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Preparation and structure of highly confined intercalated polystyrene/montmorillonite nanocomposite via a two-step method

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Abstract

A two-step approach with a combination of emulsion polymerization and melt intercalation with higher clay loading of 33 wt.% is disclosed to highly confine the polystyrene (PS) chains by montmorillonite. The product of the emulsion polymerization is an easily crushable fine powder. And the powder is readily processible by open mill to form a transparent sheet. In the melt intercalation process, further intercalation of polystyrene narrows the space among the tactoids and results a highly confined intercalated nanocomposite. The results of dynamic mechanical thermal analysis (DMTA) and differential scanning calorimetry (DSC) showed that the cooperative motions of PS segments were substantially depressed, indicative of the highly intercalated structure formed in the nanocomposites. A structural model is proposed to explain the highly confined mesostruture of the PS/MMT nanocomposite.

Keywords: Polystyrene; Montmorillonite; Nanocomposite; Confinement

1. Introduction

Polymer-layered silicate nanocomposites (PLSNs) have received much attention for their remarkably improved physical/mechanical properties at much lower content of filler compared with that of the conventional filled polymers. The unusual properties of the PLSNs are attributed to the dispersion of layered silicates on nanometer scale and the confinements of the polymeric matrix at nanometer level. There are two typical nanostructures in layered silicates/polymer complex, i.e. intercalated structure and exfoliated structure. In the exfoliated PLSNs, the single MMT platelets are dispersed in polymer matrix uniformly. In the intercalated ones, the polymeric matrix only partially intercalates into silicate layers and/or tactoids and most of the MMT maintain their stacked structures (tactoids). Generally speaking, in situ intercalative polymerization tends to form exfoliated PLSNs [1,2], while polymer intercalation tends to form intercalated PLSNs [3,4].

From the view of the confinement of polymer matrix, the polymer matrix in the PLSNs could be divided as *partially confined* polymer matrix and *highly/fully confined* polymer matrix. If the distance between parts of the MMT particles is considerably higher than the gyration

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radius of the polymer chains, part of the polymer chains are free of confinements of the MMT particles. In this case, the polymer matrix is referred as *partially confined*. When the distance between most or all of the MMT particles is comparable or less than the gyration radius of the polymer chains, most or all of the polymer chains are confined by the MMT particles. In this situation, the polymer matrix is referred as *highly or fully confined*. In exfoliated PLSNs, only 4 vol% MMT is needed to achieve a *d*-spacing of 25 nm [5]. At such a *d*-spacing, the polymer chains are fully confined. For an intercalated PLSNs, relatively larger amount of MMT concentration, for example 30 wt.%, is necessary to fully confine the polymer chain, as most of MMT is in stacked tactoids forms in the intercalated PLSNs [6]. For most of the polymers, however, formation of PLSNs with such a high MMT concentration is not easy viamelt intercalation, solution intercalation or in situ intercalative polymerization. *Fully confined* intercalated systems with higher content of MMT were rarely prepared [7,8]. The *highly or fully confined* intercalated PLSNs, in which most or whole polymer matrix is confined by the silicate layers and/or tactoids, will be of great scientific and technological importance as the *highly or fully confined* intercalated PLSNs may provide a model of true interfacial materials and the possibility of improving the physical/mechanical properties.

This work attempts to prepare a *highly confined* intercalated polystyrene/montmorillnite (PS/MMT) nanocomposite via a two-step method. First, part of polystyrene chains is introduced into the galleries of MMT layers via free radical emulsion polymerization. In the mean time, the montmorillonite is organically modified by polystyrene and/or cationic surfactant, and another part of polystyrene is formed outside of the MMT galleries as microspheres. Second, the outside polystyrene then intercalates into the expanded MMT galleries by the heat and shearing force during the following melt mixing. The preparation of polystyrene PLSNs via free radical emulsion polymerization has been well documented [8–11]. The reported polystyrene PLSNs were exfoliated or *partially confined* intercalated PLSNs, as the MMT concentration was relatively low (lower than 5 wt.%). In this paper, we report the preparation of *highly confined* polystyrene PLSN via the two-step procedure. The *highly confined* intercalated structure is substantiated by XRD, SEM and thermal analysis.

