

# The effect of lignin on processing and the properties of lignocellulose material recovered by ionic liquid

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**Abstract.** As a prospective raw material, lignin containing papermaking fibers can be easily recycled, dissolved with proper solvents and reused. However, in order to utilize this material, more eco-friendly green dissolution methods are also required. As a green solvent, ionic liquids (ILs) have been attracted too much interest in processing of lignocellulosic biopolymers, but the practical effect of lignin on this process was not clear. In this due, production of lignocellulosic bio-composite films from bleached (lignin-free) and unbleached (lignin-containing) soda pulps was studied. First, fibers were dissolved in 1-Buthyl 3-Methyl Imidazolium Chloride (BMIMCL) at 85-95 °C. Following fabrication and preparation of the lignocellulosic films, certain mechanical and physical properties of cellulose composite films were analyzed. FESEM and XRD analytical methods were applied to study the product morphology and structure. Microscopic studies showed both fibers were disappeared in the ionic liquid in less than 1 h, although the unbleached fibers took more time for complete dissolution. The results indicated that the films produced from unbleached pulp had less tensile strength and more dynamic contact angle with water droplet than the ones produced from bleached pulp. Moreover, the optical tests revealed that the lignin resulted in less transparency of the films, but increased absorption of UV radiations. This implies that even impure lignocellulose feedstock can have promising features.

## 1. Introduction

The fibers, films and composite materials made of biopolymers have attracted much attention recently, as they help decreasing dependence on oil resources, while they are biocompatible, biodegradable and also due to their high performance [1-2].

Other cellulose, which is the most abundant natural polymer in our environment, is a fibrous, tough, water-insoluble substance with unique crystalline structure that plays a substantial role in blend with different biopolymers to produce various bio-products [1–3]. Cellulose is mainly isolated from lignocellulosic resources, which are abundant renewable organic materials on earth. In order to extract cellulose from lignocellulosic feedstocks, especially lignocellulosic residues, for fabrication of various products, dissolution and further processing of cellulose is necessary [3-4].

However, usually dissolution of cellulose in common solvents is not readily achieved. Some features of this carbohydrate, such as: the strong inter and intera-molecular hydrogen bonding, high degrees of polymerization and crystallinity are some problematic factors in this respect. Although several solvent systems have been applied for preparation of regenerated cellulose materials,



generally, usual solvents are not industrially applicable due to high environmental toxicity, recovery problems or many adverse side reactions [5].

In this respect, as a solvent, ionic liquid can be named as one of the proper candidates. Ionic Liquids (ILs) have recently attracted too much attention as “green solvents” for various chemical processes. Owing to very small vapor pressure, ILs can be easily recovered and reused. They are mostly in the liquid form at relatively low temperatures (below 100 °C), while possessing thermal and chemical stability and non-flammability [6–8].

Pinkert et al. (2009), summarized a list of lignocellulosic materials which had been treated/dissolved with various ILs and different dissolution conditions [9]. Zhang et al. (2017), focused on fabricating methods of cellulose-based materials with ILs and its future trends [10]. In some studies, wood chips of different species were immersed in some of ionic liquids for even very long periods, at relatively high temperatures, but low solubility was observed [8]; while thermo-mechanical pulp (TMP) fibers or micro crystalline cellulose (MCC) particles, were readily dissolved in ionic liquids under similar conditions [4,9]. Therefore, in addition to lignocellulosic material particle size, the presence and structure of lignin may be important factors affecting the application of ILs for processing of lignocellulose materials [11], and moreover, the properties of the products.

## 2. Experimental

### 2.1 Materials

As raw fibrous material, bagasse was provided from Pars Paper mill (Khuzestan, Iran), and used for further delignification and bleaching. 1-Butyl-3-Methyl Imidazolium Chloride (BMIMCl), was purchased from Sigma-Aldrich chemical Co. (Steinheim, Germany). All other reagents were analytical grade.

