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RESEARCH ARTICLE

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Characterization of bamboo cellulose-based green composite film by NMMO technology

Abstract Bamboo cellulose, lignin and starch have been molecularly blended to form homogeneous composite films by NMMO-technology. The structural properties of the films were investigated with FTIR, WAXD and AFM technologies, respectively. The results show that bamboo cellulose, lignin and starch have been molecularly blended through NMMO-technology. There was a two-phase system consisting of ternary composite components as one phase and pores as the other on the surface of the composite film. Because of the existence of homogeneous phase structure formed by the rearrangement of the natural polymer molecules, the film shows good properties originating from the mutual supplement of different natural components.

Keywords ternary composite film, NMMO, characterization, properties

1 Introduction

Bamboo cellulose, lignin and starch are three major materials of natural polymer and they have been studied and widely applied in degradable and renewable materials. Since they could not be melted, traditionally, these natural polymers were usually added into the matrix together with other undegradable materials after they were deformed plastically or chemically modified. Thus, there is presently no use for the thermoplastic processes to extrude fibre or films from these directly. In order to make full use of these natural materials to perform overall environment-friendly function, as an alternative, a simpler and more environment-friendly NMMO (Lyocell)-technology (Gunnars et al., 2002; Fält et al., 2004; Fink et al., 2004; Tian et al., 2004; Peng et al., 2005) has received considerable interest all over the world recently.

In this study, we combined three natural polymers of bamboo cellulose, starch and lignin by employing NMMO-dissolving process to obtain a novel triple-homogenous film (CLS film). FTIR analysis, WXRD test and AFM observation demonstrated the formation of these natural green films.

2 Materials and methods

2.1 Materials

NMMO (N-methyl-morphine-oxide), 50% (w/v) solution in water was supplied by the Huatai Chemical Co., Ltd in Huaian. Bamboo pulp, with a degree of polymerization (DP) of 1000 was supplied by the Shanghai Tenbro Bamboo Textile Co., Ltd. Lignosukohinate (MN) was supplied by the Wuhan East China chemical Co., Ltd. The cornstarch was from the Shanghai starch factory.

2.2 Preparation of natural polymers-NMMO solution and film

The known amount of bamboo cellulose, starch and lignin (weight ratio of cellulose, starch and lignin was 6:3:1) together with 50% (w/v) NMMO solution in water was charged into a 250 mL three-necked round bottom flask equipped with an overhead agitator, heat mantle, reflux condenser and addition funnel, and heated to 100°C, in which vacuum was applied in order to evaporate the water to yield a polymeric solution of 10%. The aqueous solution with yellow color was finally obtained and the complete dissolution of composite natural polymers was checked by polarization microscopy (Gunnars et al., 2002).

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The films for testing were prepared with 10wt% polymer solution in NMMO on a freshly cleaned glass board pre-heated at 70°C, further precipitated in deionized water around 10°C for 10 min, and finally washed in another batch of deionized water for at least 3 h to remove the remaining NMMO. The films with thickness of 15–20 μm were dried continuously in laboratory desiccators in air at 45°C.

2.3 Methods

2.3.1 Structural characterization

FTIR analysis. Fourier transform infrared analysis was performed on a Magna-IR 550 spectrometer (Nicolet Instruments, Madison, WI). The spectrum was recorded before 32 times scanning at a resolution of 4 cm^{-1}.

Wide-angle X-ray diffraction. X-ray diffraction curves of the film samples were measured with a Japan D/max-γB X-ray diffractometer in transmission geometry employing CuK radiation (40 kV) monochromized by a Ge-crystal.

Atomic force microscopy (AFM). The AFM observation was made on SPA 300HV-DFM (Seiko Instruments Industry, Co., Ltd, Japan) in ultra-light-tapping mode at room temperature, using the micro-fabrication cantilevers with a spring constant of approximately 20 N/m. All AFM data including the height, phase shift and the 3-dimensional (3D) image as well were recorded simultaneously.

