

Synthesis and properties of polystyrene/Fe-montmorillonite nanocomposites using synthetic Fe-montmorillonite by bulk polymerization

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Fe-montmorillonite (Fe-MMT) was hydrothermally synthesized. It was modified by cetyl trimethylammonium bromide (CTAB) and successfully synthesized polystyrene/Fe-montmorillonite (PS/Fe-MMT) nanocomposites via bulk polymerization for the first time. The resulting nanocomposites were characterized by X-ray diffraction (XRD) spectra, transmission electron microscopy (TEM), high resolution electronic microscopy (HREM), thermal gravimetric analysis (TGA) and cone calorimeter. XRD, TEM and HREM indicated that both intercalated and exfoliated-intercalated structures were observed. In comparison with pure PS, the thermal stability was notably improved in the presence of clay. From cone calorimetry it was found that the peak of heat release rate (HRR) was significantly reduced by the formation of the nanocomposites. Also intercalated nanocomposites were more effective than exfoliated-intercalated nanocomposites in fire retardancy. © 2005 Springer Science + Business Media, Inc.

1. Introduction

The recent interest in polymer/clay composites with nanometer dimensions, the so-called nanocomposites [1–4], stems from the dramatic improvement in physical properties that can be produced by just adding a small fraction of clay to a polymer matrix. It has been shown that most of the properties are enhanced in the presence of a small amount of clay. For instance, incorporation of a few percent of clay in many cases increases the modulus, strength, gas barrier properties, and heat stability, compared to the pure polymers. The presence of clay takes on fire retardant properties [5].

The nanocomposites typically make up of organically modified clay and matrix polymers. The most frequently used clay is montmorillonite, MMT, which is an aluminous silicate mineral with sodium ions present between the clay layers. It is an occurring 2:1 phyllosilicate. The MMT crystal lattice consists of about 1-nm-thin layers, with a central octahedral sheet of alumina fused between two external silica tetrahedral

sheets [6]. This space between the clay layers is referred to as the clay gallery. To make compatible with polymers, the sodium ions are usually ion-exchanged with an organic ammonium or phosphonium salt to convert this material into a hydrophobic ammonium or phosphonium treated clay. The nanocomposites can be prepared either by a blending process, either melt blending or solution blending, or by a polymerization process in the presence of the organically modified clay.

The phenomenon of isomorphous replacement in montmorillonite (in the tetrahedral crystal lattice of structural level, Si^{4+} is replaced by Al^{3+} ; in the octahedral lattice, Al^{3+} is replaced by Fe^{3+} , Fe^{2+} , Mg^{2+} , Cr^{3+} , Zn^{2+} and Li^{+} etc. Due to exchange of unequal values, the electric neutrality of the structure is destroyed and some excess electrons appear, these electrons are compensated by alkali metal cations or alkali earth metal cations, the cations of compensation come into spaces between structure levels and distribute into the edges of lattices. Those cations are often replaced

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by other cations so the clay performs sorts of distinctive functions.) is very common. The types of MMT maybe possess different performances from natural MMT. Plenty of pillared clay was synthesized containing Zr, Ti, Fe, Cr, V. Their properties were discussed in many articles.

In this article, Fe-MMT was synthesized using the way which was mentioned by Nagase T [7], the type MMT has a structure as well as natural MMT. In this type of MMT, the difference is that Fe^{3+} ion replaces Al^{3+} ion in the crystal lattice. The clay containing iron and other cations were applied to catalytic field many years ago [8, 9], and they perform catalytic activity very well. Because this clay possesses the similar structure of natural MMT, guessing that has the properties of natural MMT. Maybe in other flame retardant-montmorillonite synergism systems, it will have effectiveness of catalytic inflaming retarding. This point is still waiting for verification. In this article, a new application of Fe-MMT was proved and some favorable properties comparing with pure polymer. For the first time, this type MMT was modified by CTAB. Then, Polystyrene nanocomposites were synthesized using this type of organic Fe-montmorillonite (Fe-OMT) via bulk polymerization, and obtaining intercalated nanocomposites. When clay content was reduced, exfoliated structures can be obtained. The normal characterization of structure nanocomposites required XRD spectra measurements to show changes in the d spacing of the clay and TEM to image the individual clay layers and thus show the exact nature of the clay-polymer interaction. TGA had been used and the onset temperature of thermal degradation was increased comparing to that of virgin polymer in our system. Flame retarded property was measured by the cone calorimeter.

