The potential of cuttlebone as reinforced filler of polyurethane

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ABSTRACT

The potential of cuttlebone (CB) as a biomass reinforcing filler for waterborne polyurethane (WPU) was studied in this research. The crushed CB reacted and crosslinked with the WPU pre-polymer during the synthesis process. The structure, thermal properties and mechanical properties of WPU composites were investigated. An excellent adhesion was found between WPU and CB. The changes in their chemical structure and the improvement in the thermal stability were observed due to their interaction. The stiffness and the strength of WPU were doubled by adding 7.1% CB in weight without significantly reducing the breaking elongation.

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1. Introduction

Polyurethane (PU) is the polymer which contains hard and soft segment units joined by urethane links and can be synthesized into foams, adhesives, coatings, sealants or fibers [1]. Waterborne PU (WPU), which can be dispersed in water, is widely used because it is non-toxic, non-flammable and eco-friendly [1].

PU is sometimes too soft for certain applications and reinforcing fillers are added to enhance its stiffness. Currently, glass fiber and carbon fiber are the commercial fillers for polymers [2]. Homogenous and multi-functional PU composites can be achieved with Nano-fillers, such as carbon nanotube [3–6], carbon black [7], graphene [8,9], nanocellulose [10], nanoclay [11] and nanosilica [12]. However, they are too expensive for mass production and may be harmful to human body [13]. Another focus is the biomass filler, such as bamboo [14], wood [15], rice husk [16], chitin [17] and kenaf [18], because of their cheapness, availability, safety and biodegradability.

Interaction between polymer and filler has significant effects on the composite quality. However, inorganic fillers usually have poor adhesion with polymer, resulting in final composites with poor strength [19]. Surface modification has been conducted on fillers or polymers via grafting or functionalization to enhance their adhesion in recent researches [19–22]. Cuttlebone (CB) is a natural composite containing $CaCO_3$ and β-chitin [17,23–24]. $CaCO_3$ is a stiff mineral while chitin is a polymer with abundant OH and NH groups which can crosslink with NCO groups on PU. Thus, excellent interfacial adhesion and outstanding mechanical properties are expected for PU/CB composites.

The potential of CB as an eco-filler WPU was studied in this investigation. Crushed CB reacted and crosslinked with WPU during the PU synthesis process. Their interaction was investigated from the change in their chemical structure. Its effects on the morphology, thermal properties and mechanical properties of the composite were also investigated.

2. Experimental

2.1. Materials

Polypropylene glycol 2000 (PPG 2000, Acros) and Dimethylolpropionic acid (DMPA, 99.0%, Acros) were dried at 80 °C in vacuum for 12 h. 4,4-Methylene diphenyldiisocyanate (MDI, 99.5% Acros) was stored at 4 °C before used. N-(2-Hydroxyethyl)ethylenediamine (DEA, 99%, Sigma Aldrich), acetone (99.5%, Shell) and triethylamine (TEA; 99.7%, Acros) were dried with molecular sieve 3 Å (MS3A). Dibutyltin dilaurate (DBTDL, 95%, Sigma Aldrich) was first diluted with acetone to 2% in weight and then dried with MS3A. CB was purchased from a local Chinese medicine store. It was washed with deionized water, followed by 3 h air drying and 12 h vacuum drying at 80 °C. Finally, it was crushed and sieved with a 90 μm-mesh sieve.

2.2. The preparation of CB/PU composite

CB reinforced PU was synthesized via acetone method. 1.25 g MDI was first dissolved in acetone and then was dried over

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MS3A for 10 min. The solution was mixed with 2.5 g PPG 2000 and 0.266 ml diluted DBTDL, and was then refluxed in 40 °C in N_2 for 2 h. 0.3 g DMPA was added to the mixture for another two-hour reaction. Desired mass of CB was added into the PU pre-polymer solution and reacted for 1 h. During the whole process, acetone was added to keep the solution stirrable. After the neutralization with 0.334 g TEA for 15 min, 20 ml deionized water was added dropwise with vigorous stirring. 0.158 g DEA was added into mixture for further chain extension. Finally, acetone was removed with rotary evaporator at 30 °C.

The PU solution was poured on a Teflon mound and kept stirring for even CB distribution. It was dried at room temperature for 2 days and then at 60 °C for 12 h. The sample without the addition of CB was coded as PU-Pure. The PU/CB films with the CB content of 0.1 g and 0.3 g were coded as PU/CB-0.1 and PU/CB-0.3, accounting for 2.4% and 7.1% in PU weight respectively.

2.3. Characterization

The dispersion size of PU-Pure solution was measured with ZetaPlus, Brookhaven Instruments equipped a He–Ne laser (633 nm) for 10 min. The sample was diluted in deionized water and was homogenized via ultrasonic wave treatment.

The morphology of crushed CB and CB distribution in PU films were observed via scanning electronic microscopy (SEM) with Leica Stereoscan 440(20 kV). All PU films were first frozen with liquid N_2 and then immediately snapped. Samples were put on the carbon tape and were then sputtered with gold for about 2 min.

Horizontal attenuated total reflection-Fourier transform infrared spectroscopy (HATR-FTIR) was performed on a PerkinElmer Spectrum 100 FTIR with HATR accessory. ZnSe crystal window was used. The data were collected over 4 scans with a resolution of 4 cm^{-1}.

Wide-angle X-ray diffraction (XRD) patterns were recorded with SmartLab (Rigaku, Japan) using Cu Kα radiation (0.154 nm, 45 kV, 200 mA). The diffraction angle ranged from 10° to 60° and the scan rate was 5°/min.

