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Water-induced modulus changes of bio-based uncured nanocomposite film based on natural rubber and bacterial cellulose nanocrystals

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ABSTRACT

Bacterial cellulose whiskers (BCWs) were firstly incorporated into natural rubber (NR) by an evaporation method. The structure, morphology, dynamic mechanical properties, water uptake and water-responsive behavior of modulus for NR/BCWs nanocomposite films were investigated. It was found that the hydrophilic BCWs generated a significant reinforcement effect on the storage modulus of NR. In the presence of water, the nanocomposite films showed a pronounced response in storage modulus, especially for the nanocomposite filled with highest filler content. The storage modulus of films with 20 phr (parts per hundred rubber) BCWs decreased by 95.3% after equilibrium swelling in water. This modulus change behavior was attributed to the disentanglement of hydrophilic filler network via competitive hydrogen bonding with water. NR/BCWs nanocomposite film could be used as a new type of shape-memory material for biomedical applications.

1. Introduction

Mechanically dynamic materials that respond to stimuli in selective physiological conditions are of significant current interest in biomedical applications, sensors and smart clothing (Lee and Park, 1998; Pelrine et al., 2000; Peppas et al., 2006; Shanmuganathan et al., 2010). Inspired by the stimuli-responsive behavior of sea cucumbers, which have the spectacular ability to rapidly and reversibly alter the stiffness of their inner dermis in response to threats, a new family of mechanically dynamic polymer nanocomposites have been developed (Capadona et al., 2008; Dagnon et al., 2012; Mendez et al., 2011; Shanmuganathan et al., 2009; Shanmuganathan et al., 2010). The stimuli-responsive behavior can be performed through designing a nanocomposite architecture in which a viscoelastic matrix is reinforced by hydrophilic cellulose nanofibers (also referred to as nanocrystals) extracted from a range of renewable biosources (Dagnon et al., 2012; Shanmuganathan et al., 2009; Shanmuganathan et al., 2010). In this stimuli-responsive system, the rigid percolating network formed by cellulose nanocrystals may be re-regulated under the selective physiological conditions (external stimulations). Via noncovalent or covalent bondings, the stress transfer between adjacent cellulose whiskers can be tailored according to the external stimulus, which results in changes in the strength and stiffness of the nanocomposites (Shanmuganathan et al., 2009; Shanmuganathan et al., 2010). For example, Capadona et al. extracted cellulose nanofibers from tunicates, and firstly reported the stimuli-responsive behavior of a rubbery ethylene oxide-epichlorohydrin copolymer (EO-EPI) reinforced with cellulose nanofibers (Capadona et al., 2008). This architecture exhibited a reversible change in tensile modulus, from 20 to 800 MPa, upon exposure to water (acts as chemical regulator) that mediated hydrogen bonding interaction among the whiskers. A similar water-responsive behavior was also reported for the carboxylated styrene-butadiene rubber (xSBR) nanocomposites reinforced with chitin nanocrystals prepared from chitin powder (Liu et al., 2015).

Cellulose whiskers are considered a competing candidate for polymeric green fillers owing to their biodegradability, low density, high mechanical properties and diversity of the sources (Azizi Samir et al., 2005; Bendahou et al., 2010). For the stimuli-responsive polymer composites reported previously, the cellulose nanofibers were extracted from animal and/or plant cellulose. Differing from plant cellulose, in which cellulose Iβ is the major component, bacterial cellulose (BC) predominantly consists of cellulose Iα, which shows some uniqueness in physicochemical, mechanical and biological properties (Guo and Catchmark, 2012; Wang et al., 2012). The most striking features of BC are its high crystallinity, mechanical strength, modulus and biodegradability (Heßler and Klemm, 2009). Compared with cellulose from other sources, the ultrafine three-dimensional structure and sufficient water holding capability makes BC more popular in the biomedical fields (Wang et al., 2012). As a derivative of BC, bacterial cellulose whiskers (BCWs) are elongated crystalline rod-like nanoparticles

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obtained by general acid hydrolysis of BC in order to digest the amorphous cellulosic domains. The reinforcement effect of BCWs on polymeric matrices has received increasing attention recently due to the high crystallinity, high aspect ratio and excellent mechanical properties of BCWs as well as their biocompatibility and biodegradability (George et al., 2011; George and Siddaramaiah, 2012; Soykeabkaew et al., 2012).

Bio-based materials that reduce the dependence on fossil fuel and improve the sustainability of the environment have attracted more and more research interest (Bras et al., 2010; Espert et al., 2004; Jong, 2014). Natural rubber (NR) is a widely used raw material originally deriving from the latex of *Hevea brasiliensis* (Bras et al., 2010; Rolere et al., 2015). As an environmentally friendly material, NR consists of *cis*-1,4-polyisoprene (94 wt.%), lipids (ca. 3 wt.%), proteins (2 wt.%), carbohydrates (0.4 wt.%) and minerals (0.2 wt.%), and can be disintegrated in soil by specific microorganisms (Rolere et al., 2015; Salomez et al., 2014). In comparison with synthetic rubber, NR also shows superior mechanical properties, which may be contributed by the associative structure in which phospholipids and proteins are believed to interact with the α- and ω- terminal groups of polymer chains, respectively (Tanaka and Tarachiwin, 2009; Toki et al., 2009). With the objective to improve the sustainability of environment, NR has already been studied as a natural matrix for bio-based nanocomposites with cellulosic nanofillers (Bendahou et al., 2010; Bras et al., 2010; Kargarzadeh et al., 2015). However, to the best of our knowledge, little work has been reported so far on NR reinforced with BCWs.