2. Experimental section

2.1. Materials

The majority of chemicals used in this study, including styrene(St), 2,2'-azobis(isobutyronitrile) (AIBN), Cetyltrimethyl ammonium bromide (CTAB), Acidic sodium silicate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$), iron(III)chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), magnesium chloride($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) and sodium hydroxide (NaOH)were all from Shanghai Chemistry Company.

2.2. Synthesis of Fe-montmorillonite

Fe-montmorillonite (Fe-MMT) was synthesized using the way as following: hydrous oxide was prepared by mixing $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ solutions to set the atomic ratio at Si-Fe-Mg = 4–1.7–0.3. The pH was adjusted with NaOH solution. PH was in the range of 12–12.4. Then, the slurry was sealed in a Teflon container and hydrothermally treated at 180°C for 24 h, for obtaining Fe-MMT as a transparent yellowish-brown gel without impurities. The sample was dried under dynamic at 80°C for 48 h.

2.3. Modifiability of pristine Fe-MMT

The Fe-MMT was dispersed in water, under vigorous stirring condition to form a suspension. Then the solution of CTAB was added to the suspension and stirred for 3 h at 80°C. The suspension was centrifuged and washed with boiling distilled water to remove the excess intercalative reagent, until the supernatant liquid was tested by a 0.1 mol/L AgNO_3 solution without yielding sedimentation. The product was then vacuum-dried and ground into power to get the Fe-montmorillonite (Fe-OMT).

2.4. Synthesis of PS/clay nanocomposites

The synthesis for the preparation of procedures polystyrene/Fe-montmorillonite (PS/Fe-MMT) nanocomposites were as follows. A desired amount of Fe-OMT was dispersed in styrene under supersonic dispersion at 25°C, the mixtures were charged into a four-neck reactor equipped with a baffle stirrer, a reflux condenser, a nitrogen inlet, and a rubber septum. The initiator of AIBN was added and stirred to form a stable suspension. Then the suspension was polymerized at 60°C for 10 h under a nitrogen atmosphere. After drying and removing unpolymerized monomer in a vacuum oven at 80°C, PS/Fe-MMT composites were obtained.

2.5. Characterization

2.5.1. Determination of cation-exchange capacity

For given clay, the maximum number of cations that can be taken up is constant and known as the cation-exchange capacity (CEC). It is measured in milliequivalents per 100 g (meq/100 g) of clay. The procedures for measuring CEC were as follows. Clay mineral (2–3 g) was saturated with ammonium chloride solution (25 ml) (in 25/75 wt/wt water–alcohol mixture; 0.1 mol/L; pH = 7) in a centrifuge tube by stirring overnight. The suspension was then centrifuged and the clear supernatant liquid (containing unexchanged NH_4^+ ions) was transferred into a flask. The precipitate was saturated again with ammonium chloride solution and then centrifuged. The precipitate saturation and centrifugation were repeated three times, ensuring the ion-exchange was completed. Finally, the collected clear supernatant liquid was reacted with formaldehyde and the resulting H^+ was titrated with standard NaOH solution and, thus, the molar number of concentration unexchanged NH_4^+ was determined so that the CEC of the clay could be calculated. The CEC of the Fe-MMT used was determined as 106 meq/100 g.

