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Research paper

Effect of doubly organo-modified vermiculite on the properties of vermiculite/polystyrene nanocomposites

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ABSTRACT

Vermiculite (Verm)/polystyrene (PS) nanocomposites were prepared by dispersing a doubly organo-modified Verm (DOVerm) in PS via in situ polymerization (DOVerm/PS 1/99, 3/97, 5/95, and 7/93 mass/mass ratios). The morphology of Verm/PS nanocomposites evolved three stages as the content of DOVerm decreased in the nanocomposites: intercalation at high filler content, intermediate state of intercalation to exfoliation, and exfoliation of Verm in PS matrix with a low filler content. The morphological changes of Verm/PS nanocomposites were confirmed by the X-ray diffraction (XRD) patterns and the transmission electron microscopy (TEM) images. Compared with the pure PS, the nanocomposites filled with Verm showed significant enhancements on thermal stability and dynamic mechanical properties. Interestingly, the nanocomposites filled with 1 and 7 mass% of DOVerm exhibited more pronounced effects of Verm on the properties. It was proved that the double organo-modification clearly enhanced the ultimate properties of the Verm/PS nanocomposites.

1. Introduction

Clay mineral/polymer nanocomposites (CPN) have attracted much interest for various applications in recent years owing to the excellent properties of the materials, as well as the low cost and easy availability of starting clay minerals (Alexandre and Dubois, 2000; Annabi-Bergaya, 2008; Bergaya and Lagaly, 2007; Gilman, 1999; Pavlidou and Papaspyrides, 2008; Ruiz-Hitzky and Van Meerbeek, 2006). Depending on the nature of components used and the method for preparation, intercalated, exfoliated or partially-intercalated-partially-exfoliated CPN can be fabricated (Alexandre and Dubois, 2000; Pavlidou and Papaspyrides, 2008). Usually, three main approaches are used to prepare CPN: solution blending, melt intercalation and in situ polymerization (Alexandre and Dubois, 2000). Among them, in situ polymerization is one of the most promising methods for preparing CPN with controlled morphology, especially when polymer matrix with low polarity was employed (Zeng and Lee, 2001; Zeng et al., 2002).

Since clay minerals are naturally hydrophilic and inherently incompatible with most organic polymers, the compatibility between them is vital to produce CPN with superior properties (Owusu-Adom and Guymon, 2009; Ruiz-Hitzky and Van Meerbeek, 2006; Zanetti et al., 2000). In order to increase the interactions between clay minerals and polymer matrix, clay minerals were organically modified either by intercalating of alkyl chains (Lagaly and Beneke, 1991; Lagaly et al., 2006) or introducing different functional groups (Pinnavaia, 1983; Ruiz-Hitzky and Van Meerbeek, 2006; Williams-Daryn et al., 2002). The surface treatment facilitates the intercalation and exfoliation of clay mineral layers inside the polymer matrices and thus offering reinforcing effects for the polymers.

The most used clay minerals as nanoscaled filler are based on the smectite group (Ray and Okamoto, 2003), of which montmorillonite (Mt) is a typical representative (Panwar et al., 2011) in CPN. Vermiculite (Verm) is another 2:1 phyllosilicate (Brigatti et al., 2006), which is abundant and much cheaper than Mt (Tjong and Meng, 2003). It is generally used in packaging for antishocking purposes. Most of the Verm/polymer nanocomposites were developed by using the exfoliated Verm nanolayers as raw materials in polymers with low polarity or the intercalated organo-Verm (OVerm) as fillers in polymers with high polarity (Tjong et al., 2002a,b). However, the employment of low polarity polymer and intercalated OVerm to fabricate Verm/polymer nanocomposites with desired properties is rarely reported, especially for polystyrene (PS) which is widely used as an engineering plastic. Herein, we studied the effects of organo-modification on the compatibility between PS and Verm.

