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Research paper

Mechanical and thermal properties of palygorskite poly(butylene succinate) nanocomposite

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ABSTRACT

Palygorskite (Pal) and modified Pal (OPal) by a silane coupling agent are used to improve the mechanical and thermal properties of poly(butylene succinate) (PBS) and the nanocomposites are prepared by melt blending. The synthesized palygorskite PBS nanocomposites are characterized by thermo-gravimetric analysis (TGA), X-ray diffraction (XRD), and scanning electron microscopy (SEM). The mechanical properties and dynamic mechanical and crystallization behavior have been studied. Surface modification improves the dispersion of Pal in the PBS matrix and 16% improvement in the tensile strength is observed from palygorskite PBS nanocomposites with 3 wt.% of OPal compared to pure PBS. The flexural properties and thermal stability of the palygorskite PBS nanocomposites are also enhanced significantly in the presence of OPal. Incorporation of OPal increases the storage modulus and decreases tan δ demonstrating the reinforcing effects of clay on the PBS matrix. Thermal analysis reveals that the Pal nanoparticles are effective nucleating agents accelerating crystallization. The glass transition temperature increases slightly in the presence of palygorskite except the sample with 2 wt.% clay.

1. Introduction

Polymer/clay nanocomposites have attracted much attention, because the properties of polymer can be greatly improved through modification with the clay (Gao et al., 2005; Lin et al., 2014; Wu et al., 2014). Zhou and Keeling (2013) demonstrated the preparation and evolution of clays and clay minerals providing insights and spurring applications to mining, environmental management, paleoclimate, as well as earth and extraterrestrial sciences in the 34th International Geological Congress held in 2012. Zhou et al. (2011) stated an overview on strategies towards clay-based designer catalysts for green and sustainable catalysis and prospects for the preparation of clay-based catalysts and their catalytic applications were briefly discussed. Palygorskite (Pal) is a crystalline hydrated magnesium aluminum silicate with a unique three-dimensional structure and fibrous morphology. Pal has the chemical formula of $Si_8O_{20}Mg_5(Al)(OH)_2(H_2O)_4 \cdot 4H_2O$ and the structure has been studied (Bradley, 1940; Yang et al., 2014). Pal possesses a random network composed of densely packed rods with a diameter of less than 100 nm and lengths varying from several hundreds of nanometers to several micrometers. The large aspect ratio of the Pal fibers renders them useful as fillers to reinforce rubber, plastics, and common polymers including polyvinyl alcohol (Peng and Chen, 2006), styrene butadiene rubber (Tian et al., 2003), epoxy resins (Lan and Pinnavaia, 1994; Xue et al., 2006), polyamide (Shen et al., 2005; Pan et al., 2006), polyimide (Lai et al., 2005), polypropylene (Wang and Sheng, 2005), and polyurethane (Ni et al., 2004; Pan and Chen, 2007).

Interfacial adhesion plays a key role in polymer composites (Puka'nszky, 2005). It is generally accepted that hydrophilic silicate layers are not compatible with hydrophobic polymers but more compatible with hydrophilic polymers. In order to improve the interaction between the hydrophilic Pal and hydrophobic polymer, Wang and Sheng (2005) modified palygorskite using silane and performed graft polymerization with butyl acrylate to obtain org-palygorskite/polypropylene (PP) nanocomposites and the results showed that the strength and stiffness of the PP/Pal nanocomposites were improved significantly. Preparation of Pal/hydrophilic polymer composites has also been reported. Xu and He (2001a, 2001b) studied the crystallization behavior of polyoxymethylene/Pal and compared the isothermal crystallization behavior of polyoxymethylene with and without Pal. Shen et al. (2005) prepared the nylon 6/Pal nanocomposite by in situ polymerization. However, few studies have hitherto been conducted to determine the properties of Pal reinforced poly(butylene succinate) (PBS) nanocomposites. PBS is a white crystalline thermoplastic with a melting point of 90–120 °C (similar to LDPE), glass transition temperature of about −45 °C to −10 °C (between PE and PP), tensile strength between PE and PP, and stiffness between

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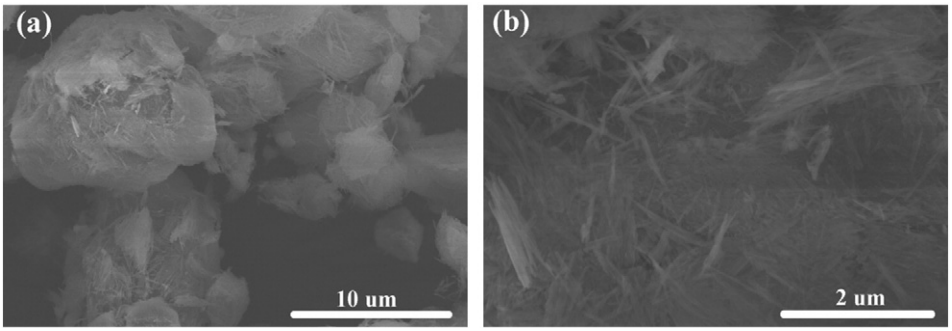

Fig. 1. SEM micrographs of (a) Pal and (b) OPal.