2. Experimental section

2.1. Raw materials

Montmorillonite (MMT) was supplied by Nanhai Nonferrous Mineral Co. Ltd. Guangdong, China. The average particle size and the cation exchange capacity (CEC) were 20 μm and 100 meq/100 g, respectively. Cetyltrimethyl ammonium bromide (CTAB) was supplied by Shanghai Juyuan Chemical Agents Co. Ltd. Styrene was supplied by Tianjing Ruijinte Chemical Agents Co Ltd. All chemicals are used as received.

2.2. Preparation of PS/montmorillonite nanocomposite

Mixture of styrene (40 g), deionized water (100 g) and CTAB (10 g) was added to a three-necked flask under continuous stirring. The mixture was emulsified for half an hour before slowly adding MMT slurry (400 g) with the concentration of 5 wt.%. Potassium peroxide disulphate (0.35 g) as the free radical was then added. The reaction was carried out at 60 °C for 3 h before adding another part of the initiator (0.35 g). The reaction was lasted for another 3 h. The mixture was then heated to 80 °C and reacted for 1 h. The product was washed by deionized water for several times and dried at 60 °C under vacuum. The product is an ultrafine powder. The conversion of polystyrene was determined as 85%. The content of MMT of the powder is 33 wt.% determined by thermogravimetric analysis. The number average molecular weight the polydispersity index of the PS is determined as 63,700 and 2.60, respectively.

The powder was melt mixed at 150 °C by a two-roll mill and then compression moulded at 190 °C for 5 min to form a 2-mm sheet.

2.3. Characterizations

The XRD was performed with a Raguku Model D/max III diffractometer. The X-ray beam was nickel-filter Cu Kα_1 ($\lambda = 0.1504$ nm) radiation operated at 40 kV and 30 mA. Corresponding data were collected from 1 to 50° at a scanning rate of 2°/min.

The dynamic mechanical thermal analysis (DMTA) was performed with TA DMA 2980 dynamic mechanical analyzer. Three point bending mode was selected and the experiment was carried out at a vibration frequency of 1 Hz form 30 °C to 150 °C with a heating rate of 5 °C/min and under nitrogen purging.

DSC analyses were carried out using a Pekin–Elmer Diamond DSC. The sample was first heated to 200 °C and kept for 5 min to eliminate the heat history. The sample was then cooled down at a rate of 10 °C/min. The sample was then reheated to 200 °C at a rate of 10 °C/min. The entire test was performed under nitrogen purging.

Thermogravimetric analysis (TGA) was carried out under nitrogen purging with a TA Instrument TGA 2050 thermogravimetric analyzer with a heating rate of 10 °C/min from 30 °C to 600 °C.

Microscopic investigation was performed with SM1530 VP scan electron microscope (SEM). The sample was brittle fractured in liquid nitrogen and the fractured surface was coated a gold film before observations.

Molecular weight and distribution was determined by GPC with a Waters apparatus Water Breeze at room temperature, differential refractometer as detector, using THF as the solvent, and calibrated with polystyrene standards.

3. Results and discussion

3.1. Structure analysis of nanocomposites

The X-ray diffraction (XRD) profiles of pristine MMT and PS/MMT nanocomposites are shown in Fig. 1. Pristine MMT shows a characteristic 0 0 1 diffraction peak around 6.95°. Two 0 0 1 diffraction peaks were observed around lower diffraction angle for the product of the emulsion polymerization (nanocomposite powder) and the moulded nanocomposite sheet. The *d*-spacing of the nanocomposite powder were calculated as 1.81 nm and 3.61 nm. The 0 0 1 diffraction around higher angle may be due to the intercalation of the cationic surfactant during the polymerization and the one around lower angle may be attributed to the polymerization of styrene between the intragalleries of the MMT. The two *d*-spacing of the nanocomposite sheet were further increased to 1.94 nm and 3.97 nm, respectively. The increases in *d*-spacing indicate the MMT layers are further intercalated by the polystyrene outside MMT galleries with the aid of the heat and shearing force during the melt intercalation process.

