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Chemical modification of palygorskite with maleic anhydride modified polypropylene: Mechanical properties, morphology, and crystal structure of palygorskite/polypropylene nanocomposites

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ABSTRACT

Maleic anhydride modified polypropylene (PP) (PP-g-MAH) was chemically grafted onto palygorskite (Pal) via the bridge linking of [3-(2-aminoethyl)aminopropyl]trimethoxysilane (Z-6020) and PP-g-MAH in the presence of ultrasonic oscillation. The modified Pal was added to a PP matrix as a nano-filler to prepare Pal/PP nanocomposites by melt blending. Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy were used to discern that PP-g-MAH and Z-6020 were chemically grafted onto Pal via acrylation between —NH_2 and anhydride groups. The Pal/PP nanocomposites were characterized by Scanning electron microscopy, transmission electron microscopy and wide angle X-ray diffraction. The toughness and strength of PP could be improved markedly by the addition of modified Pal. The modified Pal was dispersed uniformly in the PP matrix in the form of individual crystal needles, which demonstrated the presence of strong interactions between the modified Pal and PP. The modified Pal could induce the formation of β-form PP crystals and promote the motion of PP chains during crystallization.

1. Introduction

Palygorskite (Pal) is a type of clay with the chemical formula $Mg_5(Al)Si_8O_{20}(OH)_2(OH_2)_4 \cdot 4H_2O$ (Haden and Schwint, 1967). Pal is generally used as a catalyst carrier (Cao et al., 2008; Guo and Shi, 2013; Li et al., 2012; Ma et al., 2009; Pushpaletha and Lalithambika, 2011) and an adsorbent (Liu, 2007; Frost et al., 2010) because of its large surface area. Despite the presence of ribbons with a 2:1 phyllosilicate structure, Pal differs from other layered silicates because Pal lacks continuous octahedral sheets. In Pal, each ribbon links with the next via the inversion of SiO_4 tetrahedra along a set of Si—O—Si bonds, which extend parallel to the *a*-axis and their width runs along the *b*-axis of two linked chains. Because of its chain phyllosilicate structure, Pal can be broken easily by shear stress to form fiber crystals (Galan, 1996). Therefore, Pal has been used recently as a nano-filler to improve the mechanical properties of polymers (Shen et al., 2005; Wang and Sheng, 2005; Wang et al., 2008; Xue et al., 2006; Zhao et al., 2007).

Pal can significantly improve the wear resistance of polyimide and polytetrafluoroethylene (Lai et al., 2007). The effect of Pal filler on the properties of nylon 6 was also investigated by Subramani et al. (2008), where they found that Pal could act as an effective reinforcement for nylon 6. In addition, 4,4′-methylene bis(phenyl isocyanate) molecules were grafted onto Pal surfaces via chemical bonding and the modified Pal was then incorporated into a polyurethane matrix by in situ polymerization (Wang et al., 2008), where the results showed that the tensile strength and Young's modulus of polyurethane could be increased by >75% when the modified Pal content was 10 wt.%. In another study (Yuan et al., 2007), Pal was modified with hexadecyltriphenylphosphonium bromide and 3-glycidoxypropyltrimethoxysilane, and Pal/poly(ethylene terephthalate) (PET) nanocomposites were then prepared via in situ polycondensation. It was found that the flexural modulus of the Pal/PET composites filled with 3 wt.% Pal was 41.1% higher than that of pure PET.

Polypropylene (PP) is a widely used polymer with good processability, low cost, and relatively high mechanical properties, but its impact resistance is poor (Houshyar and Shanks, 2007; Lin et al., 2008; Chen et al., 2009; Song et al., 2009). To improve the impact resistance without any loss of strength, clay/PP nanocomposites have been studied for many years (Kawasumi et al., 1997; Perrin-Sarazin et al., 2005; Tarapow et al., 2009; Chen et al., 2011; Furlana et al., 2011). However, it is still challenging to prepare clay/PP nanocomposites with well-exfoliated structures.

Compatibilization plays an important role during the preparation of clay/PP nanocomposites (Karsli and Aytac, 2011). In general, maleic anhydride grafted PP (PP-g-MAH) is used to improve the compatibility

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between PP and clay such as montmorillonite (Ray and Okamoto, 2003; Hari et al., 2009), but few studies have addressed the preparation of Pal/PP nancocomposites.

In the present study, Pal was broken into individual crystal needles using ultrasonic oscillation and PP-g-MAH was then reacted with [3-(2-aminoethyl)aminopropyl]trimethoxysilane (Z-6020), which was pre-grafted onto the surfaces of the Pal crystal needles. Thus, PP-g-MAH was chemically grafted onto the surfaces of the crystal needles to improve the compatibility between Pal and PP. This good compatibility might improve the uniform dispersion of Pal in the form of crystal needles and enhance the mechanical properties of PP. Thus, the effects of modified Pal on the mechanical properties, morphology, and crystal structure of PP were also investigated.

2. Experimental

2.1. Materials

Pal clay was kindly provided by Anhui Mingguang Rare Minerals Co. Ltd, China. PP (grade F401) with a melt flow index of 2.5 g/10 min (190 °C/2.16 kg) was obtained from Langang Petrochemical Co. Ltd, China. [3-(2-aminoethyl)aminopropyl]trimethoxysilane (Z-6020), which has the formula $NH_2CH_2CH_2NHCH_2CH_2CH_2Si(CH_3O)_3$, was provided by Dow Corning Co. Ltd (USA). PP-g-MAH grafted with 1 wt.% maleic anhydride was provided by the ChenGuang Research Institute of Chemical Industry. Xylene and ethanol were analytical grade and purchased from Kelong Chemical Reagent Company (Chengdu, China).

