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Preparation and Characterization of Polyhydroxyurethane/Attapulgite Nanocomposites Via *In-Situ* Surface-Initiated Polymerization

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The polyhydroxyurethane/attapulgite nanocomposites (PHU/ATP) were prepared by *in-situ* surface-initiated polymerization of a five-membered cyclic carbonate, 2, 2-bis [p-(1, 3-dioxolan-2-one-4-yl-methoxy) phenyl] propane (B5CC) and hexamethylene diamine, from the surface of the aminopropyl attapulgite nanoparticles (APATP) for the first time. The chemical grafting of the polymer on the surface of ATP was confirmed by FTIR and the morphology of the attapulgite nanoparticles in the nanocomposites was examined by TEM. The thermal stabilities of the polyhydroxyurethane (PHU) and the polyhydroxyurethane/attapulgite nanocomposites (PHU/ATP) were compared with thermogravimetric analysis (TGA).The %G of the attapulgite nanoparticles was also calculated from the results of TGA after the free polyhydroxyurethane was washed off.

Keywords: Five-membered cyclic carbonate, polyhydroxyurethane, attapulgite nanoparticles, nanocomposites, *in-situ* surface-initiated polymerization

1 Introduction

In the last decade, nanocomposites have attracted considerable attention as their application could dramatically improve material properties such as heat resistance, radiation resistance, mechanical and electrical properties etc. It has been widely used as filler in paints, rubbers, binders, functional fibers, anti-virus materials (1, 2). The properties of nanocomposites strongly depend on the organic matrix, nanoparticles and the way in which they were prepared. Recently, there are more attempts to prepare the heterochain polymers/silica nanocomposites with chemical bonds between the polymers and the silica nanotubes. For example, polyamide/silica nanocomposites (3), poly(ethylene terephthalte)/silica nanocomposites (4), hyperbranched polymer/silica nanocomposites (5), polyurethane/silica nanocomposites (6, 7). The silica nanoparticles used in these nanocomposites had been organo-modified before the step of polymerization.

It is well known that surface modification by grafting of polymers onto inorganic nanoparticles is an effective way to improve its dispensability in an organic polymeric matrix and its compatibility with the polymeric matrix, thus enhancing the properties of the composite materials.

Attapulgite is a type of needle-shaped silicate. The diameter of the particles is 20nm approximately and the length is from several hundreds of nanometers to several micrometers. ATP is a hydrated magnesium aluminum silicate containing ribbons of a 2:1 phyllosilicate structure different from other layered silicates. There have been some reports on the use of ATP in rubbers (8), adhesives (9), Nylon (10), thermoplastic polymer (11–13), and silicate-epoxy nanocomposite (14).

Five-membered cyclic carbonates can be prepared from oxiranes and carbon dioxide under mild conditions (15), and even stereospecifically via retention of the configuration of epoxides (16). Recently, some articles have been reported that five-membered cyclic carbonates can react with amines efficiently to afford the corresponding hydroxyurethane (17, 18).

In this paper, we have successfully prepared polyhydroxyurethane/attapulgite nanocomposites (PHU/ATP) by in-situ surface-initiated polymerization in solution. The attapulgite nanoparticles can be well-dispersed in some organic solvents after being grafted with the polyhydroxyurethane.

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2 Experimental

2.1 Materials

Attapulgite nano-fibrillar clay (ATP) with the average diameter of 325 mesh, was provided by Gansu ATP Co. Ltd., Gansu, China. It was calcined before use.

γ-Aminopropyltriethoxysilane (APTES) (Gaizhou Chemical Industrial Co. Ltd. Liaoning, China) was used as received.

Bis (oxiran-2-ylmethyl) cyclohex-4-ene-1, 2-dicarboxylate resins were bought from Wuxi China. LiBr (Chemical, Shanghai, China), N, N-dimethylformamide (DMF), toluene, 1-methyl-2-pyrrolidone (NMP), hexamethylene diamine and ethanol (Tianjin Chemicals Co. Ltd., China) were all analytical reagents.

2.1.1. *Preparation of Aminopropyl Attapulgite Nanoparticles*

At first, attapulgite was purified by the procedure reported previously (19). A mixture of 5.0 g ATP nanoparticles, 300 ml toluene and 50 ml APTES in a 500 ml flask was dispersed with ultrasonic vibrations for 30 min. Then the mixture was refluxed for 8 h under stirring with a magnetic stirrer. After the reaction, the mixture was centrifuged (10^4 rpm/min for 20 min) and the precipitate was dispersed into 500 ml ethanol with ultrasonic vibrations for 30 min., and the washing operation was repeated three times. The resulting precipitate, aminopropyl attapulgite nanoparticles (APATP), was dried in vacuum at room temperature.