Figs. 2 and 3 show the SEM images of the nanocomposite powder and sheet, respectively. As shown in Fig. 2, the product of the emulsion polymerization is an ultrafine powder with particle size around 20 μm. The nanocomposite powders consists of the MMT particles with diameter of several micrometers and PS fine particles with diameter around 70 nm. According to the XRD results, the MMT particles possess intercalated structure and may be interconnected by PS chains to form relatively larger agglomerates. The fine PS particles may be formed by the polymerization of styrene outside the MMT galleries. As shown in Fig. 3, from longitudinal and cross-section view, an ordered intercalated structure is formed in the nanocomposite sheet. The heat and shearing force may be attributed to the orientation of the intercalated MMT layers. As a consequence, the very uniform and ordered intercalated structure is formed during the melt intercalation process. From the cross-section view, the thickness of tactoid is about 30 nm. The uniform dispersion of MMT in the nanocomposite may be further substantiated by the transparent appearance of the nanocomposite sheet, as shown in Fig. 4. In view of the high loading of the MMT, the transparency of the nanocomposite sheet is unusual. This fact may be explained by the mixing of the organic phase (polystyrene) and reinforcing inorganic elements (MMT) in molecular or mesoscale level, which is smaller than the wavelength of the visible light [12].

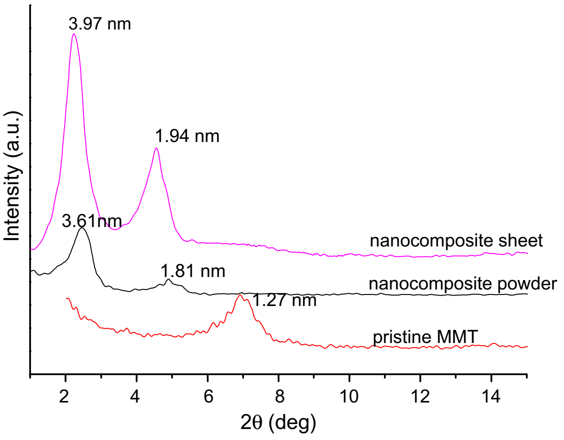


Fig. 1. XRD patterns of MMT and PS/MMT nanocomposites.

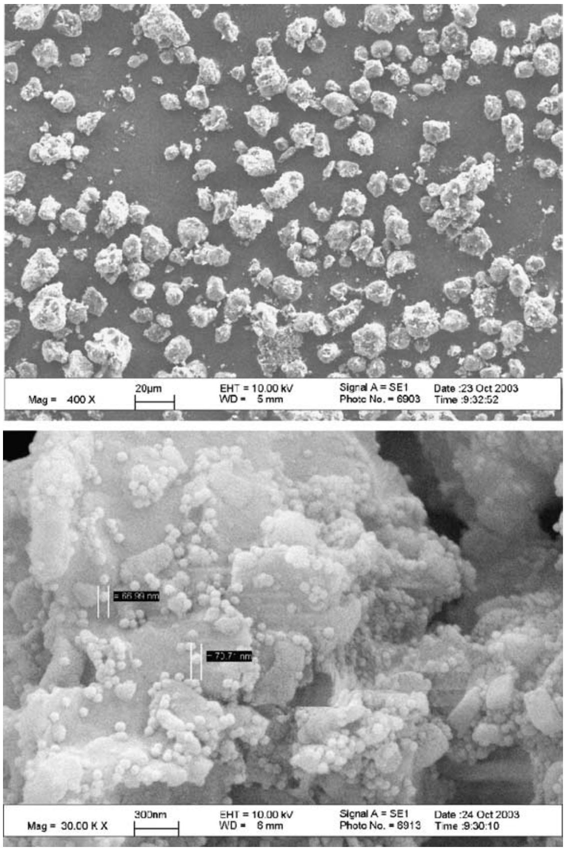
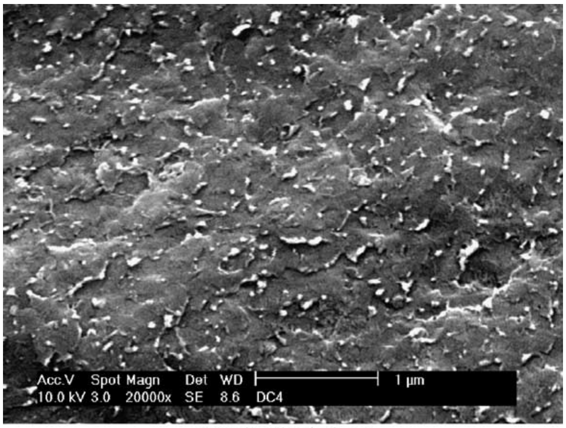
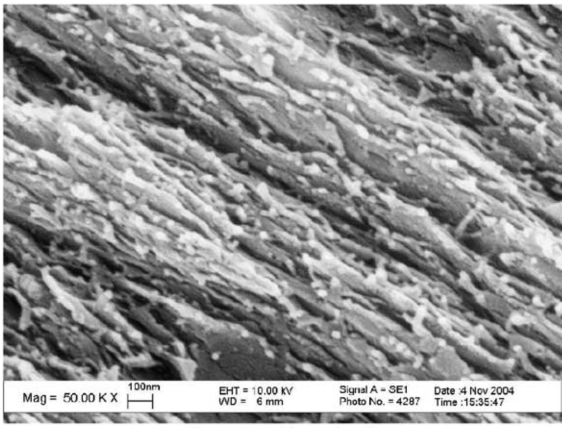