### 2.2 Pulping and bleaching of lignocellulose material

As a main delignification process, pulping was performed in a rotating digester equipped with electrical power under controlled pressure and temperature. The liquor/bagasse ratio was 8:1 and the alkaline charge 18 % NaOH, based on oven-dry bagasse weight (22.5 g/L). The time-to-temperature, pulping time and final temperature were set 15 min, 45 min and 170 °C, respectively. Following cooking process, the pulp was washed on a sieve of 200 mesh size with tap water. The pulping yield was calculated about 52 %, with final Kappa number of 16.5, according to TAPPI test method T236 om-99, at least with three replications.

Then bleaching treatment was carried out to eliminate residual lignin according to Zobel and McElwee (1958) procedure [12]. Air-dried fiber (2g) was placed in an Erlenmeyer flask, and 160 ml preheated distilled water was added. Afterwards, 20 ml of buffer solution (made from 29 ml acetic acid, 10.5 g sodium hydroxide and 170 ml distilled water) and 20 ml of sodium chlorite (34 g/l) were added respectively. Following stirring the mixture, the flask was placed in a hot-water bath at 70 °C for 2 h. Then the content of the flask was neutralized by sodium sulfite. Finally, the fibers were filtered and washed thoroughly with distilled water. The final Kappa was about 1.5. Also, the degree of polymerization (DP) of cellulose was analyzed according to TAPPI T230 om-04 test method.

### 2.3 Treatment of lignocellulose material in IL and preparation of the film

Lignocellulosic materials were firstly oven dried at  $103 \pm 2$  °C for 24h. Then, they were added calmly into BMIMCL at 85-95 °C, with 2 % concentration. Consequently, the IL-treated lignocellulosic solution was used for fabrication of the films. For this purpose, the solution was stirred on a hot plate at a constant stirring rate (about 300 rpm) under N<sub>2</sub> gas atmosphere, for 1 h. The clear lignocellulosic solution was then casted on a glass plate and kept in the ambient temperature for 24 h. Afterward, the produced gel was washed periodically for 24 h with distilled water to remove the IL. Finally, the films were gently blotted between filter papers and oven-dried at 60 °C for 12 h.

Also, for visualization of the dissolution process, some pictures were taken at 250x magnification using MICROS N-200 optical microscope (Austria), at various stages of dissolution of lignocellulosic materials in the IL.

#### 2.4 Characterization of the film samples

**2.4.1 FESEM.** To study the structure of the produced film samples, a field emission scanning electron microscope (FE-SEM) MIRA3 XMU (TESCAN, Czech Republic) was used, at accelerating voltages of 3 and 15 kV, at various magnifications. In this due, the regenerated film samples were frozen in liquid nitrogen, immediately broken and then the fractured surfaces were coated with a very thin layer of gold, prior to take micrographs.

**2.4.2 X-ray diffraction.** The crystalline structures of the produced cellulosic films were studied using a Philips X'Pert MPD diffractometer (Eindhoven, Netherlands) with Cu K $\alpha$  radiation (40 kV and 40 mA). The diffracted intensities were measured in the range of  $2\theta = 5^\circ$  to  $59^\circ$  with the step size of  $0.04^\circ$  at 0.8 s per step.

**2.4.3 Tensile strength of the films.** To Tensile strength (TS) of the samples were tested on a Universal Testing Machine (Model TVT-300Xp, Perten, Sweden), according to ASTM standard method D 882-02. In this due, the film samples were cut into rectangular pieces (5 cm  $\times$  1 cm) and the thickness was determined at 5 points. The samples were carefully placed between the grips, vertically, with 30 mm of initial grip separation distance and constant elongation rate of 10 mm/min.

**2.4.4 Contact angle measurements.** The effect of lignin on affinity of the film surface toward water droplet was evaluated using a PG-X Goniometer, Switzerland, with a droplet volume of 60  $\mu$ l, at 23  $^\circ$ C and 50 % RH.