Based on the aforementioned viewpoints, in this work, the NR/BCWs nanocomposite films were prepared by mixing BCWs suspensions with NR latex, followed by evaporation. The effects of BCWs on the structure, morphology, tensile storage modulus, water uptake and water-responsive behavior of modulus for nanocomposite films were thoroughly investigated. This study aimed to develop a new class of bio-based rubber nanocomposite with mechanically dynamic behavior.

2. Experimental

2.1. Materials

The BC pellicles were produced by Acetobacter xylinum NUST4.2. Sodium hydroxide(NaOH) and concentrated sulfuric acid (H_2SO_4, 98 wt.%) were purchased from Shanghai Lingfeng Chemical Reagent Co. Ltd. (Shanghai, China). Natural rubber latex (solid content: 60 wt.%) was purchased from Shanghai Nessen international trading Co. Ltd. (Shanghai, China).

2.2. Preparation of BCWs

The cellulose was purified by boiling the BC pellicles in 0.2 M aqueous NaOH solution for 2 h then rinsing with deionized water several times until a neutral pH was achieved. The purified pellicles were further mechanically disintegrated into a cellulosic paste. Then, about 100 g of cellulosic paste (wet weight) was added to 100 mL of H_2SO_4 (50 wt.%) and stirred for 48 h at 60 °C. After hydrolysis, the BCWs suspensions was centrifuged (12000 rpm) for 30 min, and the sedimented BCWs were further washed with deionized water until a neutral pH was achieved.

2.3. Preparation of NR/BCWs nanocomposite films

The NR/BCWs nanocomposite films were prepared by an evaporation method. BCWs aqueous suspensions were obtained by dispersing a specific amount of BCWs in deionized water. The suspensions were sonicated for 0.5 h in an ice-water bath using Elma ultrasonic cleaner (Germany) with an output power of 100 W. Then, BCWs suspensions were added into NR latex with ultrasonic treatment for 1 h to achieve NR/BCWs suspensions. The suspensions were further stirred for 4 h. After that, the suspensions were degassed under vacuum before being cast on a polytetrafluoroethylene (PTFE) mold (Zhenjiang Run Fang Seals Co. Ltd., China) with a diameter of 10 cm and a depth of 1 mm. Next, water was evaporated in a ventilated oven at 40 °C for 12 h. Each sample was further dried under vacuum at 50 °C for 12 h to obtain a NR/BCWs nanocomposite film. A series of nanocomposite films containing 3, 5, 7, 10, 15, 20 phr of BCWs were labeled as NR-BCWs n (n denoting BCWs content in the film).

2.4. Characterizations

Atomic force microscopy (AFM) was carried out on a NanoScope III D Multimode scanning probe microscope (Bruker Co. Ltd., Switzerland) in a tapping mode. The whiskers dispersion was spin-coated onto a freshly exfoliated mica substrate at 2000 rpm and dried at room temperature. Transmission electron microscopy (TEM) was performed with a JEOL-2100 transmission electron microscope (JEOL Co. Ltd., Japan) with an accelerating voltage of 200 kV. Scanning electron microscope (SEM) images were taken from the representative freeze-fracture surfaces of the nanocomposites using a Phenom Pure desktop SEM (Phenom CO. Ltd., Netherlands) and the specimens were prepared by fracturing the film in liquid nitrogen.

X-ray diffraction patterns (XRD) were recorded by a D8-Advanced X-ray diffractometer (Bruker Co. Ltd., Switzerland) with Cu Kα radiation (λ = 0.154 nm) from 5 to 50°, the scanning speed was 3° min^{-1}. Fourier transform infrared spectra (FTIR) were conducted on a FTIR-8400S spectrometer (Shimazdu Co. Ltd., Japan) at a scanning resolution of 4 cm^{-1} in the wavenumber range from 4000 to 700 cm^{-1}. The spectra of BCWs and NR/BCWs were recorded by a transmission mode of KBr pellets and a Horizontal attenuated total reflectance model, respectively.

Dynamic mechanical analysis (DMA) was investigated with a Q800 dynamic mechanical analyzer (TA Co. Ltd., USA) with a tensile mode of 1 Hz. The tests were measured over a temperature range from −70 °C to 80 °C with a heating rate of 3 °C min^{-1} under a N_2 atmosphere, and the results of three measurements were averaged.

The water swelling behavior of nanocomposites was investigated by immersing the samples in deionized water at 25 °C for 5 days. The samples were removed every 24 h, gently wiped using filter paper, weighed, and immediately re-immersed in deionized water. The swelling ratio (Q) was calculated by Eq. (1), and the results of three measurements were averaged.

$$\text{Swellingratio}(\%) = 100 \times (M_t - M_0)/M_0 \quad (1)$$

where M_0 and M_t are the weights of the sample before immersion in deionized water and after water immersion for a certain period time (t), respectively.

Water contact angle of the film surface was measured with a C601 Contact Angle instrument (Shanghai solon information technology Co. Ltd., China) by sessile drop method under room temperature. A drop of DI water (4 μL) was carefully deposited to the sample surface to avoid the effect of falling force by gravity. The contact angle values were calculated by software according to the Young-Laplace model.

3. Results and discussion

3.1. Characterizations of BCWs

The XRD patterns of BC and BCWs (Fig. 1a) showed three major crystalline peaks at 2θ = 14.5, 16.4 and 22.5°, corresponding to the (101), (101) and (002) crystal planes of cellulose I allomorph, respectively (Martínez-Sanz et al., 2011). It is predicted that BCWs prepared from BC will have a higher crystallinity due to the removal of disordered or amorphous regions of BC by acid hydrolysis. The crystallinity index (CI) was calculated from the following equation (Martínez-