In this work, the doubly organo-modified Verm (DOVerm) was prepared successively by the intercalating of cetyltrimethylammonium cations (CTA$^+$) and grafting of 3-(trimethoxysilyl)propyl methacrylate (TMSPMA) on Verm. The obtained DOVerm was dispersed in styrene monomer to create intercalated and/or exfoliated Verm/PS nanocomposites via in situ polymerization. Structure and morphology of the Verm/PS nanocomposites were studied by X-ray diffraction (XRD)

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and transmission electron microscopy (TEM). Thermal stability and dynamic mechanical properties of the Verm/PS nanocomposites were also evaluated with a special emphasis on the effect arising from the content of DOVerm.

2. Experimental section

2.1. Materials

Verm was provided by Xinlong Verm Co. Ltd., Xinjiang, China. The raw Verm with size ranging from 2.8 to 8 mm was washed several times with deionized water and dried at 70 °C for 48 h, followed by crushing in a pulverizer for 2 min, and was then passed through a 325-mesh sieve and the fraction with size less than 45 μm was utilized for experiments. The cation exchange capacity (CEC) (70 mEq/100 g) of the pretreated Verm was determined by the ammonium acetate method (Bache, 1976; Chapman, 1965). 3-(Trimethoxysilyl)propyl methacrylate (TMSPMA, Tech) was purchased from Nanjing Yudeheng Fine Chemical Co. Ltd., China and used as received. Styrene (98%), 2,2′-azobisisobutyronitrile (AIBN, CP), cetyltrimethylammonium bromide (CTA^+B^-, 99%) and other analytical grade reagents were purchased from Sinopharm Chemical Reagent Co. Ltd., China. Styrene was washed with NaOH solution and deionized water successively, and dried over anhydrous sodium sulfate and distilled under reduced pressure, and then stored at −20 °C for further use.

2.2. Preparation of CTA^+-modified Verm (OVerm)

The procedure to prepare Na^+-Verm was described in the previous paper (Wang et al., 2011). Its CEC was 86.5 mEq/100 g. The OVerm was prepared by ion-exchange reaction between the interlayer cations of Na^+-Verm and the CTA^+ cations under the optimized conditions using the hot solution method. The OVerm was recovered by filtering the solution, followed by repeated washings of the filtered cake with deionized water and ethanol to remove excess ions.

2.3. Preparation of functionalized Verm (DOVerm)

The OVerm was chemically modified using a two-step procedure to obtain the doubly organo-modified vermiculite (DOVerm). In a typical experiment, 30 mL of TMSPMA was dispersed in 600 mL anhydrous ethanol with stirring. The pH of mixture was adjusted to 3.5–5.5 with acetic acid and the hydrolysis reaction of TMSPMA was maintained at room temperature under stirring for 1 h. Subsequently, 12.23 g OVerm was added into the mixture and the dispersion was further stirred at 50 °C for silanization for 6 h. The product was collected by centrifugation followed by repeated washing with ethanol for four times and subsequently with deionized water for one time, and dried in a vacuum oven at 70 °C for 24 h.

2.4. Preparation of Verm/PS nanocomposites

Verm/PS nanocomposite samples with DOVerm contents of 1, 3, 5 and 7 mass% (abbreviated as %) were prepared via in situ polymerization of styrene in the presence of DOVerm. A typical synthesis procedure has been previously described (Uthirakumar et al., 2004; Zhong et al., 2005). Briefly, an appropriate amount of DOVerm was dispersed into the styrene monomer, and the mixture was ultrasonicated for 15 min and then mechanically stirred for 12 h at room temperature to allow the dispersion and swelling of the DOVerm in the styrene. Subsequently, the mixture was added into a 250-mL three-neck round-bottomed flask equipped with a mechanical stirrer, a reflux condenser and a nitrogen gas inlet. Then, AIBN initiator (1.0% based on styrene) was added, followed by inlet nitrogen gas for 15 min. The resulting mixture was slowly heated to 80 °C under stirring, and polymerized at this temperature for 48 h to obtain Verm/PS nanocomposites. The samples prepared were labeled as X%DOVermPS, where X stands for the mass percentage of DOVerm in the CPN. For comparison purpose, a similar procedure was employed to prepare the pure PS and X%OVermPS. The unbound polymer in Verm/PS nanocomposites was removed with toluene using a Soxhlet extraction apparatus (Kim et al., 2002), and the residual Verm-PS powders were dried at 80 °C for 24 h.