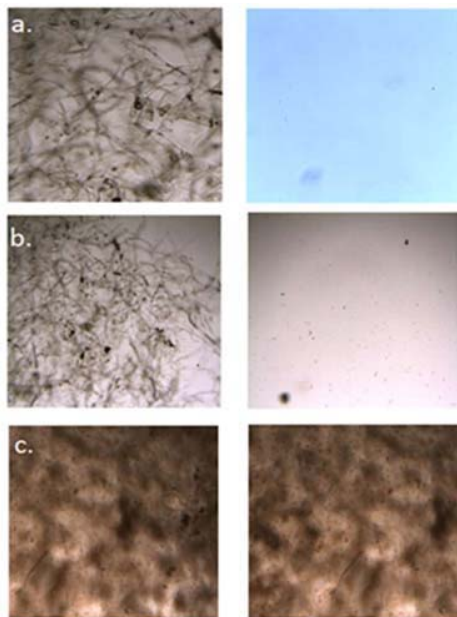
**2.4.5 UV-visible Spectroscopy (UV-vis).** In order to analyze the optical transmittance (Tr) of the films, a UV-vis spectroscope (Lambda 25, PerkinElmer, Fremont, CA, USA) was used at wavelengths between 200 to 800 nm. The samples were cut into the shape of rectangular (9 mm  $\times$  30 mm) samples, directly placed in a spectrophotometer cell and a vacant quartz compartment was used as the reference.

### 3. Results and discussion

#### 3.1 The effect of lignin on the dissolution process

Figure 1, visualizes the effect of lignin on the dissolution process of bagasse fibers in the IL. The figure demonstrates that raw bagasse fibers were not significantly dissolved in the IL, even after some hours (>12 hours) (Figure 1c), while unbleached and bleached bagasse soda pulp (UBSP and BBSP) fibers were readily disappeared in the IL within less than 1 hr. (Figure 1a and 1b). This revealed that by means of pulping and bleaching, in which lignin structure is broken up and kappa number decreases to 16.5 (after pulping) and finally to 1.5 (following harsh bleaching), the dissolution process was highly facilitated [4].

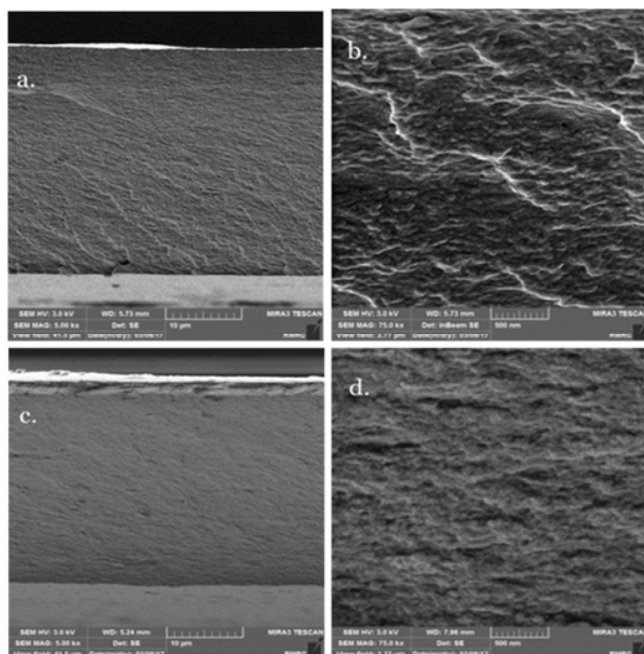
On the other hand, the DP of cellulose was analysed. The results showed the DP of cellulose in UBSP (about 400) was higher than that of BBSP (about 250). This explains that, in addition to diminishing lignin content and structure, pulping and bleaching processes may also facilitate the dissolution process due to shortening of the cellulose chain.



