Research paper

Use of ionic monomers to prepare halloysite polymer nanocomposites with reinforced mechanical performance

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ARTICLE INFO

ABSTRACT

Pristine halloysite (Hal) nanotubes were used to fabricate polymer-based nanocomposites via in situ polymerization: Methyl methacrylate (MMA) was selected as main monomer, and respectively copolymerized with a small quantity of ionic comonomer 2-(methacryloyloxy)ethyltrimethylammonium chloride (MTC) and 2-acrylamido-2-methylpropane sulfonic acid (AMPS), meanwhile Hal was added during the polymerization process. The noncovalent interactions between Hal and ionic comonomers are key factors of successful preparation of Hal P(MMA-co-MTC) nanocomposite and Hal P(MMA-co-AMPS) nanocomposite. The mechanical properties of nanocomposites were investigated in detail. The results indicate that, the nanocomposites demonstrated excellent mechanical performance due to strong interfacial adhesion ameliorated by noncovalent interactions; Hal exhibited much stronger interfacial adhesion with P(MMA-co-MTC) matrix compared to that with P(MMA-co-AMPS) matrix; and the nanocomposites containing 1.5 wt% Hal content and 10 wt% MTC content showed the highest tensile strength and flexural strength, respectively improved by 47.5% and 165.6% compared with neat PMMA. The highlight of this work is to provide a simple and feasible Hal polymer nanocomposites preparation technique with high mechanical performance improvement and slight Hal loadings.

1. Introduction

Halloysite (Hal) nanotubes are a sort of one-dimensional naturally occurring clay minerals with molecular formula of $Al_2Si_2O_5(OH)_4 \cdot nH_2O$ (Hendricks, 1938). In recent years, due to a unique combination of inorganic multi-walled tubular crystalline nanostructure, high aspect ratio, natural availability, pleasurable biocompatibility and rich functionality, Hal has captured growing attentions and been applied in a variety of fields (Pasbakhsh et al., 2013; Tan et al., 2014; Yuan et al., 2015; Zhang et al., 2016). Among them, in the field of polymer-based composites, Hal is widely utilized as nanofillers to enhance mechanical strength, thermal stability and biocompatibility (Du et al., 2010; Khunova et al., 2013; Lecouvet et al., 2014; Liu et al., 2014; Jamaludin et al., 2015; Mauler et al., 2015). Compared with other common nanofillers such as silica, carbon nanotubes and graphene, Hal exhibits weak interactions among themselves because of few hydroxyl groups and siloxane on the surfaces and their proper length (0.2–2.0 μm), which makes Hal relatively readily achieve uniform dispersion in polymer-based composites (Du et al., 2010). However, poor interfacial interactions between raw Hal and polymer matrix could easily give rise to interfacial slippage, resulting in the deterioration of the nanocomposites properties especially mechanical performance (Liu et

al., 2014). Therefore, the interface between two phases must be seriously engineered for reinforced interfacial interactions.

To improve the interfacial interactions and further optimize the properties of nanocomposites, the extensively used method is Hal modification mainly consisting of covalent functionalization (Jia et al., 2011; Joo et al., 2012; Yah et al., 2012) and noncovalent functionalization (Solomon, 1968; Du et al., 2007; Lvov et al., 2014). The covalent methods mean the selected modifiers react with hydroxyl groups of Hal to attach the surfaces of Hal through covalent bonds, while the noncovalent methods mainly utilize noncovalent interactions including electrostatic interactions, hydrogen bonding interactions, electron transfer interactions, etc. Compared with covalent functionalization, noncovalent process is relatively facile, environmentally friendly and high cost-effective, consequently becomes the hot topic. As an example, Liu et al. (2012) prepared Hal chitosan bionanocomposite films via solution casting; and the electrostatic attraction as well as hydrogen bonding interactions between two phases, increased mechanical properties and superior cytocompatibility were confirmed. In another instance, Tu et al. (2013) fabricated Hal nanocomposite hydrogels with tunable mechanical properties and drug release behavior by hydrogen bonding interactions.

