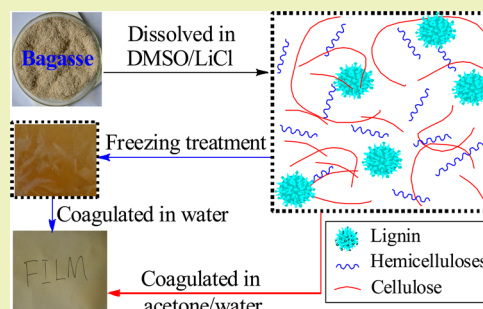


Approach to Renewable Lignocellulosic Biomass Film Directly from Bagasse

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ABSTRACT: Lignocellulosic biomass in the form of plant materials offers the most abundant renewable resource in replacing traditional fossil resources. In the present study, lignocellulosic biomass films were prepared directly from bagasse solutions in DMSO/LiCl without additional film-forming additives by coagulation either in an acetone/water (9/1, v/v) mixture or in water following a freezing treatment. The physicochemical properties of bagasse films were studied by FT-IR, UV/vis, SEM, XRD, and tensile testing. The films were semi-transparent with a yellow color and showed strong abilities in UV light blocking due to the presence of lignin. Relatively high mechanical strength comparable to cellulose–starch–lignin composite films was observed. The physical cross-link and the stress buffer of micropores formed in the freezing treatment resulted in enhanced mechanical strength of the film. The facile and environmentally friendly process creates a new strategy for converting abundant lignocellulosic materials to novel value-added bioproducts.

KEYWORDS: Films, Lignocellulosic biomass, Renewable resources, Bagasse, Biobased materials, Green materials



INTRODUCTION

Lignocellulosic biomass in the form of plant materials (such as wood, grasses, and agricultural residues) has been recognized as the most abundant renewable resource.^{1,2} These renewable bioresources have been playing an increasingly important role as fossil resources are dwindling and becoming progressively more expensive.³ In response to the finite and exhaustible fossil resources, many countries have initiated extensive research and development programs in biomass conversion and biorefinery to reduce societies' dependency on unrenewable fossil resources.⁴

Lignocellulosic biomass is a natural composite of cellulose, hemicelluloses, lignin, and extractives. It is one of the most ancient materials and continues to serve as an important material in modern society.⁵ A great number of novel materials have been developed based on lignocellulosic biomass, such as wood plastic composite,⁶ biomass-based carbon,⁷ wood ceramics,⁸ semi-conducting materials,⁹ and aerogels.¹⁰ However, it is still a major challenge to directly convert lignocellulosic biomass into valuable materials because lignocellulosic biomass has evolved complex structural and chemical mechanisms for resisting chemical and biological assault.¹¹ The cell wall structures of lignocellulosic biomass are usually compared to the reinforced concrete structures, in which cellulose, lignin, and hemicelluloses correspond, respectively, to the iron core, cement, and buffering material.¹² As a result, it is practically impossible to dissolve lignocellulosic biomass in common solvent systems, which is the major impediment to the more efficient utilization and development of this important resource.¹³

Recently, several solvent systems have been developed for completely dissolving lignocellulosic biomass.^{13–15} These solvent systems are mainly classified into DMSO-based organic solvents, including DMSO/tetrabutyl ammonium fluoride (TBAF), DMSO/N-methylimidazole (NMI) and DMSO/LiCl, and ionic liquids (ILs).¹⁶ The development of these new systems has set up improved processing strategies for the pursuit of chemicals, materials, and energy from lignocellulosic biomass.¹⁷

Biocompatible composites prepared from natural biopolymers have gained increasing interests in the past few years. Green renewable barrier films were designed from cellulose, starch, and lignin in room temperature ionic liquid (RTIL)¹⁸ and from polysaccharide-rich wood hydrolysate.¹⁹ Synthetic wood composite films containing isolated cellulose, hemicelluloses, and lignin were also prepared in a RTIL solvent.²⁰ More excitingly, composite fibers have been successfully prepared directly from raw lignocellulosic biomass solutions.²¹ These researches suggest that it is possible to directly transform raw lignocellulosic biomass into high value materials by dissolving the biomass in suitable solvents. Therefore, in the present study, the possibility of preparation of novel green, renewable, and biodegradable films was investigated directly from raw lignocellulosic biomass using DMSO/LiCl as solvent without any additional film-forming additives. The physicochemical properties of the prepared films were characterized.