Fig. 2. SEM photo of the nanocomposite powder.



(longitudinal view)



(cross-section view)

Fig. 3. SEM photo of the fracture surface of the nanocomposite sheet.

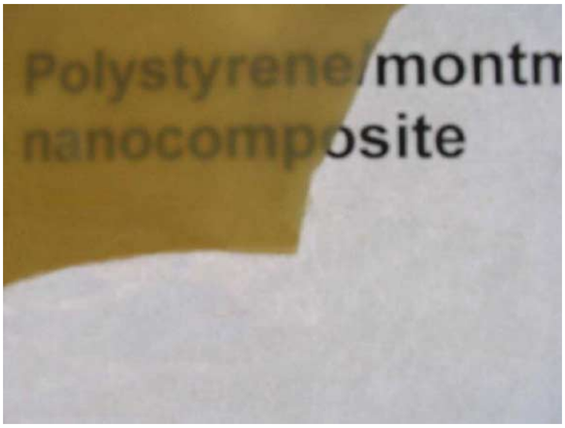


Fig. 4. Transparent appearance of nanocomposite sheet.

3.2. Glass transition of PS nanocomposite

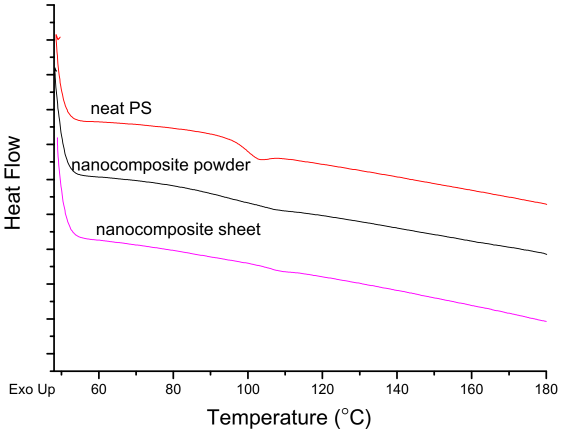


Fig. 5. DSC traces of neat PS and the nanocomposites.

Fig. 5 shows the DSC traces of the neat PS and the nanocomposite powder and sheet. The neat PS exhibits glass transition around 100 °C. For the nanocomposite powder, the T_g is too weak and/or too broad to measure, or it is suppressed due to the confinements of PS chains by the MMT layers. For the nanocomposite sheet, however, DSC does not detect any traces of thermal transitions over the experiment temperature range. The absence of glass transition is in agreement with the general observation in other fully intercalated polymer/silicates systems [7,13,14]. The absence of glass transition in the neatly intercalated polymer/silicates nanocomposites is not caused by the experimental errors [7,13]. On a local scale, intercalated polymers exhibit simultaneously fast and slow modes of segmental relaxations for a wide range of temperatures, but again with a marked suppression (or even absence) of cooperative dynamics typically associated with the glass transition.

