

Effects of Pretreatment Methods Using Various 1,4-Dioxane Concentrations on the Performance of Lignocellulosic Films of *Eucalyptus citriodora*

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In order to obtain a material that exhibits a better tensile strength, UV absorption, and transparency, lignocellulose of eucalyptus was dissolved and subsequently regenerated in ionic liquid (IL) following treatment with different pretreatment conditions. The effect of 1,4-dioxane extraction concentration was evaluated by comparing the chemical, thermal, mechanical, and optical performance of the obtained films. The results indicated that lignocellulose could be dissolved using the IL, with the regenerated film demonstrating obvious signs of phase separation. Increasing the 1,4-dioxane extraction concentration brought about an increase in the degree of crystallization, tensile stress, and ultraviolet-visible light transmittance of films. However, the lignin content and peak temperature of main decomposition for the films decreased. Compared to cellulose film, lignocellulose film showed excellent UV absorption properties due to the presence of lignin. F-90 possessed of a better tensile strength, UV absorption, and transparency. This work demonstrated the possibility that a biodegradable green functional film can be prepared.

Keywords: 1,4-Dioxane; Ionic liquid; Dissolution and regeneration; Lignocellulosic film; Performance

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INTRODUCTION

With the decrease of petroleum-based resources and growing global environmental awareness, there has been an increasing interest in the use of lignocellulosic biomass-based materials (Moniruzzaman and Ono 2012). Wood is the most abundant lignocellulosic biomass on Earth (Wang *et al.* 2011), thus making it a valuable source of raw materials. It consists of approximately 40 to 50% cellulose, 15 to 30% lignin, 15 to 25% hemicelluloses, and 1 to 10% extractives (Voitl *et al.* 2010). Cellulose microfibrils are embedded within a matrix of hemicelluloses and lignin (Doherty *et al.* 2011). A lignin-carbohydrate complex is formed between lignin and the carbohydrates by benzyl-ether, benzyl-ester, and phenyl-glycoside bonds (Lundquist *et al.* 1983; Kondo *et al.* 1990). The bonding of these components constitutes a three-dimensional network structure that is remarkably resistant against chemicals and makes it very difficult to hydrolyze (Abdulkhani *et al.* 2013). The development of new methods for the efficient utilization of wood and its structural components has been severely hampered by the insolubility of wood in common solvents (Kilpeläinen *et al.* 2007). The concept of wood dissolution and the separation of its components has encountered serious challenges in conventional methods. Energy consumption, toxic products, and

environmental pollution are just some examples of the problems that arise from current processes (Abdulkhali *et al.* 2013; Xu *et al.* 2013). Therefore, the development of new and effective solvents can be the key to effectively dissolving lignocellulose and increasing the value of wood biochemistry.

An ionic liquid (IL) is an organic salt with a generally low melting temperature (≤ 100 °C) (Sun *et al.* 2011). ILs have many attractive properties in comparison to traditional organic solvents, including good chemical and thermal stability, non-flammability, immeasurable low vapor pressure, and recyclability (Rogers and Seddon 2003), and they can be expected to play an important role in future developments aimed at sustainability of industrial processes (Sun *et al.* 2011). Certain ILs are capable of dissolving polysaccharides (Swatloski *et al.* 2002), lignin (Pu *et al.* 2007), and lignocellulose (Honglu and Tiejun 2006; Kilpeläinen *et al.* 2007; Sun *et al.* 2009) by breaking the extensive hydrogen bonding network of macromolecules. Lignocellulose can be regenerated from an IL solution through the addition of anti-solvent (Kilpeläinen *et al.* 2007). Therefore, using ionic liquids in the preparation of wood biomass composites will contribute towards a reduction in dependency on petro-materials whilst simultaneously enhancing the value of wood biomass (Muhammad *et al.* 2012). The preparation of synthetic wood composites utilizing the dissolution of cellulose, hemicelluloses, and lignin in IL has been reported before (Simmons *et al.* 2011). The synthesis of all-wood, green composites resulting from the partial or complete dissolution of wood flour (Abdulkhali *et al.* 2013; Shibata *et al.* 2013b) and lumber (Shibata *et al.* 2013a) in 1-butyl-3-methylimidazolium chloride (BmimCl) has also been recorded.