Ionic monomer is a kind of polymerizable molecules with positive and/or negative charges, exerting a tremendous fascination on increasing researchers due to favorable solubleness in water (Li et al., 2009; Sun et al., 2013; Gillespie et al., 2014). Also, hydrophilicity and small

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dimensions make pristine Hal easily dispersed in water (Liu et al., 2012). According to the characteristics of ionic monomer and Hal, preparing Hal polymer nanocomposites assisted by ionic monomer is reasonable and efficient. That is, ionic monomer attaches the surfaces of Hal through noncovalent interactions and simultaneously copolymerizes with desired monomer to prepare nanocomposite. So far this preparation method has not been reported in literature.

In this work, methyl methacrylate (MMA) was selected as main monomer, and 2-(methacryloyloxy)ethyltrimethylammonium chloride (MTC) as well as 2-acrylamido-2-methylpropane sulfonic acid (AMPS) were respectively utilized as cationic and anionic comonomer. Original Hal was used as nanofiller to improve the mechanical performance of matrix. The copolymer was synthesized via suspension copolymerization of MMA and a small quantity of ionic comonomers, meanwhile Hal was adsorbed by the copolymer through noncovalent interactions during the copolymerization process to prepare nanocomposites. Transmission electron microscopy (TEM), ^{1}H nuclear magnetic resonance (^{1}H NMR), Fourier transform infrared spectroscopy (FTIR), gel permeation chromatography (GPC) and scanning electron microscopy (SEM) were used, and the mechanical properties of achieved nanocomposites were investigated in detail.

2. Materials and methods

2.1. Materials

Hal (length: 1–3 μm; inner diameter: 5–20 nm; specific surface area: 65 m^2/g; pore volume: 1.25 mL/g; cation exchange capacity: 8.0 meq/g; refractive index: 1.54; specific gravity: 2.53 g/cm^3) was supplied by Sigma-Aldrich Co. (Milwaukee, WI). MTC was obtained from Alfa Aesar Chemical Reagent Co. (Tianjin, China). AMPS was purchased from Aladdin Industrial Co. (Shanghai, China). MMA was provided by Kermel Chemical Reagent Co. (Tianjin, China) and purified by the standard treatment with 5% aqueous NaOH and then deionized water, followed by distillation at a normal pressure and finally stored at low temperature prior to use. Benzoyl peroxide (BPO, analytical grade, Beijing Chemical Factory, Beijing, China) was used as initiator. Hydroxyethyl cellulose (HEC, analytical grade, Heda Co., Ltd., Shandong, China) was used as dispersant. Sodium dodecyl benzene sulfonate (SDBS, analytical grade, Tianjin Tianzhi Fine Chemical Co., Ltd., Tianjin, China) was used as surfactant. Other reagents were all of analytical grade. Deionized water was used throughout.

2.2. Preparation of copolymer and nanocomposite microspheres

Copolymer and nanocomposite microspheres were prepared via in situ suspension copolymerization. 60 g organic mixtures of MMA and ionic comonomer (the content of ionic comonomer MTC or AMPS is 5 wt%) and original Hal with diverse proportions (the Hal content is 0 wt%, 0.5 wt%, 1.0 wt%, 1.5 wt% and 2.0 wt%, respectively, based on the sum of organic mixtures) were ultrasonically dispersed, and the achieved mixtures of Hal and organic solution were then added to the three-neck flask followed by adding 180 mL deionized water containing 1.8 g HEC and 0.072 g SDBS. The obtained mixtures were stirred at 400 rpm bubbled with nitrogen for 30 min to obtain homogeneous suspension system, and then the reactors were heated to 75 °C. After 0.6 g BPO was added to the system, the reaction was performed for 6 h with stirrer at 700 rpm. The reaction products were repeatedly washed with deionized water, filtered and then dried in a vacuum oven overnight at 60 °C until constant mass to obtain copolymer and nanocomposite microspheres, denoted as P(MMA-co-MTC), P(MMA-co-AMPS), Hal P(MMA-co-MTC) nanocomposite and Hal P(MMA-co-AMPS) nanocomposite, respectively. The nanocomposite microspheres without ionic comonomer are marked as Hal PMMA nanocomposite.