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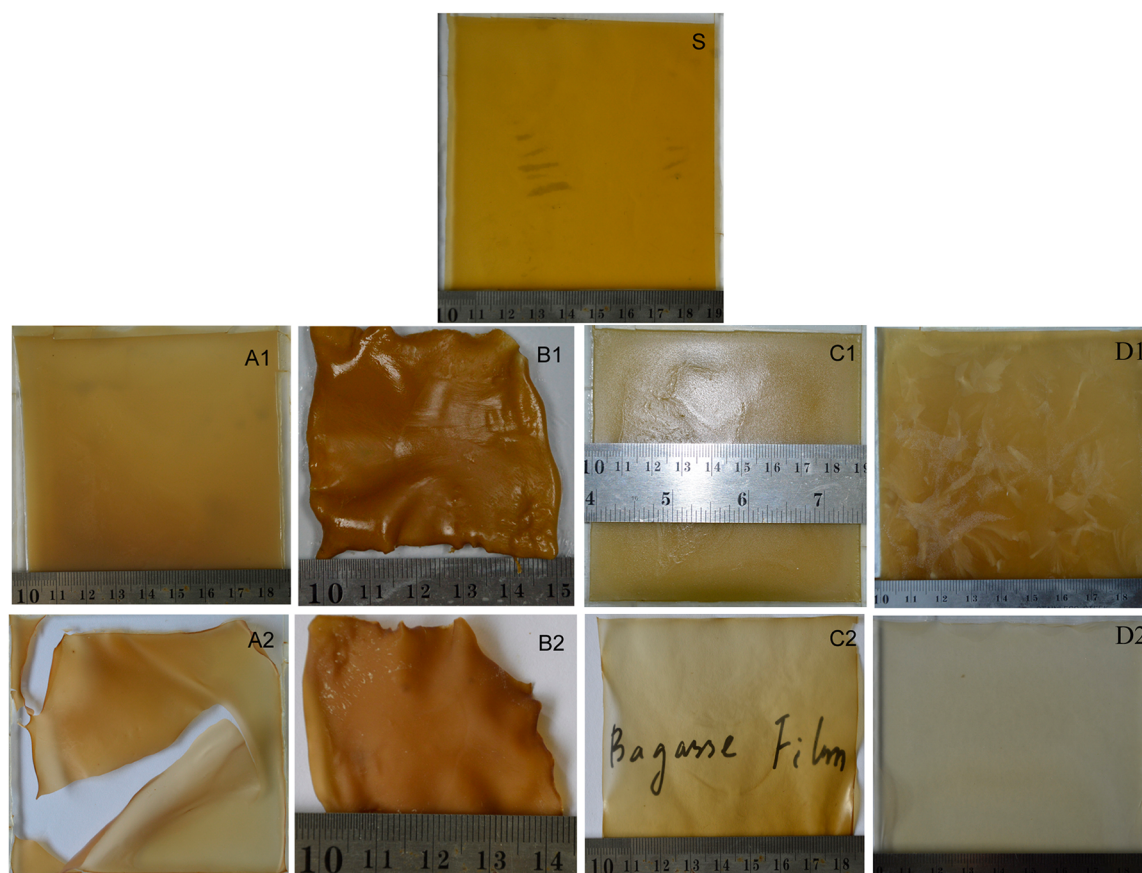


Figure 1. Film-forming solution cast on a glass plate (S), the frozen film (D), the wet films (1) coagulated in water (A), acetone (B), and acetone/water (9/1, v/v, C), and the subsequent dry films (2).

EXPERIMENTAL SECTION

Materials. Bagasse was obtained from a local factory (Jiangmen, China). It was ground and screened to prepare 40–60 mesh-sized particles. The ground bagasse was dewaxed in a Soxhlet extractor with toluene–ethanol (2:1, v/v) for 12 h and then dried in a cabinet oven with air circulation at 50 °C for a period of 24 h. The dewaxed SCB was ball-milled in a planetary ball mill for 4 h. DMSO, LiCl, ethanol, and acetone were of analytical reagent grade and were purchased from Guangzhou Chemical Reagent Factory (Guangdong, China). Water used throughout the experiments was ultrapure water.

Film Preparation. LiCl was dissolved in DMSO to prepare a DMSO/LiCl solvent system with the 6% weight ratio of LiCl. Ball-milled bagasse (0.5 g) was suspended in 9.5 g of DMSO/LiCl and stirred at 110 °C in oil bath for 5 h under a N₂ atmosphere to guarantee complete dissolution. The bagasse solution was cast onto a glass plate, immersed in the coagulation bath (water, acetone, and acetone/water) to remove DMSO and LiCl, and dried in the air to obtain the bagasse film. If necessary, the bagasse solution cast on the glass plate was frozen at –35 °C for 5 h before being immersed in water.