2.1.2. *Synthesis of 2, 2-bis [p-(1, 3-dioxolan-2-one-4-yl-methoxy) phenyl] propane*

A solution of bis(oxiran-2-ylmethyl) cyclohex-4-ene-1,2-dicarboxylate resins (47.04 g, 0.168 mol) and LiBr (0.72 g, 0.0084 mol) in 1-methyl-2-pyrrolidone (NMP, 84 ml) was charged in a three-necked flask equipped with a Dimroth condenser and CO_2inlet. The solution was stirred at 100°C with bubbled CO_2 overnight under atmospheric pressure (20). After removal of the solvent, the residue was purified by saturated baking soda, eluted by ethyl acetate to obtain a white powder product, 2,2-bis [p-(1, 3-dioxolan-2-one-4-yl-methoxy) phenyl] propane (B5CC).

2.1.3. *Graft Polymerization of B5CC from APATPs*

The APATPs 0.50 g were directly embedded into 2, 2-bis [p-(1, 3-dioxolan-2-one-4-yl-methoxy) phenyl] propane (B5CC) 2.00 g under vigorous stirring in a 50 ml flask. Hexamethylene diamine 0.52 g were added into this flask and mixed with ultrasonic vibrations in DMF for 30 min. The mixture was stirred at 100°C for 48 h. The mixture was centrifuged (10^4 rpm/min for 20 min) and the precipitate was dispersed into 500 ml ethanol with ultrasonic vibrations for 30 min. The washing operation was also repeated three times and the resulting precipitate, polyhydroxyurethane/attapulgite nanoparticles (PHU/ATP), was dried in vacuum at room temperature. ^{1}H-NMR (300MHz, DMSO-d_6): δ: 7.05–7.08 (4H, m, Ph), 6.78–6.81 (4H, m, Ph), 5.10–5.18 (2H, s, -N**H**-), 4.82–4.84 (2H, m, -CH_2C**H**(OH)-×2), 3.87–3.96 (4H, m, C**H**$_2$OH×2), 3.87–3.96 (10H, m, PhOC**H**$_2$C**H**OHC**H**$_2$O-×2), 3.54 (2H, m, O**H**×2), 3.41 (2H, m, -NHC**H**$_2$$CH_2$-), 3.08 (2H, m, -NH$CH_2$C**H**$_2$-), 1.55 (2H, m, -NH$CH_2$C**H**$_2$$CH_2$-), 1.34 (6H, m, C**H**$_3$×2), 1.21 (4H, m, -NH$CH_2$$CH_2$C**H**$_2$C**H**$_2$-) (Fig. 2).

2.1.4. *Characterizations*

The polymers cleaved from the attapulgite fiber were dissolved in deuterated chloroform and then characterized with ^{1}H-NMR using a Varian UNITY INOVA-300 FT-NMR spectrometer. Fourier transform infrared (FTIR) was performed on a Bruker IFS 66v/s infrared spectrometer. Thermogravimetric analysis (TGA) was used for the thermal stability of the nanocomposites, measured with a Perkin-Elmer TGA system from room temperature to 800 °C in nitrogen at a scan rate of 10°C/min. The morphologies of the bare attapulgite nanoparticles and PHU-ATP nanoparticles were obtained on a JEM-1200 EX/S transmission electron microscope (TEM). The powders were dispersed in DMF in an ultrasonic bath for 5 min, and then deposited on a copper grid covered with a perforated carbon film.

The percentage of grafting (%G) was calculated according to the following relationships from the TGA results:

$$\%\mathrm{G} = \text{Grafted polymer}(g)/\text{attapulgite nanoparticles charged}(g) \times 100\%$$

3 Results and Discussion

The polyhydroxyurethane/attapulgite nanocomposite (PHU/ATP) was prepared by *in-situ* surface-initiated polymerization of a five-membered cyclic carbonate (B5CC) and hexamethylene diamine from the surfaces of the aminopropyl attapulgite nanoparticles (APATP). The band at 2933 and 2870cm^{-1} is the aliphatic C-H stretch (spectrum of APATP), which indicates that the attapulgite particles had been modified with APTES. The absorption band of the C=O of -NH-CO-O- at 1667 cm^{-1}, which was absent in the FTIR spectrum of the aminopropyl attapulgite, appeared in the polyhydroxyurethane/attapulgite nanocomposite (Fig. 1). It can be seen from the ^{1}H-NMR spectrum (Fig. 2) of the polyhydroxyurethane obtained by cleaved from the attapulgite fiber that the signal **e** at 4.82–4.84 ppm could be assigned to the α-methine proton of the urethane moiety with the primary hydroxyl group. As a result, the polyhydroxyurethane had been successfully grafted to the surfaces of the modified attapulgite nanoparticles.

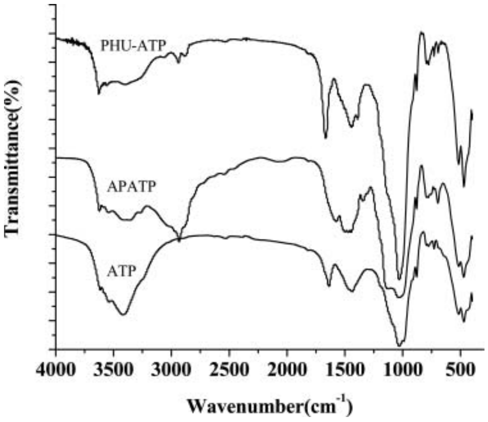

Fig. 1. FTIR spectra of ATP, APATP and PHU-ATP.

