature at which 50% degradation occurs is some measure of thermal stability, and this is 40 °C higher for all three nanocomposites. The presence of the clay does not affect the degradation process of PMMA; PMMA and its nanocomposites show three degradation steps, except for the VB16 nanocomposite in which the first step disappears. The char formation does not increase, consistent with previous work [2], [3]. The TGA curves for the nanocomposites are displayed in Fig. 5. The initial step of the degradation, which has been attributed by Kashiwagi [26] to the presence of weak links in the polymer chain, occurs at lower temperatures for allyl16 and Bz16 and is absent in VB16. The amount of this first step is decreased in the presence of the clay but it occurs at a lower temperature. This suggests, in agreement with the work of Blumstein [19] that the clay offers some templating effect. The second and third steps in the degradation occur at about the same point but, because there is less of the first step, the temperature of 50% degradation is significantly higher and the nanocomposites have enhanced thermal stability.

Table 2. TGA data of PMMA nanocomposites containing 3% clay

Composites	T0.1 (°C)	T0.5 (°C)	Char (%)	DTG (°C)
PMMA	246	334	0	236, 303, 398
PMMA-Bz16	235	374	6	183, 300, 404
PMMA-VB16	271	373	6	300, 406

PMMA-Allyl16	295	377	5	185, 306, 398
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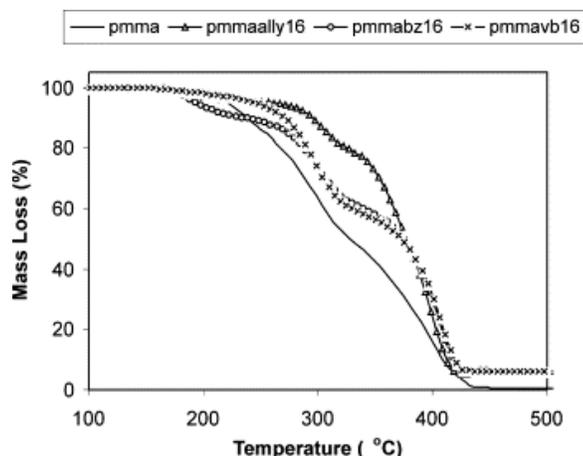


Fig. 5. TGA curves of PMMA nanocomposites.

The flammability of nanocomposites was measured by cone calorimetry and this data is shown in [Table 3](#). The PMMA nanocomposites have lower peak heat release rates (PHRR) than does virgin PMMA. The peak heat release rate for PMMA and the three nanocomposites is also shown graphically in [Fig. 6](#). While it is tempting to note that the intercalated material, Bz16, is lower than the two mixed intercalated–exfoliated nanocomposites, the typical error in PHRR is $\pm 10\%$ so the values are comparable and the reductions are comparable to those observed for polystyrene nanocomposites [\[3\]](#), [\[14\]](#). The allyl16 nanocomposite has longest time to ignition and time to burnout. These nanocomposites also show lower mass loss rate than does pure PMMA. For polystyrene-clay nanocomposites the heat release curves begin earlier for the nanocomposites than for the virgin polymer. These systems are all unfortunately flammable and cannot pass the UL-94 test for flammability. The heat release curves for the PMMA nanocomposites all begin later than that for the virgin polymer, which suggests that these systems may offer some opportunity for fire retardancy in PMMA.

Table 3. Cone data of PMMA nanocomposites containing 3% clay at 50 kW/m²

Nanocomposites	T_{ignition} (S)	PHRR (kw/m ²) (% diff) ^a	T_{PHRR} (S)	Mean HRR (kw/m ²)	ASEA ^b (m ² /kg)	AMLR ^c (g/s ⁻¹ m ²)
PMMA	13	935	118	597	141	24
PMMA-Bz16	14	676(28)	109	466	206	19
PMMA-VB16	14	706(24)	106	493	225	20
PMMA-Allyl16	29	744(20)	127	544	201	22

a% Diff=[PHRR(no clay)–PHRR(clay) / PHRR (no clay).

b ASEA: average specific extinction area.

c AMLR: average mass loss rate.

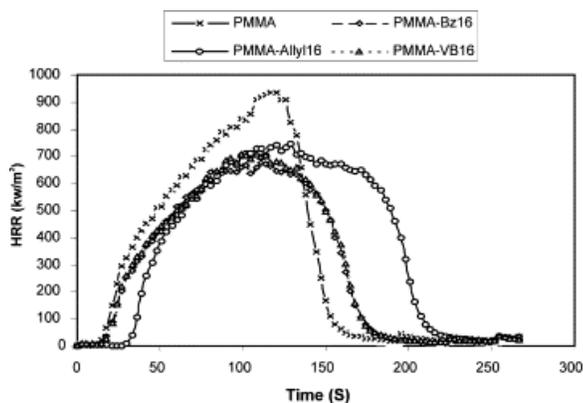


Fig. 6. Heat release rate of PMMA nanocomposites.

Tensile strength and elongation at break, representative of mechanical properties, are shown in [Table 4](#). It is well known that the mechanical properties of nanocomposites are enhanced relative to those of the polymers and that exfoliated nanocomposites are enhanced relative to intercalated systems [\[27\]](#). The strength at break increases about 30% for Allyl16 nanocomposites containing 3% clay, the increase is lower for Bz16 nanocomposite. The strength of VB16 nanocomposite is even lower than that of virgin PMMA. The elongation at break decreases for these three nanocomposites.

Table 4. Mechanical properties of PMMA nanocomposites

Nanocomposites	Tensile strength at break (MPa) ^a	Elongation at break (%)
PMMA	17.16	4.67
PMMA-Bz16	19.31 (+12%)	3.56
PMMA-VB16	13.72 (-20%)	3.90
PMMA-Allyl16	22.12 (+29%)	3.94

a In parentheses are the difference between pure PMMA and the nanocomposites.

4. Conclusions

Poly(methyl methacrylate)-clay nanocomposites have been prepared by bulk polymerization. Both intercalated and partially exfoliated structures have been obtained. The partially exfoliated structure results possibly from the grafting reaction onto the clay. Thermogravimetric analysis of nanocomposites shows that the onset temperature is higher for the nanocomposites than for the virgin polymer. Cone calorimetry measurements indicate that the peak heat release rate is reduced by formation of the nanocomposites, but less than in polystyrene-clay nanocomposites. The allyl-containing clay is better than the benzyl-containing clay for the PMMA nanocomposites.

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