Overall performance of wood biomass composites is affected by a variety of variables during their manufacture with IL. The presence of lignin in composites generally leads to the weakening of mechanical properties (Abdulkhali *et al.* 2013). Lignin has traditionally been viewed as a simple waste material or low value by-product (Casas *et al.* 2012). However, lignin has been shown to possess antimicrobial and antifungal activity (Cruz *et al.* 2001), to act as an antioxidant (Krizkova *et al.* 1999; Pan *et al.* 2006), and to absorb UV radiation (Toh *et al.* 2005). This indicates that composites containing lignin may have important implications in the future manufacture of products as diverse as medicine bottles and food packaging (Simmons *et al.* 2011). The particle size of raw materials also has an influence on dissolution time when immersed in IL. As a result, smaller wood particles are usually easier to dissolve (Kilpeläinen *et al.* 2007; Sun *et al.* 2009). Nevertheless, extensive ball-milling, which attempts to diminish the size of wood particles, causes degradation and undesired chemical modification of both cellulose and lignin (Lu *et al.* 2003; Guerra *et al.* 2006). Ultrasound pretreatment can increase the contact area between the raw material and chemical reagent, resulting in a reduction of complete dissolution time while exposed to the IL (Mikkola *et al.* 2007; Sun *et al.* 2009; Velmurugan and Muthukumar 2012).

The objective of this study was to prepare a lignocellulosic film that exhibits a better tensile strength, UV absorption, and transparency. Lignocellulose was chosen as raw material. The material was subjected to typical processing methods such as ball milling, 1,4-dioxane extraction, ultrasound, and freeze drying. The ionic liquid 1-butyl-3-methylimidazolium chloride (BmimCl) was chosen as a processing medium. It is known that acidic dioxane-water mixture can extract lignin partially from wood powder (Wu and Argyropoulos 2003), and BmimCl can dissolve lignocelluloses entirely (Abdulkhali *et al.* 2013). This manner of preparation for lignocellulosic films has not yet been reported

to the best of our knowledge. Performance of the films was tested with a scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), thermogravimetric analyzer (TG), ultraviolet-visible spectrophotometer (UV-Vis), and a mechanical testing instrument. Effects of 1,4-dioxane extraction concentration on performance of the films was explored as well.

EXPERIMENTAL

Materials

Eucalyptus citriodora was obtained in Nanning, China. After removing the bark, the air-dried eucalyptus wood bricks (about $5 \times 5 \times 5 \text{ mm}^3$) were ground in a 50 mL jar (1700 times per minute) using steel balls under liquid nitrogen conditions for 20 min. The subsequent wood powder was dried at 40 °C in a vacuum for 12 h and kept inside a ground-glass, stoppered flask. Microcrystalline cellulose was purchased from Sigma-Aldrich (USA), and was dried at 40 °C in a vacuum for 24 h.

The IL, 1-butyl-3-methylimidazolium chloride (BmimCl), was purchased from Lanzhou Institute of Chemical Physics, China. All other chemical reagents (1,4-dioxane and hydrochloric acid) were purchased from Kelong, China. All chemicals were applied without further treatment.

Methods

Pretreatment process

The ball-milled wood was suspended in 1,4-dioxane/water (Table 1) containing 0.2 mol/L HCl with a solid-to-liquid ratio of 1:20 (g/mL) and refluxed at 90 °C for 2 h. The mixture was centrifuged at 8000 rpm for 5 min and washed with the same solvents (two times). This whole operation was repeated once, and the resulting mixture was washed with deionized water until the filtrate was clear. Following this step, about 150 mL of the mixture containing raw materials and deionized water was placed in a common sonifier apparatus (Xinzhi, China) at a frequency of 20 kHz. The sonifier was equipped with a cylindrical titanium alloy probe tip 2 cm in diameter. The sonifier apparatus was worked for 2 seconds and paused for 3 s at 360 watts for 1 h. Temperature of the mixture was controlled using a water bath. Following the ultrasound, lignocellulosic materials were treated by freeze drying at -50 °C for 48 h.