3.3. Dynamic mechanical properties

The dynamic mechanical properties of PS and PS/MMT nanocomposites are shown in Figs. 6 and 7. As

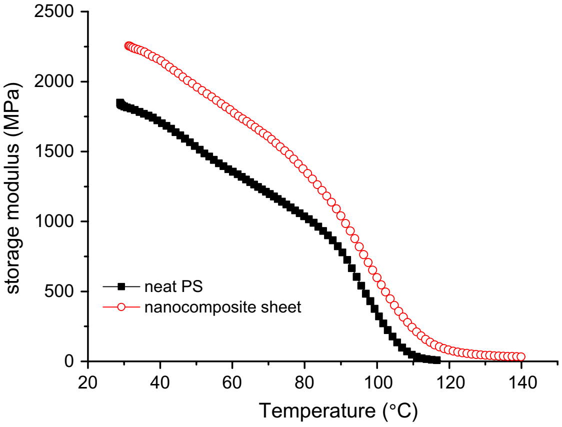


Fig. 6. Dynamic storage modulus of neat PS and nanocomposite.

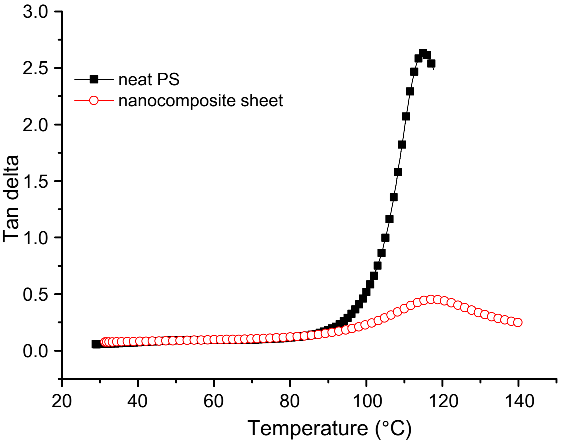


Fig. 7. Dynamic mechanical loss of neat PS and nanocomposite.

shown in Figs. 6 and 7, the dynamic storage modulus is substantially higher than that of neat PS. The tangent delta peak of the nanocomposites is highly suppressed. The increase storage modulus is attributed to the reinforcing effects of MMT layers/tactoids. The highly suppressed tangent delta peak may be also an indication of the formation of highly intercalated structure of the nanocomposites. The emergence of the weak glass transition in DMTA experiment indicates that the fully intercalation is not achieved although two-step entrapment of the PS chains was adopted. But this study exploits a general way to highly confine hydrophobic polymer chain in MMT platelets or tactoids via a facile procedure.

3.4. Modeling of the intercalated structure

To fully confine the PS chains, the distance between the MMT layers and/or tactoids should be smaller than the radii of gyration of PS chains. Under general circumstances, MMT is dispersed in polymer matrix in tactoid form, instead of single platelets. To understand the mesostructure of the prepared PS/MMT nanocomposite, an intercalated structural model is proposed by the authors and schematically showed in Fig. 8.

The polystyrene chains consist of two parts, intercalated intragallerial part between the MMT layers and the part between the packed MMT tactoids. To understand the confined environment of the PS chain between the tactoids, the distance between the tactoids, d, is computed with the average number of the MMT layer of the tactoid, n, by Eq. (1).

$$\frac{V_\mathrm{f}}{V} = \frac{\pi \times \frac{D^2}{4} \times h \times n}{(D+d)^2 \times (d + d_\mathrm{spacing} \times n)} \tag{1}$$

where V_f/V is volume faction of the MMT, equals to $0.33 * 1.1/2.35$. D is the diameter of the MMT platelet, typically of 1000 nm, h is the thickness of the MMT