Characterization. Film thickness was measured using a micrometer (Lorentzen and Wettre, precision 0.01 μm) at five different locations on each film, and the mean value was used in the calculations to determine the mechanical test measurement. Tensile testing was performed with an Instron Universal Testing Machine 5565 fitted with a 100 N load cell. The samples were cut to rectangular specimens with a width of 15 mm and length of 70 mm, and at least five replicate specimens were tested from each film. The initial distance between the grips was 30 mm, and the grips were separated at the rate of 1 mm/min. The light transmittance of the films was measured over the wavelength range of 200–900 nm with an UV/vis spectrophotometer

(TU-1810, Beijing, China). SEM was conducted on a LEO 1530VP (LEO, Germany) with an accelerating voltage of 10 kV.

FT-IR spectra were recorded on an FT-IR spectrophotometer (Bruker) using a KBr disc containing 1% finely ground samples. Thirty-two scans were taken for each sample in the region of 4000–400 cm⁻¹ at a resolution of 4 cm⁻¹ in the transmittance mode. The XRD pattern of bagasse and the prepared films was recorded on a Bruker D8 ADVANCE X-ray diffractometer (Germany) equipped with Ni-filtered Cu Kα₁ radiation (λ = 0.154 nm) at room temperature. The scattering angle range was 5–40° with an 8°/min scanning speed and a 2θ step interval of 0.02°.

RESULTS AND DISCUSSION

Films Preparation. In the present study, lignocellulosic composite films were fabricated directly from bagasse dissolved in DMSO/LiCl without any additional film-forming additives. Film-forming solution of 5% ball-milled bagasse in DMSO/LiCl was cast onto a glass plate to form wet film (Figure 1S). The wet film on the glass plate was immersed into water to remove DMSO and LiCl, and bagasse hydrogel film (Figure 1A1) was obtained. However, it was unfortunately cracked upon drying (Figure 1A2). This may be due to the combined effects of the presence of hemicelluloses, known as nonfilm-forming polymer from plant biomass,²² and the strong hydrogen-bonding interaction between polysaccharides and water, a polar solvent with strong hydrogen-bonding ability.

To avoid the cracks during drying caused by the strong hydrogen-bonding interaction, acetone was chosen to remove DMSO and LiCl. However, the bagasse film shrank extensively after DMSO and LiCl were removed (Figure 1B1) and further

shrank upon drying but without any cracks (Figure 1B2). To prevent the film from shrinking, a small amount of water was added to the acetone to form an acetone/water (9:1, v/v) mixture as the coagulating bath. The hydrogel film was obtained after the removal of DMSO and LiCl (Figure 1C1), and the film without any cracks was obtained with marginal shrinkage after drying (Figure 1C2). It suggests that a coagulating bath with suitable hydrogen-bonding ability is necessary to prepare a continuous film without any collapse. The bagasse film coagulated in the acetone/water (9:1, v/v) mixture was named as Film 1.

To compensate for coagulation drawbacks in water, film strength needed to be enhanced to resist against the cracks caused by the removal of water during drying. The enhanced physical cross-linking was reported using a freezing–thawing treatment in the preparation of aerogels.¹⁰ In the present study, the wet film cast on the glass plate (Figure 1S) was frozen at $-35\text{ }^{\circ}\text{C}$ (Figure 1D1), followed by being immersed directly into water without being thawed. A continuous film without cracks was obtained after drying (Figure 1D2), indicating the successful compensation of the film cracks by the increased physical cross-linking during freezing treatment. The bagasse film coagulated in water following freezing treatment was named as Film 2.

Chemical and Physical Structure of the Bagasse Films.

In order to monitor the chemical changes of bagasse upon film formation, FT-IR spectra of bagasse, Film 1, and Film 2 were comparatively studied, as illustrated in Figure 2. The bands

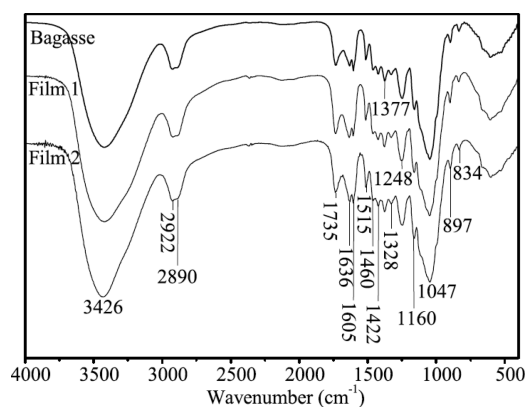


Figure 2. FT-IR spectra of bagasse and the films.