Dissolution process

Each of the lignocellulosic materials obtained after pretreatment and IL (5:95, w/w) was placed in a flask under vacuum conditions. The mixture was heated at 80 °C on a hot plate with magnetic stirring (about 500 rpm) for 30 min, to ensure the raw material was adequately mixed with the IL. Then it was heated at 100 °C under the same magnetic stirring until complete dissolution was observed. The dissolution procedure of the materials was monitored using a polarized light microscope with 400× magnification. The respective dissolution time of the materials is given in Table 1. At the same time, microcrystalline cellulose was dissolved in the IL and subsequently regenerated, to prepare the cellulose film (CF) used in the control group at the time of optical analysis.

Film Preparation

The nearly transparent, dark brown, suspension that resulted was spread onto a Telfon petri dish and placed in a constant temperature and humidity box at 30 °C and 60 ± 5 % RH for 24 h. Afterwards, the gel was repeatedly washed with deionized water to remove the remaining IL until white precipitate was no longer generated when the rinsate was placed dropwise into silver nitrate solution. Once dry, the lignocellulosic and cellulose films were obtained using standard processing methods. This included clamping the gel between two glass plates with binder clips and drying under reduced pressure at 40 °C in a vacuum oven.

Table 1. Treatment Conditions of Pretreatment Methods based on Various 1,4-Dioxane Concentrations

| Sample Code | 1,4-Dioxane Concentration (%) | Material Code | Dissolution Time (min) | Y/N |
|---|-------------------------------|---------------|------------------------|-----|
| L-95 | 95 | F-95 | 150 | N |
| L-90 | 90 | F-90 | 160 | Y |
| L-85 | 85 | F-85 | 180 | Y |
| L-80 | 80 | F-80 | 190 | Y |
| L-0 | 0 | F-0 | 300 | N |
| N: Lignocellulose could not prepare the film due to too fragile | | | | |
| Y: Lignocellulose could prepare the film | | | | |

Characterization

High-magnification images of fragile fractures on cross sections of the films were observed using SEM model Philips XL-20 after being sputtered with gold. FTIR spectra of the obtained films were recorded on a Nicolet 6700 Fourier Transform Infrared spectrometer using a KBr disc containing 1 % of very fine ground samples. One hundred scans were taken for each sample in the range of 4000 to 525 cm⁻¹ at a resolution of 4 cm⁻¹ in the transmission mode. Before data collection, background scanning was performed for correction. The crystallization patterns of the films and raw materials were recorded on an X-ray diffraction instrument (XD-3, Pu Xi, China) with Cu K α radiation (wavelength, $\lambda = 0.154$ nm) at 36 kV and 20 mA. XRD data was collected from $2\theta = 10$ to 40° at a scanning rate of $0.5^\circ \text{ min}^{-1}$. The relative crystallinity of raw materials, as expressed by crystallinity index (C_{rl}), was calculated using the following formula (Segal *et al.* 1959),

$$C_{rl} = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \% \quad (1)$$

where I_{002} is the amplitude of the (002) diffraction peak (typically for $2\theta \approx 22^\circ$) and I_{am} is the intensity at $2\theta = 18^\circ$. Thermogravimetric analysis of the obtained films and their corresponding raw materials (about 5 mg) was performed on a Netzsch Instruments TG 209 with a 100 mL min^{-1} flow of nitrogen. The sample was heated in an aluminium crucible at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ from $35 \text{ }^\circ\text{C}$ to $600 \text{ }^\circ\text{C}$. The mechanical properties of the obtained films ($30 \times 5 \times 0.15 \text{ mm}^3$) were measured on an Instron 5565 mechanical testing instrument in tensile mode at $25 \text{ }^\circ\text{C}$ and $40 \pm 5 \text{ \% RH}$. The gauge

length and drawing speed were preset to 10 mm and 10 mm min⁻¹, respectively. Optical properties of the obtained films were compared to a control cellulose film using a UV-Vis-NIR spectrophotometer (PG Instruments TU-1900). The thickness of the films was approximately 0.3 mm.