X-ray diffraction (XRD) was used to characterize the layer conformation of Fe-MMT in the composite. The operation parameters were Cu-K α ($\lambda = 1.54178 \text{ \AA}$) radiation at a generator voltage of 30 kV and current of 10 mA. The range of the diffraction angle was $2\theta = 1.5 - 10^\circ$. The structure of the composite was observed by transmission electron microscope (TEM) and high resolution electronic microscopy (HREM).

The thermal properties of pure PS and PS nanocomposites were investigated by Thermogravimetric analysis (TGA) with a Netzsch STA-409c Thermoanalyzer instrument. In each case, the 10 mg specimens were heated from 25 to 600°C at the rate of 10°C/min under nitrogen flow.

The cone calorimetry experiments were evaluated following the procedure defined in ISO 5660, on the 3 mm thick 100 × 100 mm² plaques. The cone data obtained are reproducible to within ±10% when measured at 35 kW/m² heat flux.

3. Results and discussion

3.1. Nanostructure of PS/Fe-MMT composites

Original inorganic Fe-MMT has the structure of silicate layer. The d_{001} spacing is about 15 Å (Fig. 1a). After the clay is modified by CTAB, the original inorganic Fe-MMT became hydrophobic and the interlayer galleries are also distensible. The d spacing has changed into 33 Å (Fig. 1b). This increased spacing indicates that the chain of C16 intercalates into the gallery of Fe-MMT and expands it.

Then, styrene monomers enter the interlayers and grow to form PS macromolecules going with releasing a large quantity of heat. According to the intercalative polymerization mechanism, the interlayer spacing of Fe-MMT should be enlarged and intercalated or exfoliated by the growing PS macromolecule chains and uniformly dispersed in the PS matrix. The evidence of the proposed mechanism is by XRD and TEM results. Fig. 1 shows a series of XRD patterns of PS/Fe-MMT composites containing different Fe-OMT contents. The interlayer spacing (basal spacing of the (001) plane, d_{001}) of the Fe-MMT obtained by CTAB treatment is about 33 Å and larger than that of original montmorillonite. With the decrease of the Fe-OMT content (from 5 wt% to 1 wt%), the peak relative intensity of the (001) plane became weaker. For PS/Fe-MMT composite containing 5 wt% Fe-OMT, the strong (001) plane

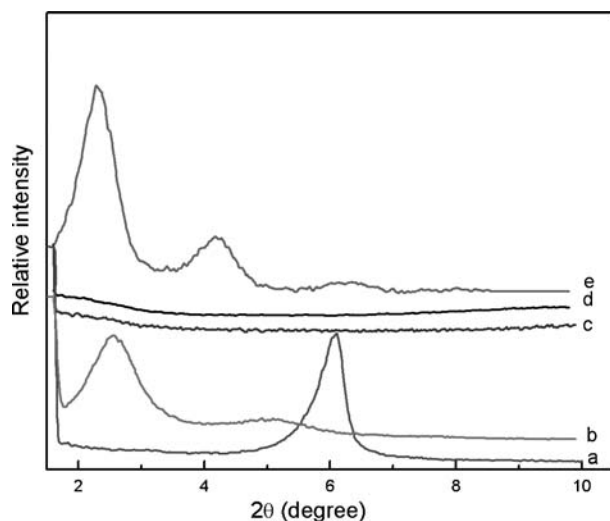


Figure 1 XRD patterns of PS nanocomposites containing different amount of (a) Fe-MMT; (b) Fe-OMT; (c) 1 wt% Fe-OMT; (d) 3 wt% Fe-OMT; (e) 5 wt% Fe-OMT.