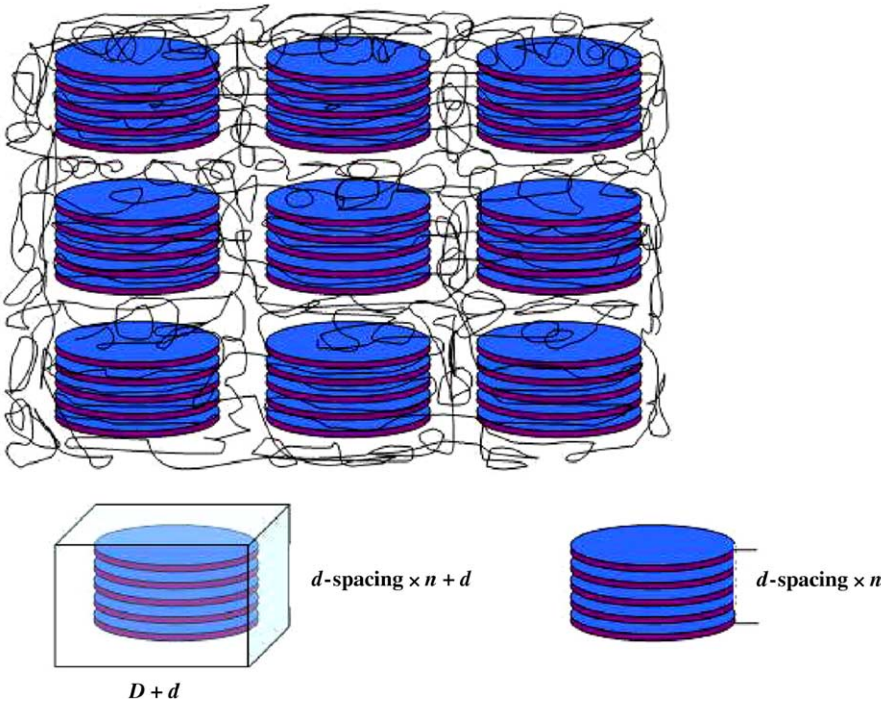


Fig. 8. Intercalated structural model of the PS nanocomposite.

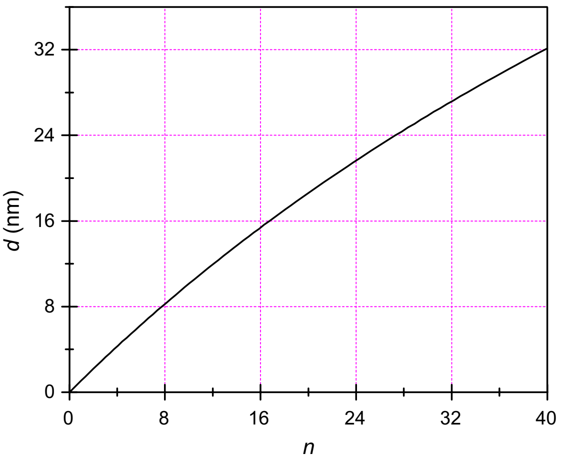


Fig. 9. Relationship between the average number of the tactoid (*n*) and the distance between the tactoid (*d*).

platelet, equals to 1 nm, *d*-spacing is basal distance of the intercalated MMT, equals to 3.9 nm, *n* is the average number of the tactoid, *d* is the distance between the tactoid.

The relationship of *n* and *d* is computerized with Eq. (1) and shown in Fig. 9. It is shown that *d* increases with *n*. For example, the *d* values corresponding to *n* of 3, 10 and 30 are 3.61 nm, 10.11 nm and 25.81 nm, respectively. To form true interfacial composite, in which all the polymer matrix is confined in interfacial region, the *n* value should be low enough to ensure that the *d* value is lower than the radii of gyration of PS chains. According to Fig. 3, the thickness of the tactoid is about 30 nm. Together with the XRD data, the *n* value is calculated as 8. As a consequence, according to Eq. (1), the *d* value is calculated as 8.3 nm, which is comparable with the radii of gyration of PS chain (8.4 nm) [15]. This result means the highly confined structure is achieved. This is well consistent with the above results of structural characterizations.

4. Conclusion

Highly intercalated polystyrene (PS)/montmorillonite (OMMT) nanocomposite could be prepared via a two-step procedure with a combination of emulsion polymerization and melt intercalation. The products of the emulsion polymerization and melt intercalation possessed typical intercalated structures. The melt intercalation of the product of the emulsion polymerization tend to further expand the *d*-spacing of MMT layers and lower the distance between the tactoids to a value comparable with the radii of gyration of PS chains. The cooperative motions of PS segments were substantially depressed, indicative of the highly intercalated structure formed in the nanocomposites.

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