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Preparation and properties of thermoset composite films from two-component waterborne polyurethane with low loading level nanofibrillated cellulose

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ABSTRACT

Thermoset nancomposite films were prepared from a two-component waterborne polyurethane (2K-WPU) incorporated with different contents of high aspect ratio nanofibrillated cellulose (NFC). Effects of NFC addition on viscosity and particle size distribution of the 2K-WPU dispersion were investigated by rotational rheometer and laser particle size analyzer, respectively. Viscosities of the 2K-WPU/NFC dispersions increased sharply and particle sizes of the 2K-WPU/NFC dispersions increased slightly with the increase of NFC content. Fractography images from scanning electron microscopy (SEM) showed rough structures appearing in the nancomposites structure, which corresponded to the microphase separation between NFC nano-filler and the 2K-WPU matrix. This microphase separation phenomenon led glass transition temperature (T_g) and break elongation of the 2K-WPU/NFC nanocomposite films decreased with the increase of NFC content. Tensile tests and dynamic mechanical analysis (DMA) indicated all the 2K-WPU/NFC nanocomposite films showed simultaneous enhancements in modulus and tensile strength, compared with those for the neat 2K-WPU (0 wt%). The enhancements can be attributed to strong interactions resulting from the formation of hydrogen bonds and chemical grafting between NFC nano-filler and the 2K-WPU matrix.

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1. Introduction

With the increasingly stringent restrictions on volatile organic compounds (VOCs) emissions in coating industry, the use of solvent-based coatings is more limited, and the environmental friendly products without or with low VOCs are more attractive. Waterborne polyurethane (WPU) using water instead of organic solvents as dispersion medium, is nonflammable, non-toxic and environment friendly, and has been widely used in coating industry [1–4]. However, different from the homogeneous film formation of solvent-based polyurethanes, the film formation of WPU is a heterogeneous phase process among water-dispersed particles. The properties of the film of WPU are not as good as that of solvent-based system. In recent years, the composite modification of WPU has become a focus in the field of environmental friendly coating industry [5–7].

Nanofibrillated cellulose (NFC) is the primary load carrying unit in plant fibers and has high tensile modulus. NFC used as reinforcement for polymers is of interest due to the properties of the fibers such as mechanical strength and stiffness (crystal modulus) approaching that of aramid fiber and steel, respectively. NFC is considered as a substitute for the more commonly used glass fibers. The recent breakthrough in isolation of NFC with low energy consumption has opened new possibilities for these green composite materials [8–10]. During the past decade, the interest in nanocellulosic based materials has gradually increased, including nanocellulose reinforced composite films [11–13].

Recent researches have shown that the properties of polymer resins, such as polycaprolactone [14], unsaturated polyester [15], polyamide [16], poly (vinyl alcohol) [17], polypropylene [18], polygalacturonic acid [19], poly (vinyl acetate) [20], acrylic resin [21], and etc, could be further improved by the addition of NFC. It was reported that polypropylene composites reinforced with NFC (10 wt%) were prepared using a compression molding. The

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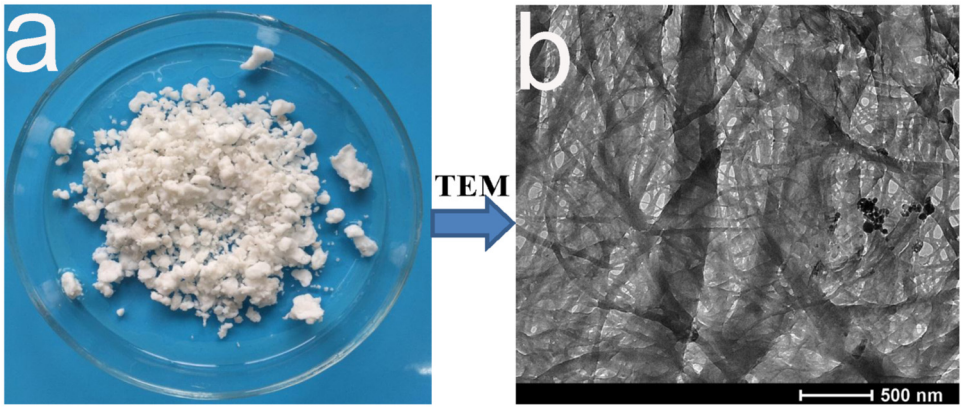

Fig. 1. NFC (a) and TEM image of NFC (b).

improvement of Young's modulus and tensile stress were 45% and 52%, respectively, compared to those of neat polypropylene [18]. Xiao et al. studied mechanical properties of NFC reinforced poly (vinyl alcohol) (PVA) film and found that tensile strength of the nanocomposite film is 1.5 times higher than that of neat PVA [22]. Young's modulus and tensile strength of polylactic acid (PLA) were increased by 40% and 25%, respectively, without reduction of yield strain after 10 wt% of NFC was added [23].