Thermogravimetric analysis (TGA) and Differential scanning calorimetry (DSC) from 25 °C to 500 °C were conducted with Mettler Toledo TGA/DSC 1 Simultaneous Thermal analyser simultaneously. 18 mg sample was heated at 10 °C/min in N_2 in each test. Differential thermogravimetric (DTG) curves were calculated.

DSC testes from −60 °C to 150 °C were conducted with Perkin-Elmer Diamond DSC in N_2. The sample was first annealed to 150 °C, followed by cooling to −60 °C and then heating back to 150 °C. The heating/cooling rate was 10 °C/min. The second heating curve was used for investigation.

The dynamic mechanical analysis (DMA) was conducted with DMA 8000, PerkinElmer in tensile mode. The temperature scanning mode was done from −100 °C to 100 °C with the frequency of 1 Hz at the heating rate of 5 °C/min. The frequency scanning mode was done with the frequency of 0.01–2 Hz at room temperature.

The room temperature stress–strain curves were obtained with Instron 4411 Tensile Compression Pull Tester Machine. The crosshead speed and the gauge length were 5 mm/min and 2 cm respectively. Two replicates were taken for each sample.

3. Results and discussions

The PU-Pure emulsion particle size distribution curve is shown in Fig. 1a. Its effective particle diameter and half width are 80.8 nm and 46.8 nm respectively. The emulsion solution is well dispersed as our WPU has enough carboxylic groups to provide high hydrophilicity [1].

The SEM image of the crushed CB is shown in Fig. 1b. It is in plate structure with the size of 30 μm and thickness of 5 μm. CB originally has the structure of lamellae supported by numerous pillars [23], which was crushed and became plate structure. CB particles with size above 90 μm were removed with the sieve. The original surface is smoother than the fractured surface because the original surface is covered by a smooth organic layer of β-chitin [23,25].

The micro-morphology of PU films is shown in Fig. 2. The neat PU-Pure film presents a smooth fractured surface, shown in Fig. 2a. No micro-bubble is found in the image with higher magnification shown in Fig. 2b. In Fig. 2c and e, PU/CB-0.1 and PU/CB-0.3 contain a thin CB–PU composite layer at the top and a pure PU layer at the bottom. CB particles are in the scale of micrometers and are still too large to stay long in the aqueous solution. They precipitated uniformly and formed a thin composite layer during the long film forming process. The CB packing density and the thickness of the composite layer increase with the CB content. Higher CB content means more CB precipitating to the bottom during the film forming process. As a result, CB has to pack more closely and build higher in the composite layer PU/CB-0.3. Moreover, composite layer of PU/CB-0.3 is found to be porous. When water was removed from WPU solution, PU coated on the CB surface and space among crushed CB was left empty. For the magnified images of PU/CB-0.1 and PU/CB-0.3 shown in Fig. 2d and f, CB is well covered by PU and only a small part of CB is exposed on the fractured surface. Their contact is very good and implies a good adhesion between fillers and PU.

To compare the appearance of different PU films, their photo is shown in Fig. 3. PU/CB composite films have excellent uniformity even in macro-scale size. Its transparency decreases with the CB content as CB is optically opaque in nature and crushed CB size is significantly larger than the wavelength of visible light.

The chemical structure of PU/CB composite was studied via XRD and FTIR for the investigation of the interaction between PU and CB. The XRD spectra of crushed CB and different PU films are shown in Fig. 4a. The XRD spectrum of CB shows sharp peaks of an aragonite $CaCO_3$ at 26.2°, 27.2°, 33.1°, 36.0°, 37.7°, 37.9°, 38.6°, 45.9°, 48.3° and 52.5°. It is because CB is mainly composed of aragonite [23]. The XRD profiles of PU-Pure films show a broad peak at about 20° and a sharp diffraction peak at about 44.5°. The broad peak at about 20° is the typical peak for PU [26] while the sharp diffraction peak at about 44.5° is the background peak due to the Iron sample holder. As there is no sharp peak for PU-Pure, it is amorphous. The peaks of CB are unobservable in PU/CB-0.1 and slightly appear in PU/CB-0.3 because of the increase in the CB packing density observed in Fig. 2.

FTIR spectra of CB, PU-Pure, PU/CB-0.1 and PU/CB-0.3 are shown in Fig. 4b. Four characteristic peaks of aragonite are observed in the FTIR spectrum of CB at 713 cm^{-1} (v_4, O—C—O in-plane bending), 856 cm^{-1} (v_2, O—C—O out-plane bending), 1084 cm^{-1} (v_1, C—O symmetric stretching) and 1486 cm^{-1} (v_3, C—O asymmetric stretching) [27]. This agrees with the XRD result that CB is composed of aragonite. The peaks of chitin are covered in the broad peaks at 1150–1650 cm^{-1} and 3150–3650 cm^{-1} [28].

The FTIR spectrum of PU-Pure has lots of peaks. The NH stretching vibration absorption peak is observed at around 3294 cm^{-1}. As the free NH stretching vibration is expected to appear at around 3420 cm^{-1}, the peak shift should be due to H-bonds between NH and carbonyl groups forming during the urethane reaction [10]. The shoulder at about 3500 cm^{-1} is due to the unreacted OH and NH groups in the precursor. Simultaneously, the C=O stretching peak can be divided two peaks at 1706 cm^{-1} and 1723 cm^{-1} in Fig. 4c, corresponding to H-bonded C=O groups and free C=O groups respectively [10]. Other major peaks are found at 1604 cm^{-1} (C=C), 1540 cm^{-1} (N—H), 1088 cm^{-1} (C—O), 1468 cm^{-1} (C—C) and 2800–2900 cm^{-1} (C—H) [5,17,29–30].