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Research paper

Synthesis of polyhedral oligomeric silsesquioxane-modified organic montmorillonites and their nanocomposites with poly(L-lactide)

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ABSTRACT

Novel montmorillonites (Mts) were prepared by reacting aminopolyhedral oligomeric silsesquioxane (POSS) with organic Mt (OMt). Poly(L-lactide) (PLLA)-based nanocomposites with Mt were produced by melt compounding. The effects of POSS modified OMt (POSS-OMt) on the gas transport, thermal properties, and morphology of PLLA were investigated. POSS in the interlayers of OMt exerted important effects on the properties of the clay polymer nanocomposites (CPN). XRD studies revealed that the layer spacing of OMt increased from 1.68 nm to 3.74 nm after intercalation with POSS. TEM findings indicated that the CPN consisted of a random dispersion of intercalated/exfoliated aggregates throughout the PLLA matrix. DSC results demonstrated that incorporation of 2 mass% POSS-OMt results in a significant increase in crystallization temperature. TGA studies further showed that the CPN prepared from POSS-OMt displays a 31.2 °C increase in decomposition temperature for 5% mass loss relative to virgin PLLA. Gas permeation analysis showed that increasing the Mt concentration in the polymer matrix leads to expected decreases in permeation values. The gas barrier properties of the CPN were comparable with those predicted by phenomenological models, such as those from Nielsen and Cussler.

1. Introduction

Clay polymer nanocomposites (CPN) are used in a wide range of applications such as structural, coating, and packaging materials because of the significant improvements observed in the mechanical, flame resistance, thermal, optical, and barrier properties of the products after loading with low levels of clay versus pristine matrix polymers or conventional clay-filled nanocomposites (Galimberti et al., 2013). Montmorillonite (Mt), one of the most commonly used clay minerals in polymer nanocomposites, features low cost, a large surface area, high aspect ratios, and low toxicity (Heinz et al., 2007). Pristine Mt is hydrophilic because of its charged nature and therefore incompatible with hydrophobic polymers; reducing the polarity of the material to improve its compatibility with most polymer matrixes is usually necessary. The two main objectives of surface modification of Mt are: (1) to expand the interlayer space, allowing large polymer molecules to enter the clay interlayer spaces, and (2) to improve the miscibility of Mt with the polymer and promote good dispersion of the layered structure within the polymer matrix (Zhao et al., 2009a). At present, clay surfaces are often treated with surfactants containing long alkyl chains, where the long alkyl chains help to expand the interlayer space of the clays to facilitate their exfoliation in polymers (Bergaya and Lagaly, 2001).

Polyhedral oligomeric silsesquioxane (POSS) reagents, monomers, and polymers are emerging as a new chemical technology for nanoreinforced organic–inorganic hybrids (Lichtenhan et al., 1993; 1995), and many studies have focused on incorporating POSS monomers into polymers(Chen et al., 2012; Song et al., 2012) because of their excellent mechanical properties, thermal stability, processing simplicity, flame retardation abilities, etc. Typical POSS monomers possess the structure of cube-octameric frameworks with eight organic corner groups, one or more of which are reactive or polymerizable. Aside from thermal stability, the POSS cage also features bulkiness, which may aid the expansion of clay interlayer spaces so that the amount of hybrid surfactants required to achieve s large expansions of the interlayer space may be decreased. POSS can be used as intercalating agents of layered silicates to prepare nanocomposites combining two types of nanoreinforcement agents (Liu et al., 2005). Several POSS-modified Mts have recently been prepared for dispersion into polymers to yield Mt polymer nanocomposites. These studies were principally motivated by the high thermal stability of POSS, which allows POSS-modified Mt minerals to withstand the high temperatures required for processing some thermoplastics. The high thermal stability of POSS may be compared with the onset temperature of nonoxidative decomposition of alkyl quaternary ammonium salts, which is around 170–190 °C (Xie et al., 2001). POSS ammonium surfactants with isooctyl substituents replacing isobutyl have also been used to prepare Mt polypropylene

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(Zhao et al., 2009b) and Mt poly(butylene terephthalate) (C.Y. Wan et al., 2008) nanocomposites.

Most of the available work on POSS-modified Mt uses POSS as a substitute for onium ions during clay modification. POSS derivatives containing short alkyl chains with amine groups behave like surfactants and POSS-modified Mts are synthesized via ion–exchange reactions. Although POSS-based surfactants could show decreased degradation, concerns on the inherent tendency of POSS compounds to aggregate or crystallize (Abad et al., 2003; Chan et al., 2005), which may hinder the exfoliation of POSS-modified clay in polymer matrices, have been raised; these concerns limit the wider application of the CPN.

In previous research, the concept of "twice functionalization" to modify clay was introduced, using an organic agent to swell the Mt and a functional agent to react with the polymer matrix and further improve interfacial interactions (Chen and Yoon, 2005a; Chen et al., 2005a, b, 2007; Li et al., 2011). In the present work, the synthesis of POSS-modified organic Mt (OMt) that had been previously modified by cationic surfactants was described. The resultant POSS-modified OMt (POSS-OMt) is then employed to prepare nanocomposites of poly(L-lactide) (PLLA). Finally, the properties of the CPN barrier membranes were investigated using extended ranges of several mathematical models to identify the benefits and limitations of CPN barrier materials.