**Figure 1:** The dissolution stages of the lignocellulosic material in the ionic liquid (IL): a. Bleached bagasse soda pulp (BBSP) fibers, b. Unbleached bagasse soda pulp (UBSP) fibers, and c. Raw bagasse fibers (RBF), before and after 1 hr stirring in the IL (magnification: 250X).

### 3.2 FESEM micrographs

Figure 2 shows the FESEM micrographs from the cross sectional view of the produced film samples. The pictures demonstrate a uniform dense micro and nano structure for both BBSP and UBSP films, in which no border line (separation line) is observed, even in the lignin containing films.



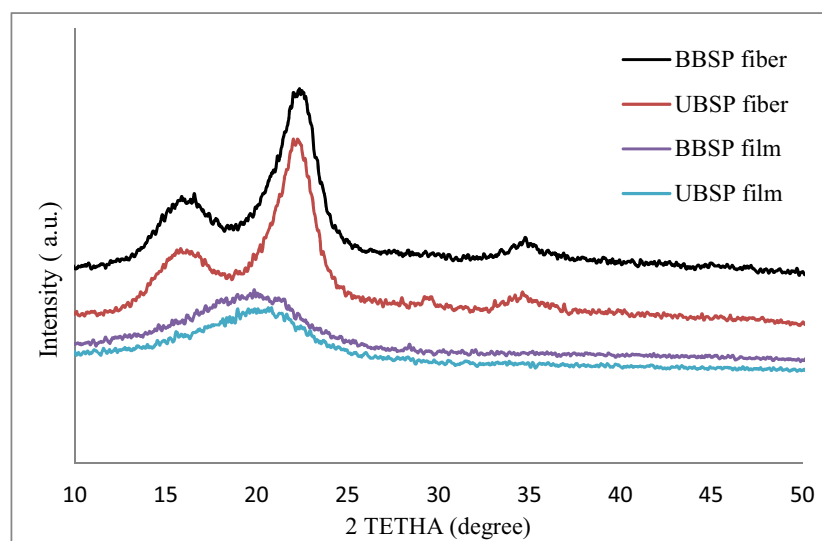
**Figure 2:** FE-SEM images from cross sectional view of the produced films (a., b. BBSP film, and c., d. UBSP film samples, at 5 kX and 75 kX magnification, respectively).

### 3.3 X-ray diffractograms

Figure 3 demonstrates the X-ray diffraction pattern for the initial lignocellulosic materials and the produced films. In the figure, the diffraction patterns for BBSP and UBSP fibers, both display the

clear peaks at  $2\theta$ :  $15.9^\circ$ ,  $22.21^\circ$ , and  $34.67^\circ$ , with the most intensity at  $2\theta$ :  $22.21^\circ$ , which show the normal pattern of cellulose type-I (native cellulose). On the other hand, the diffraction pattern of regenerated films exhibit one broad scattering in a lower angle around  $2\theta$ :  $20^\circ$  with less intensity. This broad peak (more FWHM (full width at half maximum) of the peak), demonstrated the formation of cellulose structure with less crystallite sizes, less ordered domains in the cellulose film, or both [1–3,13]. In addition, less intensity of the main peak indicates that the regenerated films predominantly consist of amorphous regions.

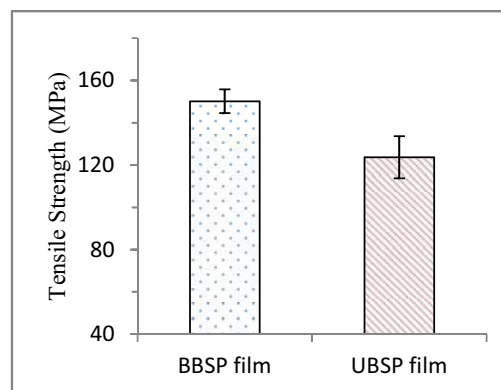
Moreover, the X-ray pattern obtained for BBSP fibers and produced films mostly resembled to that of UBSP counterparts, indicating lignin did not significantly affect the material and product crystalline structure (Figure 3).