2.3.2 Tensile testing

The mechanical properties (strength σ_{max}, elongation at the maximum force of the composite film was determined with XLW testing machine made by the Guangzhou Experimental Equipments. A 100 mm clamp separation and 100 mm/min cross-head speed were used for film testing.

3 Results and discussion

3.1 FTIR analysis

Figure 1 is the FTIR spectra of the CLS film-based Lyocell-technology. From Fig. 1, it is found that the composite film keeps the structural characteristics of cellulose to a great degree. The strong absorbance bands at 1060 cm^{-1} is the typical absorption of cellulose, and 2920 cm^{-1} is the adsorption peak of methyl and methylene from both cellulose and starch (Hassan et al., 2000). In addition, the hydroxyl groups stretch shifts from 3040 up to 3450 cm^{-1}, suggesting the dissociation of hydrogen-bonding which possibly occurred during the Lyocell-technology. From Fig. 1 it is also noted that there are absorbance peaks at 1695–1503 cm^{-1} representing typical aromatic skeletal stretch (Zhang et al., 2005). Together with the bands of 1275 and 1220 cm^{-1} of the lilac ring, we could conclude that bamboo cellulose, lignin and starch have been molecularly blended through Lyocell-technology and the homogeneously ternary film is formed.

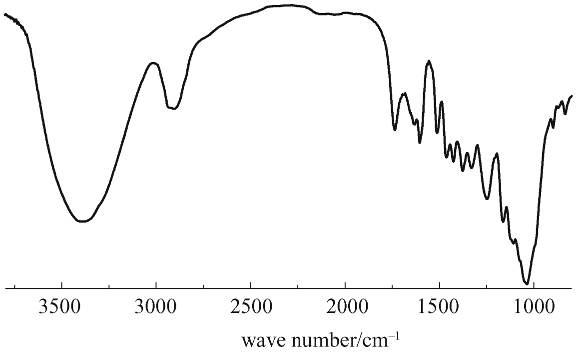


Fig. 1 FTIR spectra of the green composite film

3.2 WXRD analysis

Cellulose is a highly crystallized material and its crystal region originates from the regular and compact arrangement of hydrogen bonds formed by the numerous hydroxyl groups of the polysaccharide molecular chains, which leads to both high tensile strength and difficult processing with general melting and solution methods. From Fig. 2 it is noted that through the strong solution effect of N-methyl-morphine-oxide (NMMO), the true solution of cellulose could be formed, and the hydrogen bonds between the cellulose molecular chains could be separated. Compared with bamboo pulp (see curve a), bamboo-cellulose film based on NMMO-technology still keeps a part of the crystallization to a certain degree (see curve b), while for the bamboo-based cellulose ternary

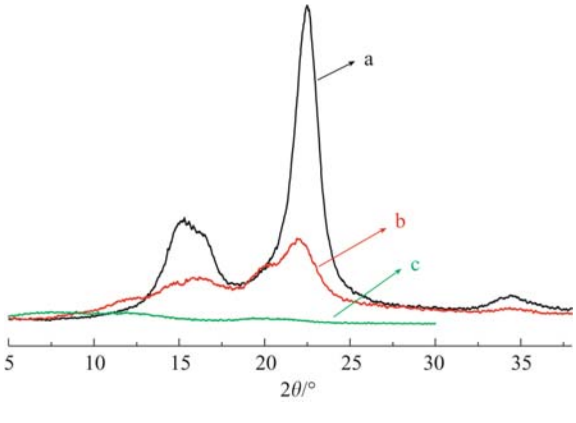


Fig. 2 XRD curves of cellulose pulp, cellulose film and CLS film and by Lyocell process

a: cellulose pulp; b: cellulose film; c: CLS film composite film (curve c), the diffraction peak of 15.20°, 16.42° disappears and the other diffraction peaks greatly weakens. This phenomenon reveals that the crystallized structure of cellulose has been destroyed with the blending of the molecular chains of starch and lignin into cellulose molecular chains. Due to the mixing of the helix molecular structure of starch and the aromatic structure of lignin by NMMO-technology, the highly regular arrangements of hydrogen bonds cannot be reformed completely between the cellulose molecules, which also imply the formation of the homogeneous structure of this ternary system.

