



# Thermoset nanocomposites from two-component waterborne polyurethanes and cellulose whiskers

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## ABSTRACT

We prepared thermoset nanocomposites from biomass-based two-component waterborne polyurethane (2K-WPU) and cellulose nanowhiskers (CNWs). Due to the formation of hydrogen bonds, the viscosity of 2K-WPU dispersion was found to be increased with the addition of CNWs. SEM images showed “sea-island structure” corresponding to the microphase separation between CNWs nano-filler and the 2K-WPU matrix. The  $\alpha$ -relaxation temperature ( $T_\alpha$ ) and glass transition temperature ( $T_g$ ) increased with the increase of CNWs content, which was due to the formation of a rigid CNWs nano-phase acting as crosslinking points in the 2K-WPU matrix. Mechanical properties from tensile test showed Young's modulus and tensile strength of 2K-WPU/CNWs nanocomposites were reinforced by the addition of CNWs. Thermo-stability of 2K-WPU/CNWs nanocomposites decreased slightly with the increase of CNWs content, which could be attributed to the increased thermal conductivity of the material after adding CNWs.

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## 1. Introduction

Given the good mechanical properties of solvent-based two-component polyurethane systems, they have been successfully used in various applications, e.g. coatings, adhesives. During the past decades, reduction of volatile organic compounds (VOCs) emissions has become the major driving force of resin developments. One approach of reducing VOCs emissions during resin industry is substituting solvent-based systems by waterborne systems. Two-component waterborne polyurethanes (2K-WPUs) which combine the environment-friendly property of waterborne resins with the good performance of two-component polyurethanes have been developed for a number of industrial applications (Chang & Lu, 2012; Melchior, Sonntag, & Kobusch, 2000; Otts & Urban, 2005; Otts, Pereira, Arret, & Urban, 2005; Wicks, Wicks, & Rosthauser, 2002). However, unlike the homogeneous film formation of solvent-based two-component polyurethane systems,

the film formation of 2K-WPUs is a heterogeneous phase process among water-dispersed particles. The mechanical properties of the film of 2K-WPUs are not as good as that of solvent-based two-component system. It is necessary to strengthen the mechanical properties of 2K-WPUs at the molecular level by chemical (Ge & Luo, 2013) or composite modification methods (Akbarian, Olya, Ataefard, & Mahdavian, 2012).

Recent researches have shown that the properties of polymer resins could be further improved by the addition of particles in the nanoscale range (Alexandre & Dubois, 2000). The nanocomposites exhibit improved mechanical properties and can improve resistance to moisture and weathering. More recently, cellulose nanowhiskers (CNWs) have been considered as potential reinforcing agents for polymer-based composite materials (Eichorn et al., 2010; Favier, Chanzy, & Cavallé, 1995; Jacob & Thomas, 2008; Klemm et al., 2011). Cellulose in plants consists of 1,4- $\beta$ -glucopyranose units associated by hydrogen bonding. It forms a semicrystalline structure where highly ordered regions (the crystallites) are distributed among disordered domains (the amorphous phase). Cellulose crystallites are in nanometer size and can be obtained by various well-documented methods (Abdul Khalil, Bhat, & Ireana Yusra, 2012; Azizi Samir, Alloin, & Dufresne, 2005; Hubbe, Rojas, Lucia, & Sain, 2008; Souza Lima & Borsali, 2004). Because of their high specific strength, modulus, and aspect ratio, they can significantly improve the mechanical properties of composites at

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loading levels as low as 5%. Other advantages of nanocrystals stem from their low density, renewable nature, biodegradability, and relatively low cost.

In order to realize property improvements, CNWs must be homogeneously dispersed in polymeric matrix. Given the high surface area and hydrophilic nature, CNWs are well dispersed in water, but difficult to be dispersed in solvent-based resins (Pu et al., 2007; Qua, Hornsby, Sharma, Lyons, & McCall, 2009; Roohani et al., 2008). One method to overcome this problem is chemically modifying the surface of the CNWs by appropriate functions, so that the polar hydroxyl groups can be converted to moieties which modifies the fiber wettability and enhances the interaction of CNWs with the matrix (Çetin et al., 2009; Habibi et al., 2008; Siqueira, Bras, & Dufresne, 2010; Stenstad, Andresen, Tanem, & Stenius, 2008). However, the chemical strategies of surface modification of CNWs are quite inefficient. It is difficult to efficiently reinforce most of the classical resin matrices. Since stable suspensions of CNWs can be easily prepared in water, their incorporation in waterborne resin to prepare cellulose nanocomposites is an efficient strategy for the utilization of CNWs without modification. So far, CNWs have been reported to be filled into thermoplastic one-component waterborne polyurethanes, resulting in a significant increase of strength and Young's modulus (Cao, Dong, & Li, 2007; Lee & Kim, 2012; Oliveira Patricio et al., 2013; Zou et al., 2011).

As an abundant carbon-neutral renewable resource and a viable supplement to fossil fuel resources, biomass is gaining extensive research attention for producing energy and materials. In our previous work, a biomass-based 2K-WPU was prepared by a polyol (WPOL) dispersion from the raw material turpentine and a hydrophilically modified hexamethylene diisocyanate (HDI) tripolymer (Wu et al., 2013). Different from the particle merging mechanism of the film formation of one-component waterborne polyurethanes, the film formation process of 2K-WPU contains not only particle merging but also crosslinking reaction between different components. In this work, we prepared novel 2K-WPU/CNWs nanocomposites by incorporating CNWs suspension, which was hydrolyzed from microcrystalline cellulose (MCC), into the biomass-based 2K-WPU. The abundant active hydroxyl groups on the surface of CNWs can take part in the crosslinking reaction with isocyanate groups of HDI, resulting in strong interfacial adhesion between the matrix and the filler. The crosslinking reaction, structure, and properties of the prepared nanocomposite materials were investigated by rotational rheometer, scanning electron microscopy (SEM), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), and tensile tests.