RESULTS AND DISCUSSION

Dissolution of Lignocellulose

The dissolution of lignocellulose in the IL, contingent upon various pretreatments, was studied. After heating for about half an hour at 100 °C, under vigorous magnetic stirring speeds, the colors of the solutions were rapidly converted to dark brown and their viscosities distinctively increased. The phenomenon was consistent with previous reports in the literature, making it apparent that the dissolution of lignocellulose occurred (Wang *et al.* 2011; Abdulkhani *et al.* 2013). The dissolution procedure for lignocellulose was monitored with a polarized light microscope. Results showed that the complete dissolution time of lignocellulose decreased as 1,4-dioxane extraction concentrations increased (Table 1). Lignin, which acts as a cementing agent when bonded to hemicelluloses, is the main obstacle in the dissolution of lignocellulose (Wang *et al.* 2011). Because the lignin content of raw materials was reduced by increases in 1,4-dioxane extraction concentration, the complete dissolution time of the entire lignocellulose decreased. However, L-0 and L-95 could not prepare lignocellulosic films in the IL as they proved too fragile. The failure of the L-0 is probably due to an inherently higher lignin content of wood powder. The fragility of the L-95 may have resulted from damage to molecular cellulose chains resulting from raw material extractions by high concentrations of 1,4-dioxane under acidic conditions.

SEM Characterization

SEM images provide information regarding the interfacial bonding of lignocellulosic films. Figure 1 shows SEM microphotographs of the fractured cross-sections of regenerated film (F-90).

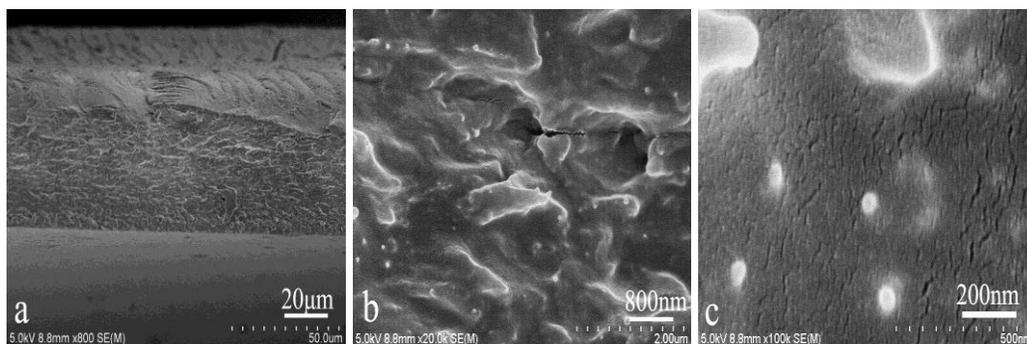


Fig. 1. SEM images of the fractured cross-sections of F-90

From these microphotographs it is clear that F-90 had a rough cross-section (Fig. 1 (a) and (b)), indicating that phase separation occurred there. In addition, nano-fibrils about 50 nanometers in diameter (Fig. 1 (c)) were observed on the fractured cross-

sections of F-90. These nano-fibrils acted as reinforcing agents in the fracturing process of the film.

FTIR Spectra

Infrared spectroscopy is a widely used method for the determination of molecular structure and identification of compounds in biological samples (Xu *et al.* 2013b). The IR spectra of the obtained films are illustrated in Fig. 2. Characteristic peaks of lignin at 1592/1506 cm^{-1} (C=C stretching of aromatic ring in lignin) are observed (Yu *et al.* 2011). F-85 and F-80 show obvious lignin peaks, while F-90 has hardly any lignin peaks. In addition, the absorption peak's intensity for F-80 is distinctly stronger than F-85's, thereby implying that F-80 has a higher content of lignin than F-85. This demonstrates that the lignin content of the films decreased with increasing 1,4-dioxane extraction concentrations for raw materials.

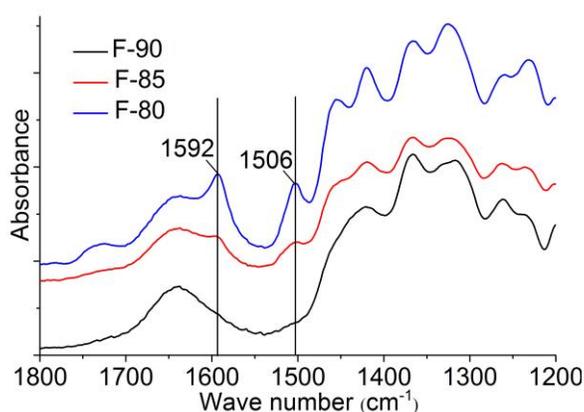


Fig. 2. FTIR spectra of the obtained films

Crystalline Structure

The crystalline structures of raw materials and regenerated films were tested using XRD (Fig. 3). The X-ray diffraction curves of raw materials exhibited typical diffraction peaks around 16°, 22°, and 34°. This corresponds to the (110), (002), and (004) planes of crystals and belong to the crystalline structure of cellulose I (Isogai *et al.* 1989; Oh *et al.* 2005).