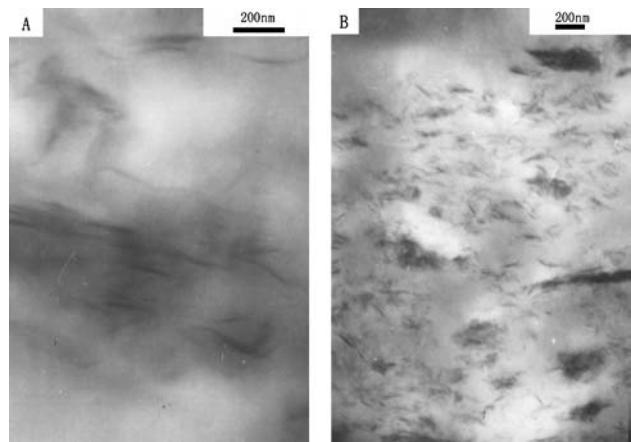


Figure 2 TEM of 3% Fe-OMT PS/ Fe-MMT and 5% Fe-OMT PS/Fe-MMT nanocomposite.

peak corresponding to d_{001} (about 37 Å) (Fig. 1e) is clearly observed, resulting from this kind of composite: intercalated nanocomposites, or at least intercalated structural shape occupied majority. Along with Fe-OMT content depression, the diffraction peak of (001) plane is not detectable (Fig. 1c and d). It declares intercalated morphology is reductive and the exfoliated morphology is incremental. Furthermore, the exfoliated morphology has taken up mass. It considers the samples of containing 3 wt% and 1 wt% Fe-OMT formed intercalated-exfoliated nanocomposites. So when the clay is decreased, nanocomposite structures change from intercalation to exfoliation.

TEM and HREM observation are used to argument XRD analysis of the nanostructure. Fig. 2 shows the TEM micrograph of the PS/Fe-MMT composites, where the bright region represents the polymer matrix and the dark narrow stripes represent the secondary particles Fe-MMT. From Fig. 2A and B where Fe-OMT composite contains 3 and 5 wt% respectively, it can be observed the Fe-MMT was dispersed in the matrix. But the layers are not watched. In Fig. 3 (HREM micrographs of 5% Fe-OMT PS/Fe-OMT nanocomposites), it is found that Fe-MMT layers were uniformly dispersed in the PS matrix. Silicate layers with an interlayer spacing of about 37 Å are observed, which is consistent with the XRD analysis. This exhibit some

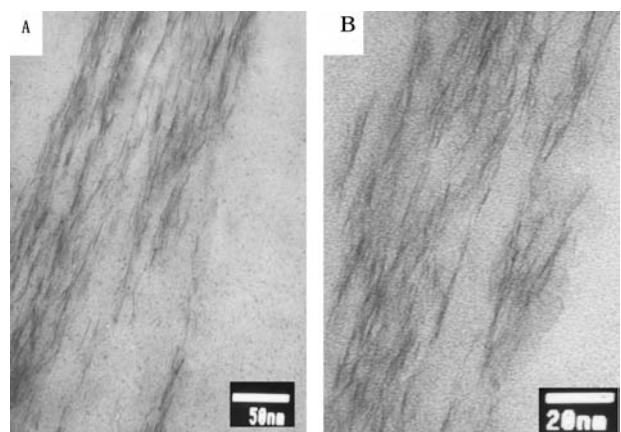


Figure 3 HREM micrograph of PS/Fe-MMT composites containing 5% of Fe-OMT.