## 2. Experimental

### 2.1. Materials

Terpinene-maleic ester type epoxy resin (TME) was synthesized from raw material turpentine (Wu, Kong, Huang, Chen, & Chu, 2007). It is an alicyclic epoxy resin with endocyclic structure and has an epoxy value of  $3.5 \text{ mmol g}^{-1}$ . Polyethylene glycol (PEG) ( $M_n = 4000$ ) was purchased from Guangdong Xilong Chemical Co., Ltd., China. Trimethylolpropane (TMP) and microcrystalline cellulose (MCC) were purchased from Aladdin Industrial Co., China. Boron fluoride ethyl ether was supplied by Shanghai Lingfeng Chemical Reagent, Co., Ltd., China. Acetone was obtained from Nanjing Chemical Reagent, Co., Ltd., China. The hydrophilically modified HDI tripolymer with NCO content of 13 wt% and solid content of 80 wt%, was supplied by Wuhan Shiquanshi Decorative Coating Co., Ltd., China. Sulfuric acid ( $\text{H}_2\text{SO}_4$ ) was purchased from Sinopharm Chemical Reagent Co., Ltd., China.

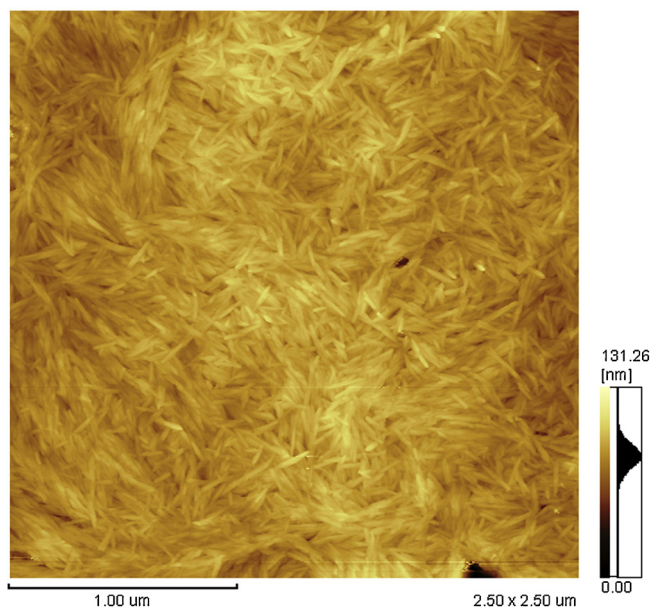


Fig. 1. AFM image of CNWs.

### 2.2. Preparation of WPOL and WPOL dispersion

The synthesis of WPOL has been described in details in our previous work (Wu, Kong, Chen, & Jiang, 2011), and therefore only a brief description follows. A 500 ml four-necked flask equipped with stirrer, dropping funnel, thermometer, condenser, and heating mantle was charged with 86.6 g TME, 15.6 g PEG and 14.5 g TMP. After the temperature inside the flask increased to  $90^\circ\text{C}$ , 0.87 g boron fluoride ethyl ether diluted in 6.1 g acetone was added with constant stirring. The reaction was continued for 1.5 h at  $110\text{--}120^\circ\text{C}$ , producing a yellow transparent product WPOL. By churning at 500–1000 rpm, at  $50\text{--}90^\circ\text{C}$ , 210 g distilled water was added slowly to disperse the produced WPOL, generating a milk-white dispersion (WPOL dispersion) with 35 wt% solid content.

### 2.3. Preparation of CNWs

CNWs were prepared according the reported studies (Bondeson, Mathew, & Oksman, 2006). 10.0 g MCC was mixed with 110 ml sulfuric acid solution (63.5 wt%). The mixture was stirred vigorously for 2 h at  $44^\circ\text{C}$ . The formed suspension was diluted with 500 g distilled water to stop the reaction. Then the suspension was repeatedly centrifuged and washed with distilled water. Dialysis was performed to remove the residual acid in the suspension. After concentrated under vacuum and adjusted with distilled water, a stable CNWs suspension with solid content of 3.0 wt% was obtained through 30 min ultrasonic treatment. The stereoscopic information of the CNWs collected with an atomic force microscope (AFM) is shown in Fig. 1. The rod-like CNWs are observed having the width of 20–40 nm and the length of 200–300 nm.

### 2.4. Preparation of 2K-WPU/CNWs nanocomposite films

CNWs suspension was mixed with the WPOL dispersion under sonication for 10 min. Then the mixture was blended with hydrophilically modified HDI tripolymer at a hydroxyl group to isocyanate group molar ratio of 1:1.2. The generated blend called 2K-WPU/CNWs dispersion was first diluted with distilled water to the solid content of 30 wt%, and then degassed under vacuum at ambient temperature. Subsequently, the 2K-WPU/CNWs dispersion was cast in square Teflon molds and dried at  $30^\circ\text{C}$  for 1 week.

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