**Figure 3:** X-ray diffraction pattern of BBSP, UBSP fibers and their regenerated films.

### 3.4 Mechanical Strength

The tensile strength (TS) of the films was studied as shown in Figure 4. The figure shows that the TS of BBSP film samples ( $150.15 \pm 5.6$  MPa) was higher than that of UBSP ones, although the DP of cellulose was higher in UBSP. This may indicate that lignin, as an impurity in the cellulose matrix, had negative effect on hydrogen bonding during regeneration of cellulosic films [1, 14].



**Figure 4:** Tensile strength (TS) of the films.

### 3.5 Contact angle

Generally, the contact angle (CA) of the material surface with water droplets implies to the hydrophilicity of the samples. Furthermore, the morphology and roughness of the surface may affect the wettability. If the CA is smaller than  $90^\circ$ , the film surface is considered hydrophilic [3].

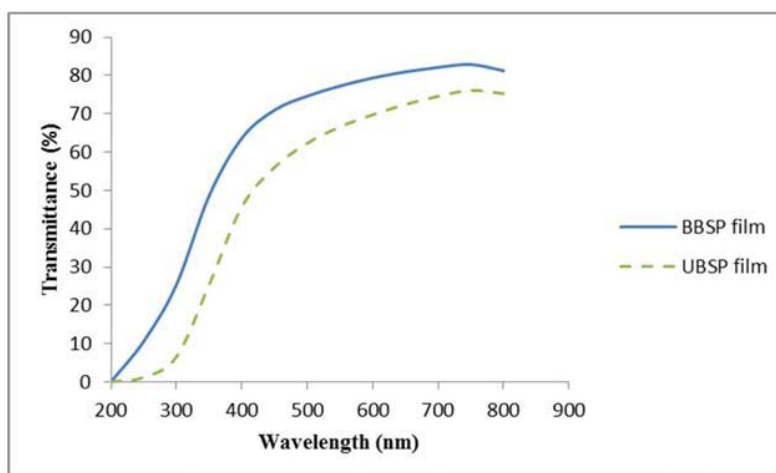
**Table 1.** The contact angles of the films with water droplet

Samples	Contact angle at collision moment ( $^\circ$ )
BBSP film	$69.2 \pm 4.6$
UBSP film	$82 \pm 8.8$

Table 1 presents the data of contact angles of water droplets at the collision moment with the films. BBSP and UBSP films. The results, indicates that BBSP and UBSP films, both had hydrophilic properties, while the increase in CA as a result of UBSP film may be attributed to effect of lignin, as lignin is reported to help the film surface smoothness and also to reduction of available hydroxyl groups on the film surface [15-16].

### 3.6 UV-visible spectra

Figure 5 depicts the transmittance spectra of the films in the range of 200-800 nm. The graph demonstrates the proper transparency (Tr) of the films in the evaluated range, although the data show that lignin caused a minimal reduction of Tr, while, instead, it caused increased UV absorption (for UBSP film in the range of 200-400 nm).



**Figure 5:** Transparency (Tr) of the films.

## 4. Conclusion

1. Microscopic studies showed both BBSP and UBSP fibers were disappeared in the ionic liquid in some minutes, although the lignin containing unbleached type of fibers took more time for complete dissolution, while prior to pulping, the compact structure of lignocellulose structure of raw bagasse fibers did not allow significant dissolution in the IL.
2. The results indicated that the BBSP films had higher tensile strength, although the DP of cellulose was less for it.
3. Presence of the lignin resulted in an increase in the dynamic contact angle of the films with water droplet.



4. The lignin resulted in less transparency of the films, but increased absorption of UV radiations.
5. The above mentioned results showed that even impure lignocellulose feedstock, specially following pulping process can have promising features.

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