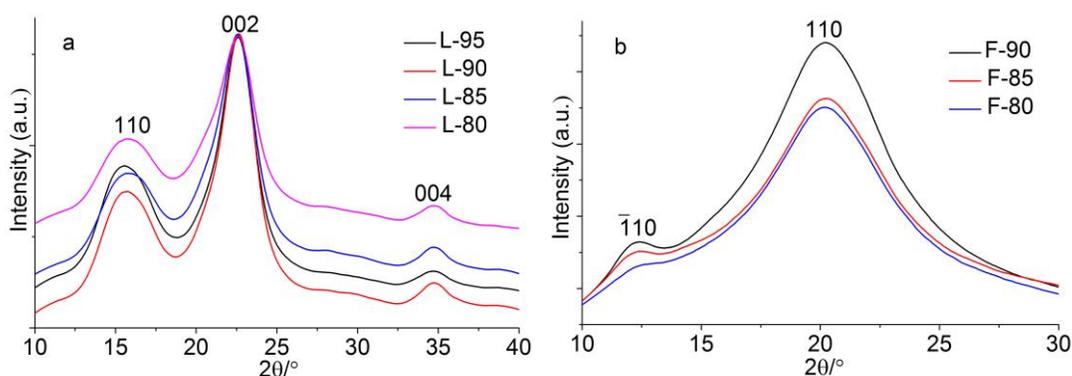


Fig. 3. X-ray diffraction curves of raw materials (a) and the obtained films (b)

After dissolution and regeneration, the crystalline structures of the obtained films had been transformed. The typical diffraction peaks found near 16° , 22° , and 34° disappeared and were replaced by broad crystalline peaks around 12° and 20° . These peak changes are consistent with the presence of (110) and (110) planes of cellulose II crystals (Isogai *et al.* 1989). It was reported that crystalline structures are transformed from cellulose I to cellulose II in cases where lignocellulose is regenerated from IL (Kilpeläinen *et al.* 2007; Zhang *et al.* 2014).

As for curves of raw materials, the value of relative crystallinity of L-80, L-85 and L-90 was 59.7%, 63.4%, and 66.9%, respectively. These values may be attributed to the fact that the relative content of cellulose in raw materials increased along with increasing 1,4-dioxane extraction concentrations. It is worth noting that the relative crystallinity (66.4 %) of L-95 showed no significant change when compared with the L-90 sample. This implies the crystalline region of L-95 may have been damaged. With regards to the curves of regenerated films, the degree of crystallization of F-90 was higher than that of F-85 and F-80 (according to compared half-peak widths). This indicates that an amorphous structure of F-90 was formed with greater difficulty. In addition, the degree of crystallization of F-85 was higher than that of F-80. Compared with the diffraction curves of raw materials, the intensities of the diffraction peaks in the regenerated films were lower. This revealed that IL destroyed both inter and intramolecular hydrogen bonds among lignocellulose, leading to lower crystallinity in regenerated films. The result is in agreement with literature (Wang *et al.* 2009).

Thermal Properties

The thermal properties of films are very important for their utilization in packing material. In thermal analysis of wood components, hemicelluloses have the lowest thermal stability (Bourgois *et al.* 1989). Lignin degradation starts at relatively low temperatures and proceeds over a wide range (Nassar and MacKay 1984). Cellulose presents higher thermal stability than both hemicelluloses and much of the lignin (Sebio-Punal *et al.* 2012). Weight loss for hemicelluloses, cellulose, and lignin usually happens at 220-315 °C, 315-400 °C, and 160-900 °C respectively (Yang *et al.* 2007). Figure 4 shows DTG curves, which are time derivatives of TG curves, corresponding to raw materials and regenerated films.