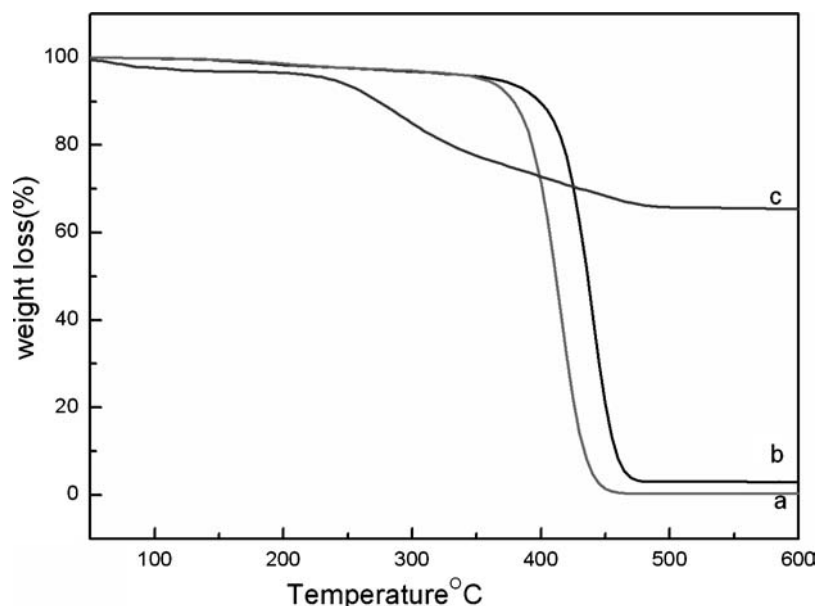


Figure 4 Fe-OMT, pure PS and PS/Fe-MMT nanocomposite characterized by TGA (a) pure PS, (b) 3 wt%Fe-OMT of PS/Fe-MMT nanocomposite, (c) Fe-OMT.

suggests that the nanoscale Fe-MMT layers are flexible and can be distorted in the PS matrix. This is different from traditional microcomposites, for instance, glass-fibre reinforces polymer composites in which, although the aspect ratio of glass fibres is very large, they remain straight in the polymer matrix.

In summary, from the analysis of XRD, TEM and HREM, we can draw the conclusion that intercalated PS/Fe-MMT nanocomposites result from bulk polymerization, and that silicate layers of Fe-MMT are intercalated into one another nanometric secondary particles (several silicate layers stacked against) and are uniformly dispersed in the polymer matrix.

3.2. Thermal stability of PS/Fe-MMT nanocomposites

In our experimental conditions, the thermal properties of pure PS, PS/Fe-MMT nanocomposites and Fe-OMT are characterized by TGA in Fig. 4 and Table I. It can be seen that the thermal stability of the PS/Fe-MMT nanocomposites is noticeably improved by adding Fe-OMT into the PS matrix. The data shows the temperatures at which 10% degradation occurs, $T_{0.1}$, as a measure of the onset of the degradation, and at which 50% degradation occurs, $T_{0.5}$, as the midpoint of the degradation process, and the residue that is nonvolatile at 600°C, are shifted to higher temperature with increasing Fe-OMT content in the nanocomposites. The

decomposition increases by as much as 30–40°C. The origin of the noticeable increase in the decomposition temperatures mainly results from strong interaction between polymer and clay. Polymer chains subjected to the silicate layers. Surface features of silicate layers make many polymer chains extremes link the same silicate layers. So those layers act as cross-bonding points. Superior cross-bonding density makes the thermal property of this polymer nanocomposite improve. In the Table I, 5% Fe-OMT PS/Fe-MMT nanocomposite has the highest thermal property of the three types of nanocomposites. It is possible that the presence of iron does lead to some radical trapping which enhances thermal stability, and this is more important for intercalated than for exfoliated nanocomposites [10].

Thermal decomposition of the Fe-OMT takes place at around 200°C and proceeds according to the Hofmann degradation mechanism [11, 12]. The initial step is the loss of an olefin, followed by the loss of the amine, leaving an acid proton on the surface of the montmorillonite in the place of the ammonium cation. In Fe-OMT, adsorptive water and interlamellar water are lost before 200°C. At nearly 240°C, the intercalant CTAB decomposed and/or vapourized from MMT. The weight loss rate eventually slowed and the residue was 71.9 wt% at about 480°C. With the temperature increasing, the weight loss rate becomes slower, which resulted from the fact that at high temperature, the structure of Fe-MMT is destroyed and structural H₂O molecular within the layers leaves. Table I, PS/Fe-MMT nanocomposites is close to that of the Fe-OMT at 600°C, showing that the nanocomposites had reached the limit of thermal resistance of the inorganic montmorillonite.

