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Helical polyurethane@attapulgite nanocomposite: Preparation, characterization and study of optical activity

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ABSTRACT

Helical polyurethane@attapulgite (BM-ATT) based on R-1,1′-binaphthyl-2′,2-diol (R-BINOL) composite was prepared after the surface modification of attapulgite (ATT). BM-ATT was characterized by Fourier-transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HTEM) and vibrational circular dichroism (VCD) spectroscopy. FT-IR and XRD analyses indicate that the helical polyurethane has been successfully grafted onto the surfaces of the modified ATT without destroying the original crystalline structure of ATT. BM-ATT exhibits the rod-like structure by SEM, TEM, and HTEM photographs. BM-ATT displays obvious Cotton effect for some absorbance in VCD spectrum, and its optical activity results from the singlehanded conformation of helical polyurethane.

1. Introduction

Recently the focus has turned on the natural clay minerals, including montmorillonite [1], kaolin [2], mica [3], smectite [4] attapulgite [5] and sericite [6], for the preparation of nanocomposites due to their low-cost and unique properties. Attapulgite (ATT) is a kind of crystalline hydrated magnesium aluminum silicate with unique three dimensional structures and has a fibrous morphology with exchangeable cations and reactive –OH groups on its surface. ATT has the structural formula $Si_8O_{20}Mg_5(Al)(OH)_2(H_2O)_4 \cdot 4H_2O$ and its ideal structure is studied by Bradley early in 1940. Because of its structural morphology and high surface areas, ATT has received considerable attention with regard to the adsorption and the removal of heavy metal ions [7–9], but there are few reports about its use in the nanocomposites grafted with helical polymers.

Helical polymers are special polymers, which possess not only the advantages of polymers such as low density, high strength, tractability, and so on, but the unique optical activity. Their unique helical structure and optical activity provide the possibility to use helical polymers in many applications. Helical polymers and their composites have attracted great attention due to their helical structure, various supramolecular architectures, and, more importantly, their potential applications in chiral and sensing materials, molecular switches, data storage, optical devices, chromatographic chiral separation, and liquid crystals display [10–17]. The synthetic polymers with right or left-handed conformation can be optically active without any chiral component. This is because these polymers contain singlehanded helical chains and they are chiral essentially [18]. If the polymer backbone is rigid enough, or the steric repulsion of side groups is large enough to maintain a stable conformation, there is the possibility of obtaining helical optical polymers. Binaphthyl units can just provide the rigid backbone and the chiral origin due to its axial chirality and conformational stability [19–21]. In this paper, helical polyurethane@attapulgite (BM-ATT) nanocomposite based on R-1,1′-binaphthyl-2′,2-diol (R-BINOL) was prepared and characterized. BM-ATT exhibits rod-like structure and it is coated by a optically active shell. BM-ATT possesses many potential applications in chiral and sensing materials, optical devices and so on owing to its optical activity.

2. Experimental section

2.1. Materials

Attapulgite, provided by Hong-fei Company (Jiangsu, China), was treated with 36.5% hydrochloric acid for 24 h, followed by washing with distilled water until pH 6.5 and drying in vacuum at 50 °C for 24 h. R-1,1′-binaphthyl-2′,2-diol was synthesized and separated according to the literature [22,23]. 4,4′-diphenylmethane diisocyanate (MDI, TCI Co. Ltd.) was dried and purified under vacuum. N,N-dimethylformamide (DMF, Shanghai Chemical Reagent Co.) was dried over 40 nm molecular sieves

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for 1 week. Other solvents were all obtained from Shanghai Chemical Reagent Company and used as received without further purification.

2.2. Preparation of MDI-ATT (M-ATT)

Two grams of ATT and 10 mL DMF solution of 0.5 g MDI dispersed into 80 mL dried toluene with ultrasonic agitation for 1 h in a 250 mL flask and the ultrasound power was 600 W. After that the mixture was refluxed at 100 °C for 8 h with stirrer, condenser, and nitrogen inlet. After cooling to room temperature, the mixture was filtered and thereafter thoroughly washed with acetone. Then it was dried in vacuum at 40 °C for 12 h to obtain the M-ATT. The process is shown in Fig. 1(1).

2.3. Preparation of helical polyurethane@attapulgite based on R-BINOL

Forty millilitres of DMF solution of 1.144 g R-BINOL was firstly conducted in a 150 mL four-necked round-bottom flask equipped with stirrer, condenser, nitrogen inlet, and heated to 100 °C gradually. Then, 10 mL DMF solution of 0.5 g MDI was added into the reactor drop by drop slowly at 100 °C and reacted for 5 h to obtain the prepolymer. Then, M-ATT was dispersed into reactor and reacted at 100 °C for 6 h. After cooling to room temperature, the mixture was centrifugalized at the speed of 3000 r/min. After taking off the upper layer floccules, the product was thoroughly washed with ethanol and dried in vacuum at 40 °C for 24 h to obtain BM-ATT. Fig. 1(2) displays the scheme of this process.

