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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 $K\alpha_1$ ($\lambda = 0.1504$ 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 sam-