TABLE I TGA results of PS/Fe-MMT nanocomposites and Fe-OMT

Fe-OMT content (%)	$T_{0.1}$ (°C)	$T_{0.5}$ (°C)	Residue at 600°C (wt%)
0	350.6	416.3	0.09
1	368.3	426.4	1.36
3	372.5	439.5	3.22
5	370.8	448.3	5.29
100	283.6	/	70.07

3.3. Fire performance of nanocomposites

The Fig. 5 shows the cone calorimetric results for PS/Fe-MMT nanocomposites and pure PS. It is normal for nanocomposites that time to ignition is earlier than that of virgin polymer. This has been observed with

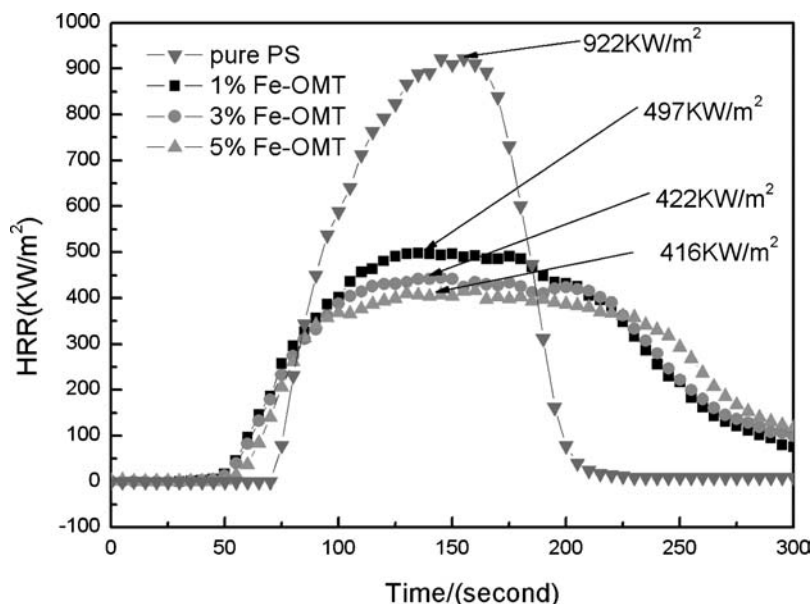


Figure 5 Peak heat release rates for polystyrene and the nanocomposites.

other nanocomposites and correlates with the observation that nanocomposites will usually burn. One invariably finds that nanocomposites have a much lower peak heat release rate (PHRR) than does the virgin polymer. When the clay content is 1%, the peak HRR value is as 54% as that of pure PS. The peak heat release rate falls as the amount of clay increases. The suggested mechanism by which clay nanocomposites function involves the formation of a char that serves as a barrier to both mass and energy transport [13]. It is reasonable that as the fraction of clay increases, the amount of char that can be formed increases and the rate at which heat is released is decreased. There has been a suggestion that an intercalated material is more effective than is an exfoliated material in fire retardancy.

4. Conclusions

Fe-MMT was hydrothermally synthesized without impurities, for the first time, we modified it by CTAB.PS/Fe-MMT nanocomposites were successfully synthesized via bulk polymerization intercalative polymerization. XRD patterns, TEM micrographs and HREM indicate that partially exfoliated and partially intercalated structures. TGA results showed that these nanocomposites exhibited well-improved thermal stability in comparison with pure PS. TGA results indicated that part of the PS chains stay immobilized inside and/or in that layered silicates and that the interactions between the nanometric silicate layers and polymer segments are strong, so that the nanocomposites are well resistant to common solvents of PS. In conclusion, the unique properties of the nanocomposites result from the strong interactions between the silicate structural layers and the polymeric chains and the iron maybe have the important site of radical trapping. From cone calorimetry, it is found that the rate of heat release is

significantly reduced by the formation of the nanocomposites.

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