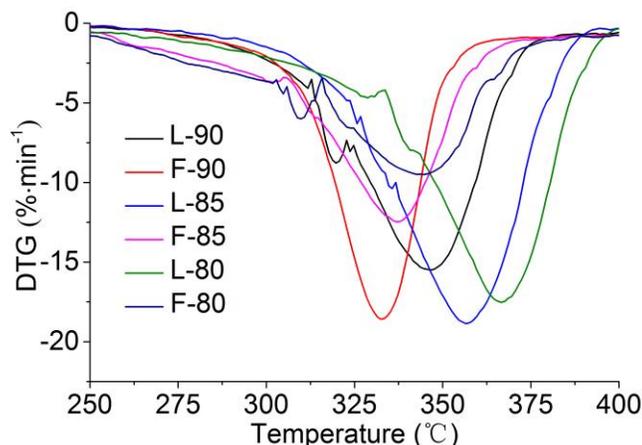


Fig. 4. DTG curves of raw materials and the obtained films

The peak temperatures of main degradation for F-90, F-85, and F-80 were lower than those for W-90, W-85, and W-80, respectively. This is because the degree of crystallization of regenerated films is lower than that of raw materials. In the case of raw materials, decomposition temperature ranges were widened, with final temperatures and peak temperatures increasing as 1,4-dioxane extraction concentrations decreased. As lignin content of raw materials increased with decreasing 1,4-dioxane extraction concentrations, thermal stability was improved, thus leading to differently degraded behaviors. In the case of the films, the trends of weight loss were similar to those of the raw materials. Due to lower lignin content, F-90 experienced a faster degradation rate between 300 and 350 °C.

Mechanical Properties

The mechanical properties of the composite materials, which can provide important information about the internal structure of materials, are strongly influenced by their microstructure (Abdulkhani *et al.* 2013). The representative stress-strain curves of the obtained films are shown in Fig. 5, and summaries of the mechanical properties are listed in Table 2. The F-90 had a higher tensile strength, modulus, and elongation at break than F-85 and F-80. On one hand, this can be attributed to the fact that F-90 has less lignin than F-85 and F-80, as is shown in Fig. 2. However, the higher degree of crystallization for F-90 compared with F-85 and F-80 can also account for this. What is more, it can be seen that the tensile strength of the films increased with increasing 1,4-dioxane extraction concentrations.

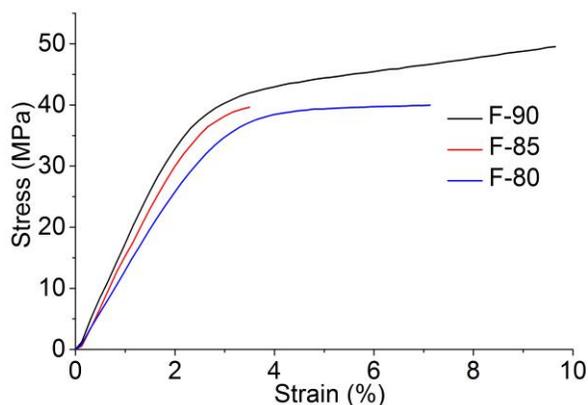


Fig. 5. Tensile properties of the obtained films

In addition, it should be noted that the tensile properties of the films in the present case were much better than those previously reported in literature. For example, the breaking stress for F-90 here was 50 MPa compared to just 5.3 MPa reported by Shibata *et al.* (2013b), and 17.8 MPa by Abdulkhani *et al.* (2013). The reason behind these significant improvements on the mechanical properties of the films may have been expounded by the fact that the lignin of raw materials was partially extracted using 1,4-dioxane. It was reported that the tensile strengths of green composites increase following increases in cellulose concentration (Abdulkhani *et al.* 2013), but the polymers would degrade along with the dissolution time (Wang *et al.* 2011). However, ultrasound pretreatments could increase the contact area between raw materials and chemical reagents (Luo *et al.* 2014) to allow for the quick dissolution of lignocellulose in IL.