2. Experimental

2.1. Materials

The OMt, I.24TL-Mt (Cation Exchange Capacity (CEC) is about 143 meq/100 g), was purchased from Nanocor Co., USA, and was purified by dissolution in ethanol at 70 °C for 4 h to remove any contaminants. The structure of the organic modifier is: $HOOC\text{-}(CH_2)_{17}\text{-}NH_3^+$. The POSSs used to modify OMt were commercial products, e.g. aminoethylaminopropylIsobutyl POSS (AEP-POSS), aminopropylisooctyl POSS (APO-POSS), and aminopropylIsobutyl POSS (APB-POSS), purchased from Hybrid Plastic Co. USA. PLLA was manufactured by Weihua Co. (Shenzhen, China) with a weight-average molecular weight of 2.4×10^5.

2.2. Preparation of POSS-OMt

The typical procedure of POSS-OMt is described as follows: the mixture of I.24TL-Mt (5 g) and excess thionyl chloride ($SOCl_2$) was heated and stirred vigorously in an oil bath with reflux at 80 °C for 24 h. The product was then filtered and repeatedly washed with hexane at room temperature to obtain the acyl-chloride functionalized OMt (OMt-COCl), a kind of gray powder. Then the OMt-COCl was mixed with 10 g of aminoPOSS and excess re-steamed THF. The mixture was heated and stirred vigorously in an oil bath with reflux at 75 °C for 24 h. The product was then filtered and repeatedly washed with re-steamed THF to yield the POSS-OMt. The POSS-OMt was dried in a vacuum oven at 50 °C for 24 h in order to remove the residual solvents. The synthetic schematic diagram of POSS-OMt is shown in Fig. 1.

2.3. Preparation of Mt PLLA nanocomposites

The nanocomposites of Mt and PLLA were prepared by melt compounding of PLLA with Mt using HAAKE torque rheometer at 190 °C under 60 rpm for 5 min. The resulting products were then hot pressed at 190 °C for 1 min under 4 atm to prepare the sheets with a thickness of approximately 0.5 mm. The molded sheets were then quickly cooled prior to their use for the various characterizations.

2.4. Characterization

The morphology of the CPN was analyzed by TEM (JEOL 2000FX) with an acceleration voltage of 120 kV. All the ultrathin sections (<100 nm) were microtomed with a Super Nova 655001 instrument (Leica, Switzerland) with a diamond knife and were then subjected to TEM observation without staining. The basal spacing of the Mt and the Mt PLLA nanocomposites was measured with an X-ray diffractometer (Bruker AXS, D8) with CuKα radiation at 45 kV and 50 mA. The diffraction patterns were collected in the range $0.5° < 2\theta < 10°$ at a scanning rate of 1°/min. Thermal gravimetric analysis (TGA) was performed on a Setaram TGA 92 Thermobalance, by heating the samples with 10 °C/min heating rate from ambient temperature to 900 °C at nitrogen atmosphere. The crystallinity of PLLA and its nanocomposites was measured by a differential scanning calorimeter (DSC) and the experiments were performed with a PerkinElmer DSC 7 series instrument (Norwalk, CT) at nitrogen atmosphere. The samples were analyzed by the following temperature program: heated up from 0 °C to 190 °C at 20 °C/min to eliminate the heat history of specimen; maintained for 5 min at 190 °C, followed by cooling the specimen down to 0 °C by liquid nitrogen; and maintained for another 10 min before heating up again to 190 °C at 10 °C/min.

Gas permeabilities of the pure PLLA and the Mt PLLA nanocomposites were measured in an automatic tightness tester which was a home-made according to the standard of ISO2782. Ultra high purity nitrogen was used for purging and analyses. The film specimens were cut into a circular shape with a diameter of 8 cm, and then tested at 60 °C and under 0.57 MPa. The membranes were placed in a stainless steel cell with chambers of known volume on each side. The nitrogen permeation rate was then calculated by multiplying the measured transmission rate by the average sample thickness. Each sample was measured at five points oriented in a cross pattern over the testing area, and the results were averaged. The CPN systems were tested for permeability using

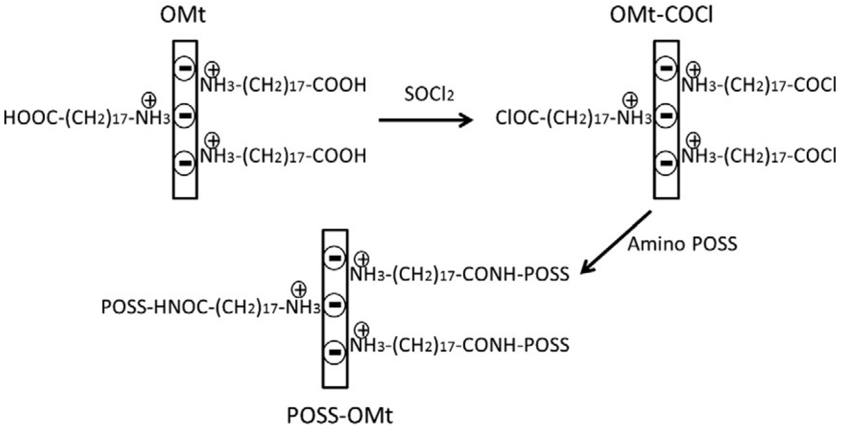

Fig. 1. The preparation of POSS-OMt.