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Role of starch nanocrystals and cellulose whiskers in synergistic reinforcement of waterborne polyurethane

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ABSTRACT

Starch nanocrystals (SN) and cellulose whiskers (CW) were fabricated successfully from the sulfuric acid hydrolysis of waxy maize starch granules and cotton linter pulp, respectively, and were characterized by transmission electron microscopy, atomic force microscopy and wide-angle X-ray diffraction. The nanocrystals and whiskers were embedded in waterborne polyurethane (WPU) matrix using a casting/evaporation technique. A synergistic reinforcing role of SN and CW in WPU was observed for the first time. With incorporation of 1 wt.% SN and 0.4 wt.% CW, the tensile strength, Young's modulus and tensile energy at break of the WPU based nanocomposites were significantly enhanced by 135%, 252% and 136%, respectively, and the elongation at break remained basically compared to pure WPU. WPU/1% SN/0.4% CW system also exhibited a much better reinforcing effect than all of WPU/SN and WPU/CW systems. Furthermore, the WPU based nanocomposites possessed greater thermal resistance. The results clearly revealed that the different polysaccharide nanocrystals and whiskers combined together to form strong hydrogen bonding networks, leading to the synergistic reinforcement of WPU. This work provides a new eco-friendly pathway to prepare polymer nanocomposites with high performance by using natural nanocrystals and whiskers together.

1. Introduction

A possible source of inspiration for the design of new high performance materials is the nature and its wonderful nanocomposite structures (Habibi & Dufresne, 2008). Many living organisms have the ability to biosynthesize polymer crystals. During the last decade, a kind of novel nano-materials derived from natural polymers, named as "green" bionanocomposites (Darder, Aranda, & Ruiz-Hitzky, 2007), has been developed, in which natural polymers can act as the matrix, the nanofiller or both. Usually, natural nanofillers are the crystalline residue with a uniform structure after acidic or alkaline hydrolysis of natural polysaccharides. The crystalline nanoparticles from different sources have different geometrical characteristics, such as rod-like nanocrystals or whiskers of cellulose (van den Berg, Capadona, & Weder, 2007a) and chitin (Lu, Weng, & Zhang, 2004), and platelet-like nanocrystal of starch (Angellier, Choisnard, Molina-Biosseau, Ozil, & Dufresne, 2004). They have provided wide applications because of their potential nanoparticle properties. Many attempts have been reported to blend polysaccharide nanocrystals with polymeric matrices (Goetz, Mathew, Oksman, Gatenholm, & Ragauskas, 2009; Kristo & Biliaderis, 2007; Paralikar, Simonsen, & Lombardi, 2008; van den Berg, Schroeter, Capadona, & Weder, 2007b). The resulting nanocomposite materials display outstanding mechanical properties and thermal stability. For example, starch nanocrystals (SN) present the originality to consist of crystalline nanoplatelets about 6–8 nm thick with a length of 20–40 nm and a width of 15–30 nm (Labet, Thielemans, & Dufresne, 2007). They have been used as a new kind of fillers, showing interesting reinforcing and barrier properties in natural rubber (Angellier, Molina-Boisseau, Lebrun, & Dufresne, 2005a; Angellier, Molina-Boisseau, & Dufresne, 2005b). On the other hand, cellulose whiskers (CW) are considered to be an ideal loading-bearing constituent in developing new and inexpensive biodegradable materials due to their high aspect ratio, high bending strength of about 10 GPa and high Young's modulus of approximately 150 GPa (Sturcova, Davies, & Eichhorn, 2005).

Polyurethanes (PUs) are one of the most versatile polymeric materials with regard to both processing methods and mechanical properties (Lu & Larock, 2008). However, the conventional PU products usually contain a significant amount of organic solvents and sometimes even free isocyanate monomers (Modesti & Lorenzetti, 2001). Therefore, these solvent-based PUs have been gradually replaced by the waterborne polyurethanes (WPUs) in past decades because of the increasing need to reduce volatile organic compounds (VOCs) and hazardous air pollutants (HAPs) (Wicks, Wicks, & Rosthauser, 2002). WPUs present many advantages,

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including non-toxic, non-flammable, non-pollution, low viscosity at high molecular weight and good applicability, and are now one of the most rapidly developing and active branches of PU chemistry and technology (Jeon, Jang, Kim, & Kim, 2007). Recently, a series of researches focus on the addition of nanosized particles, especially polysaccharide nanocrystals, in the WPU matrix to improve the thermal resistance and mechanical properties of WPU materials (Cao, Dong, & Li, 2007; Chen et al., 2008; Lee & Lin, 2006; Wu, Henriksson, Liu, & Berglund, 2007; Wang & Zhang, 2008). These novel materials are eco-friendly and biodegradable, which have a potential application in medical and biologic fields.

It is proved that the extent of the reinforcement depends on such factors as the dispersion of the nanofillers in the polymer matrix and the interfacial adhesion between nanofillers and polymer matrix (Nair & Dufresne, 2003). Few literatures have been reported on the nanofillers with different geometrical characteristics for improving the properties of polymer matrix (Tang et al., 2008; Zhang, Phang, & Liu, 2006). However, no report on using the natural nanocrystals and whiskers together as a reinforcing phase is observed. In the present work, we make a good effort to improve the mechanical properties and thermal stability of WPU by using both starch nanocrystals and cellulose whiskers simultaneously. Their morphology, structure and performance were investigated in detail by transmission electron microscopy, dynamic mechanical thermal analysis, thermogravimetric analysis and tensile testing to judge the reinforcing mechanism of these two fillers. This work may contribute some meaningful information for the application of polysaccharide nanocrystals in producing high performance polymeric materials.