2.5. Characterization

X-ray diffraction (XRD) patterns were recorded using a Bruker D8 Advance diffractometer (40 kV, 40 mA) with nickel-filtered Cu Kα radiation ($\lambda = 1.54$ Å) and scintillation detector over the range of 1 to 15° (2θ) at a scanning rate of 1.5°/min by a step of 0.005 2θ. All samples were dried at 70 °C for 12–24 h before analysis. The specimen for XRD measurement was prepared by dropping powder into the cavity of a plastic sample holder and simply pressing it with a glass slide by applying a normal force to make the surface of the powder mount smooth and flat. Transmission electron microscopy (TEM) images of the Verm/PS nanocomposites were obtained using a JEOL JEM-2200 transmission electron microscope operating at an accelerating voltage of 150 kV. The samples of Verm/PS nanocomposites for TEM observation were ultramicrotomed to obtain thin sections with thickness of 70–100 nm using Leica Ultracut UCT ultramicrotome. The thin sections were deposited on carbon coated Cu grids for TEM observation. Fourier-transform infrared spectroscopy (FTIR) measurements were conducted on a BIO-RAD FTS 165 instrument from 400 to 4000 cm^{-1} with 16 scans at a resolution of 4 cm^{-1} using KBr method. All samples were dried at 100 °C for 12 h to remove adsorbed water prior to the analysis. Thermogravimetric analysis (TGA) was performed on a thermogravimetric analyzer (TGA, NETZSCH STA 449C) under a nitrogen flow from 50 to 800 °C with a heating rate of 20 °C/min. The TGA data were processed into differential thermogravimetry (DTG) curves to identify the bonding interactions between organically modified Verm and polymer matrix. Dynamic mechanical analysis (DMA) was carried out on a dynamic mechanical analyzer (DMA-Q800, TA Instrument) at a fixed frequency of 1 Hz with an oscillation amplitude of 25 μm and in a temperature range of 25 to 150 °C with a heating rate of 3 °C/min.

3. Results and discussion

The aim of double organo-modification for Verm is to design silicate nanolayers which are compatible with styrene monomer and more convenient to be intercalated or exfoliated by PS matrix. The overall scheme for Verm treatment and polymerization is shown in Fig. 1. The introduction of long alkyl chain and silane coupling agent on Verm offers two major functions: (1) to increase the interlayer space of Verm layers for the insertion of styrene molecules and to convert the surface of Verm layers from hydrophilic to hydrophobic (Lee and Lin, 2006; Osman, 2006); (2) The silane treatment of Verm introduces C═C groups on Verm surface, which can participate in the polymerization process, further improves the compatibility of silicate with PS. Finally, depending on the different contents of DOVerm added into the polymer matrix, three types of Verm/PS nanocomposites (intercalated, exfoliated, and intermediate state of intercalation to exfoliation) were prepared via in situ polymerization.

3.1. Organically modified Verm

The XRD patterns of the Verm, Na^+-Verm, OVerm and DOVerm are shown in Fig. 2 (Lower panel). In the case of Verm, the treatment of sodium chloride and hydrochloric acid was applied with a consideration that Na^+ ions can be easily exchanged by alkylammonium cations, and the diluted hydrochloric acid can remove some insoluble salts on the surface of Verm and further purify the material (Carrado et al., 2006). Compared with the reflections of the Verm, which agree