2.4. Measurements

FT-IR spectra were carried out on a Bruker Tensor 27 FT-IR spectrometer at room temperature using KBr pellets. FT-IR spectra were obtained at a 4 cm^{-1} resolution and recorded in the region of 4000–400 cm^{-1}. The samples and background scanning times were both 16. Thermal analysis experiments were performed using a TGA apparatus operated in the conventional TGA mode (TA Q-600, TA Instrument) at the heating rate of 10 K/min in a nitrogen atmosphere and sample size was about 50 mg. X-ray diffraction (XRD) measurements were recorded using a Rigaku D/MAX-R with a copper target at 40 kV and 30 mA. The power samples were spread on a sample holder and the diffractograms were recorded in the range 5–70° at the speed of 5°/min. Transmission electron microscopy (TEM) was performed with a Hitachi H-600 microscope operating at 120 kV. High resolution transmission electron microscopy (HTEM) was performed with a JEM-2010 UHR microscope operating at 200 kV. Samples were prepared by placing drops of the colloids dispersion on a Cu grid (200 mesh; placed onto filter paper to remove excess solvent) and allowing the solvent to evaporate at room temperature. Scanning electron microscopy (SEM) was obtained on the microscope of LEO-1530VP. Vibrational circular dichroism (VCD) spectra were carried out on a Bruker Tensor 27 FT-IR spectrometer attached by PMA50 (Bruker) at room temperature using KBr pellets and the scanning time is 8 h.

3. Results and discussion

3.1. FT-IR analysis

Fig. 2 shows the FT-IR spectra of (a) ATT, (b) M-ATT and (c) BM-ATT. After the assembly of MDI to ATT, the 2270 cm^{-1} band of isocyanate groups is found in the FT-IR spectrum of the MDI-ATT (Fig. 2b). This result indicates that when a diisocyanate molecule is linked to surface of ATT by the reaction between one isocyanate and –OH on the surface of ATT, the remaining isocyanate group is unlikely to react with other ATT due to the reduced reactivity of immobilized molecules [24]. In addition, the absorptions of amide I and amide II appear at 1545 and 1512 cm^{-1}, respectively, and the absorption band of C = O is overlapped by asymmetric –COO stretching and results in a broad absorption band at about

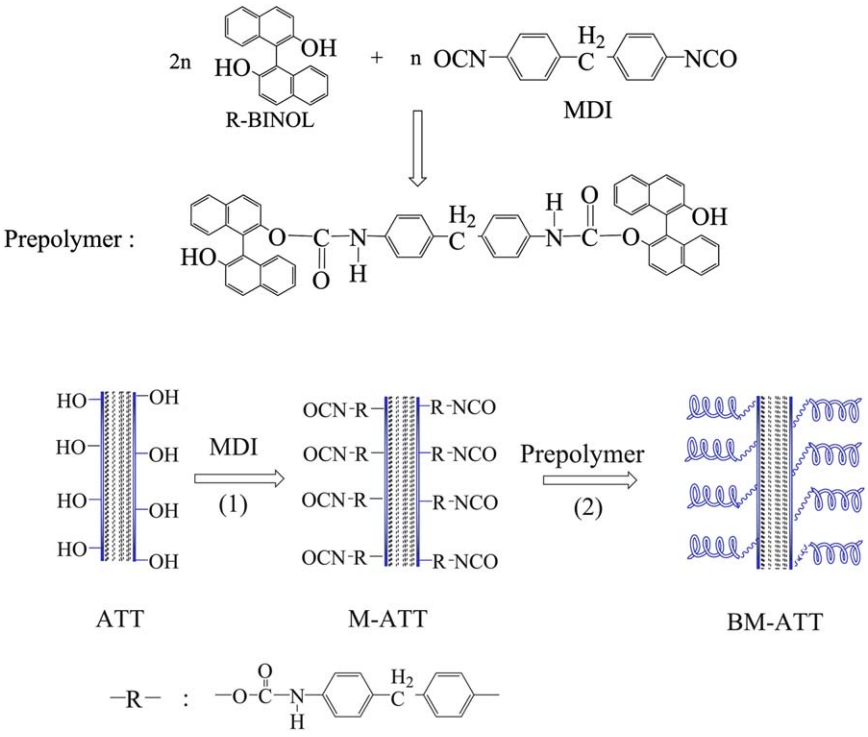

Fig. 1. The scheme of preparation of BM-ATT.