from 2922 to 2890 and 1460 and 1047 cm^{-1} are assigned to C–H stretching, C–H deformation, and C–O stretching, respectively, in lignin and carbohydrates.²³ The absorbances at 1605, 1515, 1422, 1328, and 834 cm^{-1} correspond to the aromatic skeletal vibrations and ring breathing with C–O stretching in lignin.²⁴ Lignin was reported to be extracted by dissolving lignocellulosic biomass in ionic liquids followed by precipitation in an acetone/water (9:1, v/v) mixture.²⁴ However, no obvious changes of the characteristic bands of bagasse were observed during the film formation process in the present study, indicating that lignin and carbohydrates were not substantially extracted during the dissolution and regeneration.

Previous studies showed that the cellulose I crystalline structure was completely destroyed by the dissolution–regeneration process, and the crystalline pattern of regenerated cellulose was converted to cellulose II.²⁵ However, the bagasse films, regenerated from DMSO/LiCl, did not show any signs of

cellulose II (Figure 3) in the present study. This difference of lignocellulose from isolated cellulose may be due to the

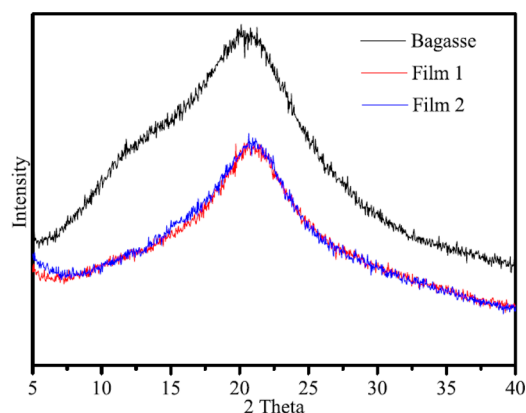


Figure 3. XRD curves of bagasse and the films.

destruction of the cellulose macromolecules by the ball-milling treatment and the presence of amorphous lignin and hemicelluloses, which may prevent cellulose macromolecules from forming cellulose II in the regeneration process. In addition, the crystallinity of cellulose in the films decreased compared with that in bagasse.

The SEM images of the surface and cross-sectional areas of Film 1 and Film 2 are given in Figure 4. Film 1 displayed

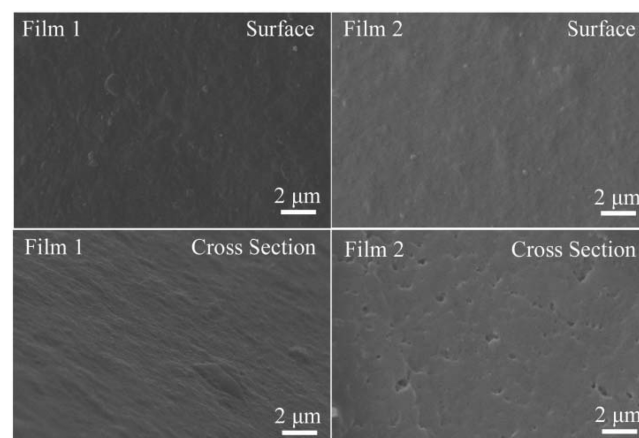


Figure 4. SEM images of the bagasse films.

homogeneously dense architecture structures from the interior to the surface. Comparatively, the outer surface of Film 1 was much rougher than that of Film 2. More importantly, the cross section of Film 2 showed some micropores as expected, which was caused by the crystals of DMSO and LiCl during the freezing process. These micropores were probably the key to the successful compensation of the film's cracks.

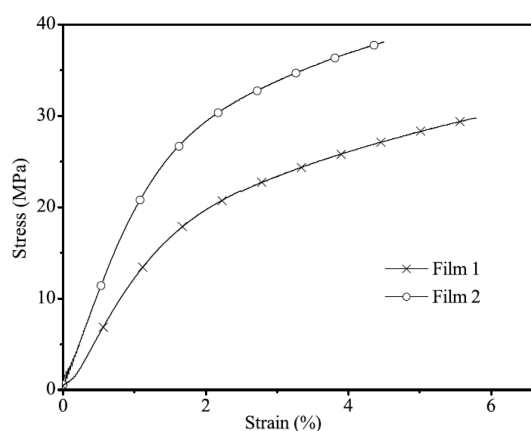
Mechanical and Optical Properties. The thicknesses of the prepared bagasses Film 1 and Film 2 varied between 25 and 45 μm . Table 1 lists the mechanical properties of Film 1 and Film 2. The tensile strength of the films was between 30–40 MPa, substantially higher than the 1 MPa reported for xylan films²² and comparable to the 28–40 MPa values reported for cellulose–starch–lignin composite films,¹⁸ indicating the relatively high mechanical strength of the prepared films. Clearly, Film 1 had a lower modulus of elasticity (1.40 GPa) and tensile strength and higher elongation at break, while Film