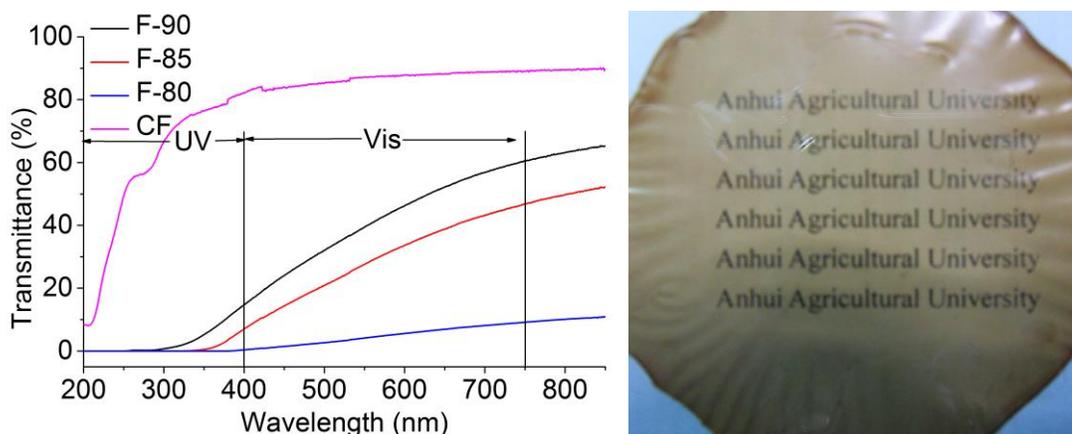
Table 2. Result of Tensile Test of the Obtained Films (n≥5)

| Material | Tensile strength (MPa) | Young's modulus (GPa) | Elongation at break (%) |
|----------|------------------------|-----------------------|-------------------------|
| F-90 | 49.8 ± 3.2 | 1.9 ± 0.1 | 9.8 ± 1.0 |
| F-85 | 40.6 ± 2.4 | 1.7 ± 0.1 | 4.0 ± 1.2 |
| F-80 | 38.6 ± 3.4 | 1.3 ± 0.1 | 7.1 ± 1.3 |

Optical Transparency

High transparency and strong UV absorption is important for films used in the packaging of food and medicine (Simmons *et al.* 2011). Figure 6 shows the optical transmittance of both lignocellulosic films and cellulose film, as well as a photograph of F-90. Compared to cellulose film, lignocellulosic films showed strong absorption in the ultraviolet spectrum due to the presence of lignin. However, cellulose film did have excellent transmitting properties in the visible and near-infrared spectrum on account of their higher transparency (Gindl and Keckes 2005; Nogi *et al.* 2009). The lignocellulosic films exhibited strong absorption in the low wavelength region of the visible spectrum because of influences derived from the films' color. The films appeared brown in color (photograph of F-90) as a result of absorption in the blue to violet region of the visible spectrum (Simmons *et al.* 2011).

In addition, by increasing the 1,4-dioxane extraction concentration, the ultraviolet-visible light transmittance of lignocellulosic film was increased. This is because raw materials contain more lignin and make dissolution more difficult in the ionic liquid (Sun *et al.* 2011). The resulting dimension of dispersed phase was larger than the wavelength of the visible spectrum which caused light generated at a higher refraction and diffused the reflection. The fact that lignocellulosic films clearly outperformed the cellulose films in absorption of ultraviolet radiation and also had better transparencies may have important implications in applications such as medicine bottles and food packaging.

**Fig. 6.** UV-Vis curves of the obtained films (left figure). Right figure shows a photograph of F-90

CONCLUSIONS

1. Lignocellulose, obtained through conventional processing methods such as ball milling, 1,4-dioxane extraction, ultrasound, and freeze drying, can be used to prepare lignocellulosic films through dissolution in the ionic liquid BmimCl and subsequent regeneration using an anti-solvent. In addition, there was obvious phase separation in the films while nano-fibrils acted as reinforcing agents in the fracturing process of the film.
2. The peak temperature of main decomposition and the complete dissolution time of raw materials decreased along with increasing 1,4-dioxane extraction concentrations. However, relative crystallinity of raw materials increased at the beginning and then tended to remain stable.
3. The degree of crystallization, tensile stress, and ultraviolet-visible light transmittance of the films increased with increases in 1,4-dioxane extraction concentrations. Nevertheless, lignin content and peak temperature of main decomposition of the films decreased. Compared to cellulose film, lignocellulosic films showed excellent UV absorption properties due to the presence of lignin.
4. Regenerated film specimens corresponding to condition F-90 (prepared with a 1,4-dioxane concentration of 90%) possessed of better tensile strength, UV absorption, and transparency in comparison to the other obtained films

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