Given hydrophilic nature, NFC products are always swelling in water, and are difficult to be dispersed in water-insoluble resins, such as epoxy resin, unsaturated polyester, polyamide, polylactic acid, polypropylene and etc. One method to overcome this problem is to exchange the medium water with acetone by placing NFC in an acetone bath [15]. However, this solvent exchange strategy of NFC is quite inefficient and environment-unfriendly. Since stable suspensions of NFC can be easily prepared in water, their incorporation in waterborne resin to prepare cellulose nanocomposites is an efficient strategy for the utilization of NFC. During the past decade, NFC has been reported to be filled into water-soluble resins, such as poly (vinyl alcohol), resulting in a significant increase of strength and Young's modulus [17,24–26].

Two-component waterborne polyurethane (2K-WPU) coatings which integrate the environment-friendly property of water-dispersed coatings with the good performance of two-component polyurethanes, are gaining extensive research attention [27–29]. In our previous work, thermoset nanocomposite films with uniform distribution of cellulose nanowhiskers (CNW) in 2K-WPU matrix and significant reinforcement were prepared by low loading level CNW [30]. The film formation process of 2K-WPU contained not only particle merging but also crosslinking reaction between hydroxyl groups (OH) of polyols and isocyanate groups (NCO) of hexamethylene diisocyanate (HDI). The abundant active hydroxyl groups on the surface of CNW could take part in the crosslinking reaction with isocyanate groups of HDI, resulting in strong interfacial adhesion between the matrix and the filler. Important distinctions are between acid-hydrolyzed rod-like whiskers (CNW) and NFC. NFC tends to have high aspect ratio and is more flexible and prone to formation of physical entanglements [31]. NFC forms network structures with very interesting mechanical behavior such as substantial plastic deformation and high strength [32]. Also, NFC can be prepared in a cost-effective way by enzymatic pretreatment of wood pulp and has the potential for large scale industrial use [8]. In this work, the 2K-WPU/NFC nanocomposite films were prepared by directly incorporating NFC suspension into water dispersed 2K-WPU, without solvent exchange. The rheological behavior, structure and properties of the prepared nanocomposites with different NFC contents were investigated by rotational rheometer, scanning electron microscopy (SEM), differential scanning calorimetry (DSC), thermogravmetric analysis (TGA), dynamic mechanical analysis (DMA), and tensile tests.

2. Experimental

2.1. Materials

NFC with water (25% NFC and 75% water, Fig. 1a) was purchased from Daicel Corporation, Japan. The stereoscopic information of the NFC collected with a transmission electron microscope (TEM) was shown in Fig. 1(b). The technical parameters of NFC provided by Daicel were as follow: width 10–50 nm and length 400–600 μm. Terpinene-maleic ester type epoxy resin (TME) was synthesized from raw material turpentine (Wu et al., 2007). It is an alicyclolic epoxy resin with endocyclic structure (Fig. 2) and has an epoxy value of 3.5 mmol g^{-1}. Polyethylene glycol (PEG) (M_n = 4000) was purchased from Guangdong Xilong Chemical Co., Ltd, China. Neopentyl glycol (NPG) was 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. TME based polyol (WEPol) dispersion with OH content of 4.3 wt% and solid content of 35 wt% was prepared according the reported studies [33,34]. The hydrophilically modified HDI tripolymer (Fig. 2) with NCO content of 14 wt% and solid content of 85 wt%, was supplied by Shanghai Siwo Chemical Co., Ltd., China.

2.2. Preparation of WEPol and WEPol dispersion

The synthesis of WEPol has been described in details in our previous work [33,34], 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 16.9 g NPG. After the temperature inside the flask increased to 90 °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 110–120 °C, producing a yellow transparent product WEPol. By churning at 500–1000 rpm, at 50–90 °C, 210 g distilled water was added slowly to disperse the produced WEPol, generating a milk-white dispersion (WEPol dispersion) with 35 wt% solid content.

2.3. Preparation of the 2K-WPU/NFC nanocomposite films

NFC was used as received. Different dosages of NFC were mixed homogeneously in the WEPol dispersion under sonication for 30 min with an ultrasonic cell disruptor. Then the obtained mixture was blended with hydrophilically modified HDI tripolymer at

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