Table 1. Mechanical Properties of Bagasse Films

entry	coagulating bath	tensile stress (MPa)	tensile strain (%)	Young's modulus (GPa)
Film 1	acetone/water ^a	30.0 ± 2.1	5.66 ± 0.77	1.40 ± 0.11
Film 2	water ^b	38.3 ± 2.4	4.40 ± 0.82	2.32 ± 0.14

^aCoagulated in acetone/water (9:1, v/v). ^bCoagulated in water following freezing treatment.

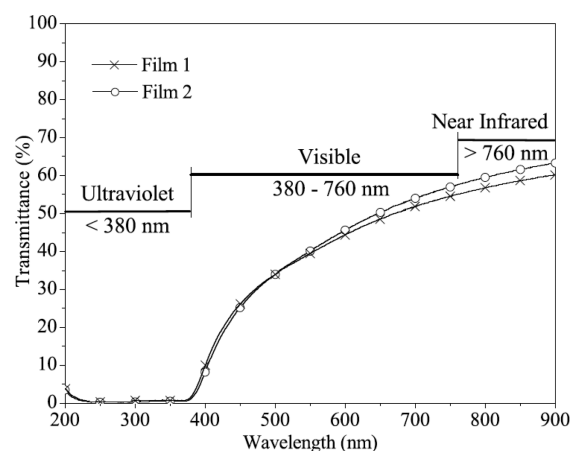
2 exhibited the increased modulus of elasticity (2.32 GPa), much higher than that of cellulose–starch–lignin composite films,¹⁸ together with enhanced tensile strength, except the decreased elongation at break. Figure 5 illustrates the

**Figure 5.** Strain–stress curves of bagasse films.

representative stress–strain curves of Film 1 and Film 2, indicating the significantly different mechanical properties of bagasse films prepared with the two procedures. The difference was probably attributed to the positive effect of the freezing treatment for successful compensation of the film cracks. In the frozen state, the macromolecules of the biopolymers were squeezed due to the solidification and crystallization of DMSO and LiCl. Consequently, more strong hydrogen bonds were formed between the squeezed polysaccharide macromolecules in the frozen state,¹⁶ resulting in partial recrystallization of cellulose, which could serve as cross-link points to form a physical cross-link structure.¹⁰ In addition, the pores, as shown in SEM, could buffer the stress in the film. These combined effects resulted in the higher mechanical properties of Film 2, compared with those of Film 1.

The prepared bagasse Film 1 and Film 2 were at least semi-transparent with a yellow color. Their optical properties were studied with a UV/vis spectrophotometer (Figure 6), and the results indicated that light transmittance values of the films at 600 nm were approximate $44.5 \pm 0.5\%$, which was much lower than that of regenerated cellulose films²⁶ due to the presence of hemicelluloses and lignin. Both of the bagasse films showed strong absorption in the violet region, which was probably attributed to the light absorption of lignin in the ultraviolet region.²⁷ These results suggest promising applications of bagasse film in UV light blocking.

Comparatively, Film 2 exhibited relatively high modulus of elasticity and tensile strength, whereas Film 1 had relatively high elongation at break. The freezing treatment applied in the preparation of Film 2 was probably responsible for these marginal differences. More importantly, there were no obvious

**Figure 6.** UV/vis spectra of the bagasse films.

differences of chemical and crystalline structures or optical properties of these lignocellulosic biomass films directly prepared from sugar cane bagasse.

CONCLUSIONS

In summary, the preparation of renewable, green, and biodegradable lignocellulosic films was achieved directly from solutions of bagasse in DMSO/LiCl without any additional film-forming additives. The continuous films without any cracks can be prepared by using an acetone/water mixture as the coagulating bath or using water as the coagulating bath following a freezing treatment. The facile and environmentally friendly process creates a new strategy for converting abundant lignocellulosic materials to novel value-added bioproducts.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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