Colloids and Surfaces A: Physicochem. Eng. Aspects 377 (2011) 312–317

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Preparation and characterization of well-dispersed waterborne polyurethane/$CaCO_3$ nanocomposites

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ARTICLE INFO

Article history:
Received 15 November 2010
Received in revised form
30 December 2010
Accepted 7 January 2011
Available online 18 January 2011

Keywords:
Waterborne polyurethane
$CaCO_3$
Oleic acid
Surface modification

ABSTRACT

In this study, in order to improve the dispersion and increase the compatibility between nanoparticles and waterborne polyurethane (WPU) matrix, $CaCO_3$ nanoparticles were firstly modified with oleic acid (OA). A series of WPU/$CaCO_3$ nanocomposites were prepared by further in situ polymerization. SEM examination of the fractured surfaces of nanocomposites showed that OA–$CaCO_3$ achieved well dispersion in WPU matrix. FTIR analysis suggested no major changes in the chemical structure of WPU in the presence of 2 wt% $CaCO_3$. Thermal stability of WPU measured by TGA was greatly improved with the addition of OA–$CaCO_3$. Meanwhile, the mechanical properties of the nanocomposites, examined by tensile tests, showed higher tensile strength than that of the pure WPU, especially incorporation of OA–$CaCO_3$.

1. Introduction

Polyurethane (PU) is one of the most interesting classes of synthetic polymers that have unique properties [1–4]. It has been widely used in adhesives, coatings, synthetic leather, construction, automatic industries, etc. Compared with the conventional organic solvent-based PU, waterborne polyurethane (WPU) shows many excellent features, with the advantages of non-pollution and nontoxicity [5,6]. However, WPU still has some drawbacks such as weak water-resistance, low adhesion in the moist environment, relatively low heat-resistance and mechanical properties, which inhibits the extensive application of WPU [7,8]. Hence, the research and development work is focused mainly on WPU for both academic and commercial reasons in PU industry.

Polymer-based nanocomposites exhibit remarkable improvements in mechanical, dielectric magnetic, thermal optical and acoustic properties compared with the pure organic polymers [9–12]. Hence, incorporation of nano-fillers into WPU is one of the interesting fields in PU industry [13,14]. As one of most important nano-fillers, $CaCO_3$ nanoparticles have been widely studied and utilized in academic and industry society because of its commercial availability and the substantial improvement in properties of polymers [15–17]. Furthermore, due to the super mechanical properties and high thermal stability, $CaCO_3$ nanoparticles are filled in many kinds of polymers by in situ polymerization method [18–22]. However, to our best knowledge, the research on the in situ polymerization of WPU in the presence of $CaCO_3$ is very seldom. The foremost challenge of using $CaCO_3$ in WPU is to achieve its uniform spatial distribution in matrix due to their incompatible interface. What is more, nanoparticles tend to aggregate together since they have a large specific surface area and high surface tension. It is extremely difficult to homogenize WPU matrix with $CaCO_3$ nanoparticles just relying on the shearing force in melt-blending. Surface modification of nanoparticles is an effective way to reduce their surface tension and increase the compatibility between them and WPU matrix. Oleic acid (OA) is one of the most popular modifying reagents for $CaCO_3$, and nanosized OA–$CaCO_3$ have been incorporation in PP, PMMA, etc [23,24]. However, to our best knowledge, it has not been used in WPU.

In this study, in order to improve the dispersion of $CaCO_3$ and increase the compatibility between nanoparticles and WPU matrix, $CaCO_3$ was firstly modified with oleic acid (OA). Afterwards, $CaCO_3$/poly(propylene glycol) (PPG) dispersions were prepared by mechanochemical approach. A series of WPU/$CaCO_3$ nanocomposites were prepared by further in situ polymerization. The influences of OA on the surface characteristics of $CaCO_3$ and the dispersion of nanoparticles in WPU, the thermal and mechanical properties of nanocomposites incorporation of 2 wt% $CaCO_3$ were investigated by water contact angle, thermogravimetric analysis (TGA), fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) and universal mechanical testing machine.

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doi:10.1016/j.colsurfa.2011.01.025

2. Experimental

2.1. Materials

Calcium oxide (CaO) was made by Menghe Chemical Reagent Factory. 2,2-Bis (hydroxymethyl) propionic acid (DMPA) was purchased from Alfa Aesar, America. Oleic acid (OA), toluene diisocyanate (TDI), dibutyltin dilaurate (DBTL), 2,5-dimethylfuran (DMF), triethylamine (TEA) and acetone were all analytical degree. Poly(propylene glycol) (PPG) with molecular weight 1000 was dried for 4 h at 110 °C under vacuum to eliminate moisture before use.

2.2. Preparation and surface modification of $CaCO_3$ nanoparticles

68 g of CaO was digested in 1000 ml distilled water at 100 °C to form $Ca(OH)_2$ slurry. After 12 h, the slurry was filtered through a 200 meshes sieve. The carbonization reaction monitored by pH value of the slurry was carried out at 18 °C in water bath. The gas mixed by CO_2 and N_2 with a molar ratio of 1:2 was bubbled into the mixture through a tube at a flow rate of 3 L/min. When pH of the slurry reached 7, the reaction was stopped. The precipitates were collected after filtration and washing with water for three times. The final white powders were dried at 90 °C overnight in an oven [25].

Surface modification experiment was carried out at 80 °C. Dried $CaCO_3$ nanoparticles were suspended in water with mechanical stirring. Then 2% (weight ratio to $CaCO_3$) OA was dissolved in ethanol and mixed with nanoparticles in a flask, keeping the temperature at 80 °C for 2 h with continuous stirring. The precipitate was collected and washed 3 times with distilled water to remove the by-products, and then dried at 70 °C under vacuum condition for 24 h.