For Hal P(MMA-co-MTC) nanocomposite, the extra nanocomposite microspheres with 0 wt%, 0.5 wt%, 1.0 wt%, 1.5 wt% and 2.0 wt% Hal content (the MTC content is fixed at 10 wt%) and the nanocomposite microspheres with 1.0 wt% Hal (the MTC content is fixed at 15 wt%) were prepared respectively with the same procedure as described above.

2.3. Preparation of specimens for mechanical tests

Obtained polymer and nanocomposite microspheres were mixed with MMA by the mass ratio of 1:1 and introduced into the resin dough, which then was put into the mold and pressed in a pressing apparatus. The mold was placed in water and heated. After cooling to room temperature, the specimens were removed and polished for further mechanical tests. The standard of tensile specimens was 50 × 7 × 2 mm^3 and that of flexural specimens was 64 × 10 × 3.3 mm^3.

2.4. Characterization

Examination of the morphology of original Hal was performed on a Philips Tecnai G2 F20 TEM. The sample was prepared by dropping a dispersion sample in deionized water on a Cu grid coated with a carbon film.

The ^{1}H NMR spectra of neat PMMA (hereafter "neat PMMA" is designated as "PMMA"), P(MMA-co-MTC), P(MMA-co-AMPS), Hal P(MMA-co-MTC) nanocomposite and Hal P(MMA-co-AMPS) nanocomposite were recorded using an INOVA 500 MHz NMR spectrometer (Varian, USA) with CDCl$_3$ as the solvent. The magnetic field strength is 11.75 T. Chemical shifts were reported in ppm units with tetramethylsilane as an internal standard.

Prior to FTIR measurement, Hal PMMA nanocomposite, Hal P(MMA-co-MTC) nanocomposite and Hal P(MMA-co-AMPS) nanocomposite were Soxhlet extracted with refluxing acetone for 48 h, and then dried in a vacuum oven at 60 °C to remove the acetone. The extracted Hal from Hal PMMA nanocomposite, Hal P(MMA-co-MTC) nanocomposite and Hal P(MMA-co-AMPS) nanocomposite are denoted as Hal-1, Hal-2 and Hal-3, respectively. FTIR spectra of original and extracted Hal samples were recorded by a Nicolet Magna Nicolet-5DX FTIR spectrometer in the scan range of 4000–450 cm^{-1} using KBr disc technique. The leaching solution with acetone precipitated by adding deionized water and dried to remove the acetone before used to detect the molecular weight by a Viscotek TDA305 GPC. The molecular weight of PMMA, P(MMA-co-MTC) and P(MMA-co-AMPS) was also detected in the same way.

The morphologies of Hal PMMA nanocomposite, Hal P(MMA-co-MTC) nanocomposite and Hal P(MMA-co-AMPS) nanocomposite microspheres as well as the tensile fracture surfaces of specimens for mechanical tests were observed by a Hitachi S4800 SEM after they were sputter coated with a thin layer of gold.

2.5. Mechanical tests

The tensile and three-point bending tests were carried out at room temperature by using a Testometric Universal Tester M350-20kN at a crosshead speed of 2 mm/min and 5 mm/min, respectively. The span between loading points for bending tests was 50 mm. At least five specimens were tested for each sample and mean value was reported.

3. Results and discussion

3.1. Structure characterization of the Hal, copolymer and nanocomposites

Fig. 1 displays the TEM micrograph of the original Hal with a predominant tubular structure. One can see that Hal are polydisperse in length, mostly ranging between 0.5 μm and 2.0 μm. The average outer diameter and inner empty lumen diameter of Hal is around 40 nm and 15 nm, respectively.