2.2. Synthesis of Z-6020-Pal and Z-6020-MAH-Pal

Z-6020-Pal was synthesized as follows. First, 20 g Pal was dispersed in 400 mL of deionized water using ultrasonic oscillation. Next, 0.4 g of completely hydrolyzed Z-6020 was added to the reaction container and the mixture was kept at 30 °C for 3 h. The product was then filtered and washed three times with deionized water to remove any free Z-6020. The hybrid Pal obtained was dried at 80 °C in a vacuum for 12 h.

Z-6020-MAH-Pal was synthesized as follows. First, 10 g Z-6020-Pal was dispersed in 200 mL of xylene using ultrasonic oscillation. Next, 20 g PP-g-MAH was dissolved in 300 mL of boiling xylene and added to the Z-6020-Pal suspension, and the mixture was then heated at 120 °C for 6 h. The entire process was performed in a nitrogen atmosphere with ultrasonic oscillation. The final product was filtered and washed three times with hot xylene to remove any unreacted PP-g-MAH. The hybrid Pal obtained was dried at 120 °C in a vacuum for 12 h.

2.3. Preparation of Pal/PP nanocomposites

The Pal/PP nanocomposites were prepared by melt blending in a two-roll mill at 190 °C with a residence time of 8 min. The Pal content was varied from 0.5% to 5% by weight of PP. The composites obtained were molded in a platen press at 10 MPa pressure and 190 °C for 10 min, and then cooled to room temperature in another platen press at 10 MPa pressure. Specimens measuring 1 mm and 4 mm in thickness were cut from the plaques for different analyses.

2.4. Characterization of the modified Pal

Fourier transform infrared spectroscopy (FTIR) analysis of the modified Pal was performed on a Tensor 27 FTIR spectrometer (Bruker) using the KBr pressed disk technique. Sample disks were prepared by mixing 1 mg of the samples with 500 mg of KBR (Merck) in an agate mortar. Scans were run at a resolution of 4 cm^{-1} from 4000 to 400 cm^{-1} with acquisition times of approximately 1 min. The samples were extracted in boiling xylene for 72 h to remove the unreacted PP-g-MAH before scanning.

X-ray photoelectron spectroscopy (XPS) analysis of the modified Pal was performed using a Kratos XSAM 800 spectrometer with an Al Kα X-ray source (1486.6 eV) at a power of 180 W (12 kV and 15 mA) and a pressure of 2×10^{-7} Pa. Spectrometer pass energy of 160 eV was used for full scan, while 20 eV pass energy was used for the high resolution scans. All of the binding energies were calibrated according to the C1s peak at 284.8 eV. The binding energy scale of spectrometer was calibrated using the metallic Cu 2p3/2 lines and Ag Fermi Edge of the respective reference metals. The samples were extracted by boiling in xylene for 72 h before scanning.

2.5. Mechanical properties

The notched Izod impact strengths of Pal/PP nanocomposites were measured with a ZQK-20 (Dahua Material Testing Technical Co., China) according to GB/T 1043–93 (China). The tensile strength was tested according to GB/T 1040–92 (China) using a CMT 4104 system (Sans Material Testing Technical Co., Shenzhen, China) with a cross-head speed of 50 mm/min. The samples were kept at 23 °C for 24 h before the mechanical tests.

2.6. Morphological characterization

2.6.1. Scanning electron microscopy (SEM)

The impact fracture surface morphologies of Pal/PP nanocomposites were observed using a Philips SEM instrument with an accelerating voltage of 20 kV. The surface was coated with a thin layer of gold to reduce the charge build-up on the surface and to improve the conductivity.

2.6.2. Transmission electron microscopy (TEM)

TEM observations were performed using an H-7100 (Tokyo, Japan) instrument with an accelerating voltage of 100 kV. Ultrathin samples with a thickness of 50 nm were microtomed at 20 °C using a Reichert Ultracut cryoultramicrotome without staining.

2.7. Wide angle X-ray diffraction (WAXD)

The crystal structures of PP and Pal/PP nanocomposites were assessed in wide angle X-ray diffraction experiments at room temperature using a Philip X'Pert Pro diffractometer, where the X-ray beam comprised nickel-filtered Cu Kα ($\lambda = 0.1542$ nm) radiation, which was operated at an acceleration voltage of 40 kV and a current of 35 mA. The corresponding 2θ data were collected from 5° to 40° with a step-size of ca 0.02°. Scan speed, counting time and slit width were 6°/min, 0.3 s, and 1.0°, respectively.

2.8. Differential scanning calorimetry (DSC)

The melting behaviors of the PP and Pal/PP nanocomposites were determined in a constant nitrogen flow using a Mettler Toledo DSC 1 differential scanning calorimeter thermal analyzer. Approximately 5 mg of each sample was placed in a standard aluminum crucible and heated from room temperature to 200 °C at a rate of 10 °C/min.

3. Results and discussion

3.1. Surface modification of Pal

The silane coupling agent could be chemically grafted onto the surface of Pal by hydrolysis condensation. First, the —NH_2 group in Z-6020 reacted with PP-g-MAH. Thus, PP-g-MAH was chemically grafted onto Pal via the bridge linking of Z-6020 and PP-g-MAH. FTIR and XPS measurements were obtained to verify this reaction. The FTIR spectra of the original Pal and the modified Pal are shown in Fig. 1, which shows that some new adsorption bands were present in the