2. Experimental

2.1. Materials

All of the chemical reagents used in this work were of analytically grade, and were purchased from commercial sources in China. Commercial waxy maize starch containing 0.5 wt.% protein, 0.15 wt.% fat and 0.15 wt.% ash was a gift of Gansu Xue Jing Biochemical Co., Ltd. (China). Cellulose (cotton linter pulp) was supplied by the Hubei Chemical Fiber Group, Ltd. 2,4-Toluene diisocyanate (TDI) was purchased from Jiangbei Chemical Reagents Factory (Wuhan, China). TDI was redistilled before use. Polypropylene glycol (PPG) having weight-average molecular weight (M_w) of 2000 was supplied by Sinopharm Chemical Reagent Co. Ltd., and vacuum-dried at 120 °C for 1 h before use. Dimethylol propionic acid (DMPA) was obtained from Chengdu Polyurethane Co. in China. Triethylamine (TEA), sulfuric acid and acetone were purchased from Shanghai Chemical Co. in China. TEA and acetone were treated with 3 Å molecular sieves to dehydrate. Starch and cellulose were vacuum-dried at 105 °C for 5 h before use.

2.2. Preparation of nanocrystals

Waxy maize starch granules (25 g) were mixed with 200 mL of 3.16 M sulfuric acid for 5 days at 40 °C, with a stirring speed of 100 rpm. Then the suspension was diluted with distilled water, and then centrifuged (10,000 rpm for 15 min). The process was repeated three times to wipe off the excess sulfuric acid. The resultant suspension, which had a weight concentration of about 5 wt.%, was treated with ultrasonic. Then, it was freeze-dried to obtain starch nanocrystal powder (SN) (Wang & Zhang, 2008).

Cotton linter pulp (20 g) was dispersed in 175 mL of a 30% (v/v) sulfuric acid, and the mixture was added to a three-necked flask equipped with a mechanical stirrer and a thermometer. The flask was placed into a water bath at 60 °C and stirred vigorously for 6 h. The suspension was then diluted with distilled water, and centrifuged at 8000 rpm for 15 min. The process was repeated three times to remove the excess sulfuric acid. The resulting suspension was dialyzed for 2 h in running water and then overnight in distilled water, until the pH reached 4. Finally, the dispersion was treated with ultrasonic, and freeze-dried to obtain cellulose whisker powder (CW) (Wang, Cao, & Zhang, 2006).

2.3. Processing of nanocomposite films

PPG2000 (116 g, 0.058 mol) and DMPA (2.68 g, 0.02 mol) were introduced into a four-neck flask equipped with a thermometer, mechanical stirrer, dropping funnel, and condenser, and the mixture was heated to 80 °C; then TDI (20 g, 0.111 mol) was added dropwise, and the reaction was carried out in dry nitrogen atmosphere for 2–3 h until the –NCO content reached a desired value, which was determined by using the standard dibutylamine titration method. Subsequently, 30 g acetone was poured into the flask to reduce the viscosity of prepolymer and then cooled to 60 °C. After neutralization of carboxylic groups of DMPA with TEA (2.1 g, 0.02 mol) for 30 min, the product was dispersed with distilled water under vigorous stirring. After the mixture was stirred at room temperature overnight, the acetone was removed by rotary vacuum evaporating at 30 °C, and the solid content of the WPU was 20 wt.% finally.

SN and CW were firstly dispersed in distilled water and ultrasonicated for 15 min to avoid the aggregations. Then, the suspensions of nanocrystals and WPU were mixed with SN content ranging from 1 to 5 wt.% and CW content from 0.2 to 1 wt.% (with respect to WPU), followed by stirring for 5 h. Subsequently, the resulting mixtures were degassed for 3 h under vacuum. Nanocomposite films with a mean thickness of 0.2 mm were prepared by drying the mixtures in some hydrophobic glass plates at room temperature for 2 weeks. Before various characterizations, the films were conditioned at room temperature in a desiccators containing P_2O_5 with 0% relative humidity (RH).

2.4. Characterizations

Transmission electron microscope (TEM) observation of the morphology of SN and the nanocomposite film was carried out on a JEM-2010 TEM (JEOL TEM, Japan). SN were dispersed in distilled water and ultrasonicated for 15 min. Then, a small droplet of the dilute suspension was deposited on a polycarbon film, which was supported on a copper grid. A thin layer was suspended over the holes of the grid. The specimen was dried in air at ambient pressure, and then was imaged on TEM at an accelerating voltage of 200 kV. The film was cut into thin strips with the cross-section of about 0.2–0.3 mm^2. They were embedded in Epon 812 epoxy resin and cured at 40 °C for 60 h. The embedded specimens were first trimmed with a razor blade and then with an ultra-cut microtome equipped with a glass knife. An extremely smooth trapezoidal top surface was obtained with the cross-section of the polymer strip. ALKBIII microtome was used for ultra-thin microtomy. The top layer (about 1 mm) was first removed using a glass knife, then, ultra-thin sections of about 100 nm thickness were cut with a Diatome diamond knife at room temperature. The ultra-thin sections were stained by OsO_4 and mounted on 200 mesh copper grids for TEM observation.

Atomic force microscopy (AFM) analysis of CW in suspension was carried out on an XE-100 microscope (PSIA Co., Korea). A droplet of the dilute CW suspension was coated onto a flake of mica, and the water was evaporated at room temperature for 24 h. Wide-angle X-ray diffraction patterns were recorded on X-ray diffraction (XRD-6000, Shimadzu, Japan), using Cu Kα radiation (λ = 0.154 nm) at 40 kV and 30 mA with a scan rate of 1°/min.