3.3 AFM observation

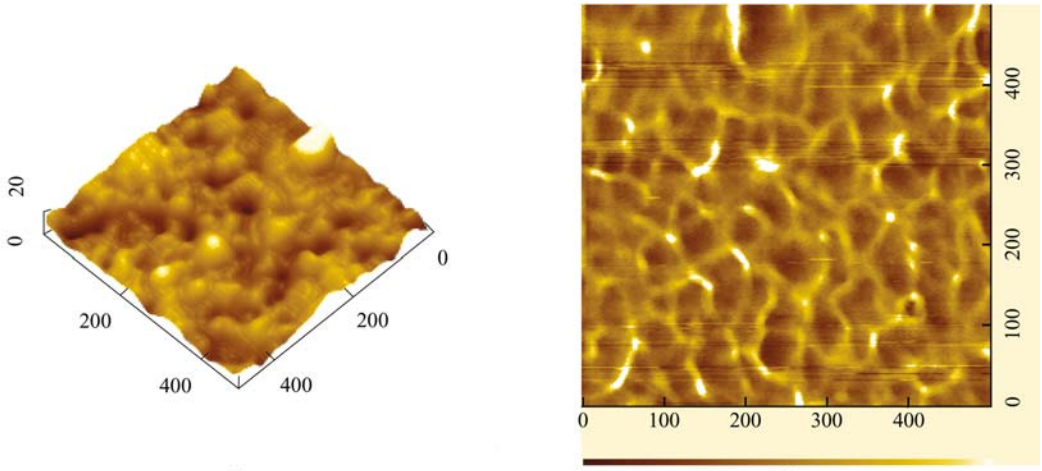
Figure 3 illustrates the AFM images of the prepared triple-homogeneous film. The height variation and rough topography exhibited across the surface were believed to be the result of the phase separation. Generally, the phase image in Fig. 3b exhibited two-phase separated surface morphology consisting of natural triple-polymers as one phase and pores as the other, and the size of the nanoscale domain was around 10–100 nm. From the topographic image (Fig. 3a), we also noted that the film surface shows a mean surface roughness of around 100 nm. The larger domain value and the higher surface roughness should originate from a much more viscous solution in this NMMO-dissolving system, because a controlled roughness could be obtained by varying the concentration of the materials according to reference (Chen et al., 1998; Ganster and Fink, 2006). This AFM result also demonstrated that triple-homogeneous structure forms because there were no phase interfaces observed among these three kinds of polymers.

3.4 Mechanical properties

Strength and elongation for the bamboo-cellulose film and CLS film are given in Table 1. Comparatively higher strength and lower elongation values for the single cellulose film were found, while CLS composite film improves the elongation greatly at the cost of sacrificing the strength a little. This result should originate from the inter-complementing structural property of the ternary homogeneous film.

4 Conclusions

Bamboo Cellulose-based ternary green composite film by NMMO Technology was prepared for the first time. The structures and properties of the green composite film were investigated with FTIR, WAXS and AFM, respectively. Results show that bamboo-cellulose, lignin and starch could be truly blended homogeneously in a molecular grade and forms a composite film with thermoplastic property, which may originate from the rearrangement of hydrogen bond and the dissociation of the crystalline region of cellulose. Due to the formation of the film after the removal of solvent by water washing, a separated microphase structure is formed.



(a)

(b)

Fig. 3 3D topographic and phase images of CLS green composite film (unit: nm)
(a) 3D topographic image; (b) phase image

Table 1 The mechanical properties of bamboo-based cellulose film and CLS composite film

bamboo-cellulose/%	lignin/%	starch/%	strength at break/MPa	elongation at break/%
100			19.18	15.70
60	10	30	17.25	80.90

Because of the inter-complementing property of the composite components in the film, the mechanical properties of the composite film are improved greatly.

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