Figure 3 shows TGA curves of the bare attapulgite nanoparticles, aminopropyl attapulgite (APATP), polyhydroxyurethane grafted attapulgite nanoparticles (PHU-ATP), and polyhydroxyurethane/attapulgite nanoparticles (PHU/ATP). PHU-ATP nanocomposite begin to decomposite at about 270°C and PHU/ATP nanocomposite begin to decomposite at about 165°C. Therefore, the thermal stability of the PHU-ATP would be better than the PHU/ATP nanocomposite. Weight losses at the temperature $<200°$C resulted from the release of the moister adsorbed. The polymer weight losses of PHU-ATP and PHU/ATP were found to be about 21.0% and 61.5%, respectively. After the *in-situ* surface-initiated polymerization, the polymer grafted attapulgite nanoparticles were filtered and extracted thoroughly with DMF and then to remove soluble ungrafted polymers. The percentage of grafting (%G) calculated from TGA result is about 22.8%.

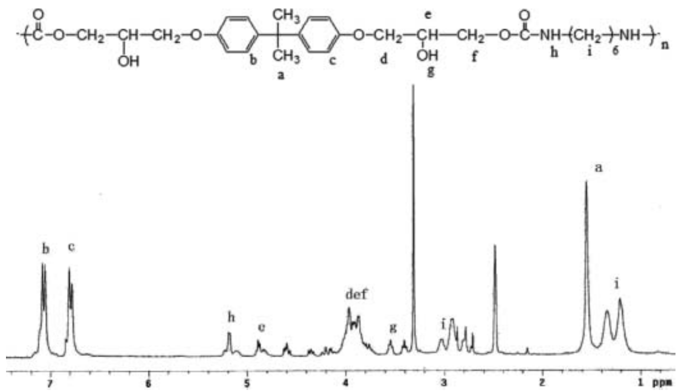

Fig. 2. ^{1}H-NMR spectra of polyhydroxyurethane.

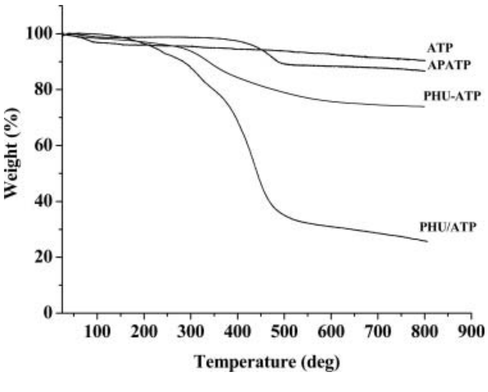

Fig. 3. TGA curves of ATP, APATP, PHU-ATP and PHU/ATP.

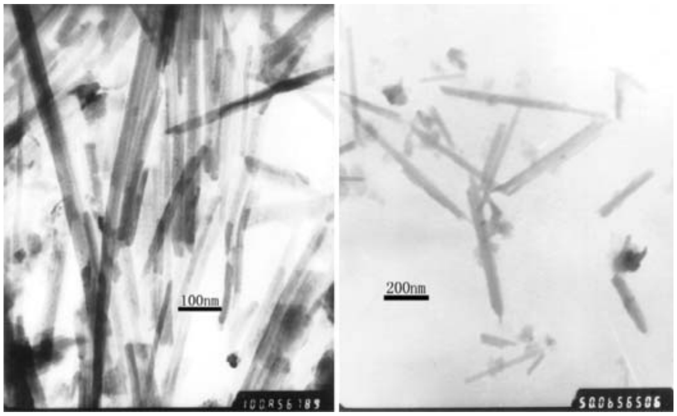

Fig. 4. The TEM of image of the ATP and the PHU-ATP nanocomposites.

The morphology analysis of the images of the bare attapulgite nanoparticles and the polymer grafted attapulgite nanoparticles were demonstrated in Figure 4. Both of the diameters of the aggregates were larger than the diameter of single attapulgite nanorob (20 nm). It might be the result from the hard agglomeration of attapulgite nanoparticles formed in the storage period. It can be seen that the dispersivity of the polymer grafted attapulgite nanoparticles is better than the bare attapulgite nanoparticles. It could be concluded that the organo-modification could break up some of the soft agglomeration of the ultra-fine particles and improve their dispersibility in organic solvent.

4 Conclusions

The opening five-membered cyclic carbonates had been achieved successfully by the *in-situ* surface-initiated polymerization of the five-membered cyclic carbonate groups with the amino groups on the surfaces of APATP from the analysis results of FTIR and ^{1}H-NMR. The grafted attapulgite nanoparticles have better dispersibility than the bare attapulgite nanoparticles in polymer or organic solvents. It is expected to be used as corrosion protections, secondary batters materials, etc.

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