LDPE and HDPE (Park et al., 2006). PBS can be processed on polyolefin processing machines to form various products (Park et al., 2006; Liu et al., 2013; Qi et al., 2013a, 2013b, 2013c). Furthermore, PBS is a biodegradable polymer after polymerization by butanediol and succinic acid and the materials are potentially bio-based renewable sources. Hence, composites fabricated with the biodegradable polymer PBS as the matrix and natural clay as enhancement fillers are also biodegradable and they have received much attention due to progress in environmental protection as well as government regulations (Wambua et al., 2003). Chen (2008) modified Pal using the hexadecyltrimethylammonium bromide surfactant and prepared Pal PBS nanocomposites by melt blending. The nucleation effect was observed, but the mechanical properties such as Young's modulus of the PBS nanocomposites were not affected as there was no strong interaction between the surfactant and Pal.

In this work, Pal was modified using the silane coupling agent KH-570 and palygorskite PBS nanocomposites produced by the simple melt compounding approach possess in a twin-screw extruder improved mechanical and thermal properties due to the good dispersion of OPal in the PBS matrix.

2. Experimental details

2.1. Materials

Poly(butylene succinate) was obtained from the HKH National Engineering Research Center of Plastics Co. Ltd. The melt flow index was 5 ± 1 g/10 min and density was 1220 kg/m^3. Palygorskite was bought from Xuyi Company, Jiangsu, China (200 mesh sieve and specific surface area 150 m^2/g). The γ-methacryloxypropyl trimethoxysilane (KH-570) utilized as the coupling agent was purchased from Beijing Chemical Reagent Company, Beijing, China. All the other chemicals in this study were reagent grade and used without additional purification.

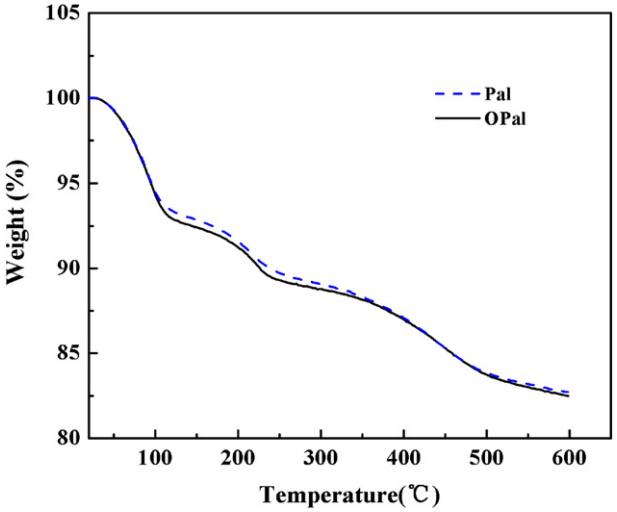

Fig. 2. TGA curves of Pal and OPal.

2.2. Preparation of OPal

Hydrochloric acid was used to remove impurities such as quartz and carbonate from Pal. To improve the compatibility of Pal with the PBS matrix, a silane coupling agent KH-570 was used to modify Pal (Wang and Sheng, 2005). 150 g of Pal was dispersed in 300 g of concentrated HCl solution ultrasonically and a certain amount of KH-570 (1.5 wt.% relative to Pal) isopropyl alcohol solution was added to the dispersion and hydrolyzed under acidic conditions. The dispersion was heated to 60 °C for 2 h and then the Pal dispersion was centrifuged, rinsed with alcohol several times, and dried in vacuum at 80 °C for 4 h. The obtained organic Pal was ground into powders (Wang and Sheng, 2005).

2.3. Preparation of palygorskite PBS nanocomposites

The Pal and PBS granules were dried at 90 °C for 2 h in a conventional oven and then at 80 °C for 5 h in a vacuum oven before use. PBS and Pal were mixed according to different contents of Pal (0, 1, 3, 5, and 8 wt.%), and then prilled by a melt-compounding method using a twin-screw extruder (SHJ-35, Nanjing Juli Chemical Machinery Co., Ltd. China) at a screw speed of 200 rpm. In the process, the temperature profile was 146, 149, 150, 150, 148, 155, 153, and 156 °C from hopper to die. The sample was designated as Pal PBS nanocomposites. Using the same method, OPal instead of Pal was obtained from the OPal PBS nanocomposites.

2.4. Characterization

2.4.1. Mechanical properties

The samples for mechanical testing were prepared using an injection molding machine (DH-90, Ningbo Haitian Plastics Machinery Co., Ltd. China) at a barrel temperature of 145–155 °C and an injection pressure of 400 bar. The tensile samples were injected into dog-bone specimens with dimensions of 150 × 10 × 4 mm^3. The tensile tests were carried out on a universal materials testing system (GB/T1040-1992, China) at room temperature at a crosshead speed of 20 mm/min. The samples for the flexural tests had dimensions of 150 × 10 × 4 mm^3. The bending tests were carried out according to the GB/T9341-2000 protocol at a crosshead speed of 2 mm/min. All the data reported here represented the average of at least five specimens.

2.4.2. Dynamic mechanical analysis

The storage modulus and tan δ of the palygorskite PBS nanocomposites were measured from −50 to 110 °C under N_2 using a dynamic mechanical analyzer (DMA, Seiko SII Model DMS6100). The specimen dimensions were 40 mm × 8 mm × 0.2 mm. A slow heating rate of 2 °C/min was used to thermally equilibrate each specimen in the