2.3. Preparation of $CaCO_3$/PPG dispersions

0.6 g of the unmodified or OA-modified $CaCO_3$ was dispersed into 10 ml acetone solution with 30 min ultrasonation, respectively. Then, 20 g of PPG was put in to get a mixture suspension. Afterward, the mixture suspension was kept at 80 °C for 2 h with stirring. And then, various dispersions were obtained.

2.4. Preparation of WPU/$CaCO_3$ nanocomposites

A glass reactor equipped with a mechanical stirrer, a charging and sampling port, a nitrogen inlet and outlet was charged with $CaCO_3$/PPG dispersion and excess TDI (pure PU obtained in the absence of $CaCO_3$ dispersion, the weight percent of $CaCO_3$ is 2%). The reaction took place at 80 °C for 2 h. The temperature was then reduced to 60 °C, DMPA and the catalyst DBTL were added and conducted to react with the isocyanate (–NCO) for 2 h. The NCO- terminated prepolymer was obtained. During this stage, acetone was added to reduce the viscosity. After the reaction mixture was cooled to 40 °C, TEA was added to neutralize the carboxylic groups of DMPA, and then deionized water was added to emulsify for 30 min. Acetone was removed from the above dispersion under reduced pressure at 40 °C, and WPU/$CaCO_3$ nanocomposite emulsion was obtained. Afterwards, WPU/$CaCO_3$ nanocomposite emulsions were poured into polypropylene mould and dried at 60 °C for 24 h. WPU/$CaCO_3$ nanocomposite was obtained.

2.5. Characterization

Fourier transform infra-red (FTIR) spectroscopy of the samples were examined in the wave number range from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1} using a JIR-5500 (JEOL) spectrophotometer at room temperature.

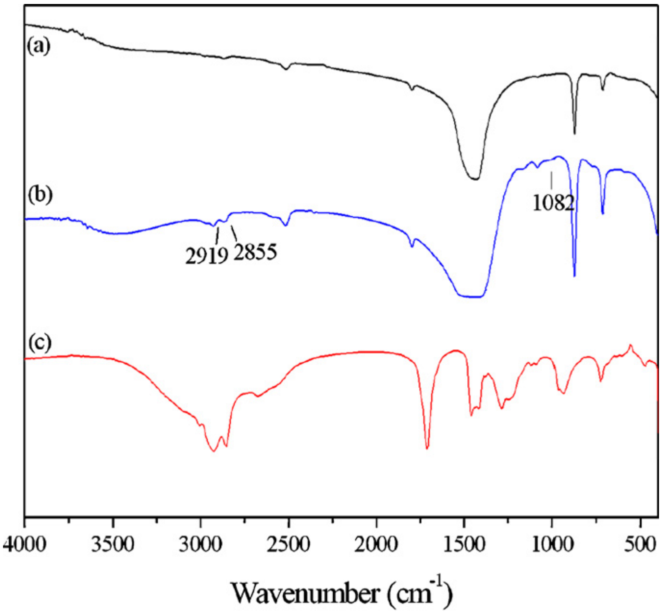

Fig. 1. FT-IR spectra of (a) unmodified $CaCO_3$, (b) OA–$CaCO_3$, and (c) OA alone.

Water contact angle of sample was measured by using a JC2000C2 contact angle goniometer (Shanghai Zhongchen Powereach Company, China) by the sessile drop method with a microsyringe at 25 °C.

Scanning electron microscopy (SEM) (XL30 ESEM FEG) was used to observe the dispersion of $CaCO_3$ in WPU. The freeze-fractured surfaces of WPU/$CaCO_3$ nanocomposite obtained at liquid nitrogen temperature were examined. All samples were coated with gold before SEM observations.

Thermogravimetric analysis (TGA) was carried out using a DTG-60H (SHIMAPZU) analyzer. The pure WPU and WPU/$CaCO_3$ nanocomposites were examined in nitrogen atmosphere from 100 to 600 °C at a heating rate 20 °C/min. The weight of samples used was about 5 mg.

Tensile measurement was performed at 25 °C using a universal mechanical testing machine (AGS-J) made in Japan. The conditions of tensile measurement were as follows: sample size was 20 mm × 4 mm × 0.8 mm; sample length between jaws was 10 mm; crosshead speed was 50 mm/min. For each data point, five samples were tested, and the average value was taken.

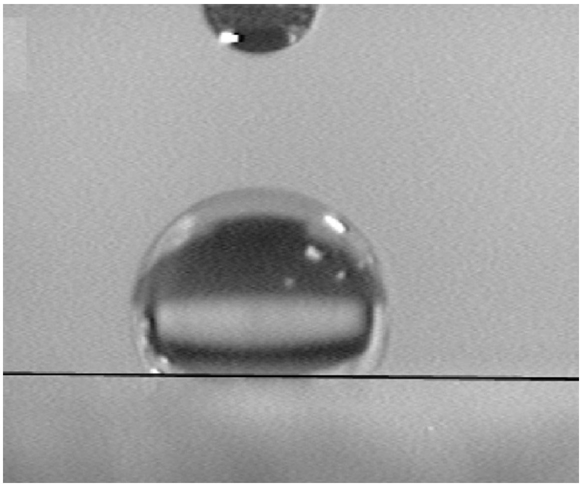

Fig. 2. Contact angle of OA-modified $CaCO_3$.