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Comparison of physical properties of regenerated cellulose films fabricated with different cellulose feedstocks in ionic liquid

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ABSTRACT

With the serious "white pollution" resulted from the non-biodegradable plastic films, considerable attention has been directed toward the development of renewable and biodegradable cellulose-based film materials as substitutes of petroleum-derived materials. In this study, environmentally friendly cellulose films were successfully prepared using different celluloses (pine, cotton, bamboo, MCC) as raw materials and ionic liquid 1-ethyl-3-methylimidazolium acetate as a solvent. The SEM and AFM indicated that all cellulose films displayed a homogeneous and smooth surface. In addition, the FT-IR and XRD analysis showed the transition from cellulose I to II was occurred after the dissolution and regeneration process. Furthermore, the cellulose films prepared by cotton linters and pine possessed the most excellent thermal stability and mechanical properties, which were suggested by the highest onset temperature (285 °C) and tensile stress (120 MPa), respectively. Their excellent properties of regenerated cellulose films are promising for applications in food packaging and medical materials.

1. Introduction

Nowadays, the public have more and more concerns with the environmental problems such as "white pollution" and the decrease in natural resources. However, the demand for petroleum based materials is increasing day by day (Satgé, Granet, Verneuil, Branland, & Krausz, 2004; Mahmoudian, Wahit, Ismail, & Yussuf, 2012). Therefore, more efforts on the exploitation of new materials from biomass resources as alternative for petroleum based materials have been made in recent years (Liu, Pang, Zhang, Wu, & Sun, 2013).

Cellulose is the most abundant natural polymer and renewable resource on the earth (Jia, Li, Ma, & Sun, 2012). As the prime source of biofuels and value-added product, cellulose is considered as a promising alternative to non-renewable natural resources for the sustainable supply of fuel and chemicals in the future due to its significant industrial applications and unique physicochemical properties like biocompatibility and biodegradability (Klemm, Heublein, Fink, & Bohn, 2005; Jia, Li, Ma, Sun, & Zhu, 2011; Wan, Wu, Yu, & Wen, 2006). Recently, extensive research is being carried out worldwide to identify and study chemical or biological transformation pathways to convert cellulose into biofuels, feedstock chemicals and bio-based materials (Turner, Spear, Holbrey, & Rogers, 2004). Until now, several successful studies about cellulose fibers, beads, films, and cellulose derivatives have been reported (Luo & Zhang, 2009; Zhang et al., 2009).

Nevertheless, application of cellulose is limited due to the rather complex fashion of cellulose where an extended intra- and intermolecular network of hydrogen bonds is indicated as the basis of cohesion between cellulose molecules. It is believed that intramolecular hydrogen bonds provide chain stiffness, while, on the other hand, intermolecular hydrogen bonds allow the linear polymer molecules to assemble in sheet-like structures (Medronho & Lindman, 2014). Therefore, such a stable structure of cellulose resulted in the insolubility of the biopolymer in almost all common organic and inorganic liquids. Various more or less exotic solvents were developed to overcome this problem and to make cellulose accessible for tailored modification (Liebert, Heinze, & Edgar, 2010). Over the past decades, several cellulose solvent systems were reported for dissolving cellulose, such as *N*-methylmorpholine-*N*-oxide (NMMO) (Swatloski, Spear, & Holbrey, 2002), ammonium fluorides/dimethylsulfoxide (DMSO) (Köhler & Heinze, 2007), and NaOH/urea aqueous solution (Tang, Chang, & Zhang, 2011). Although several of these as solvents for fabricating of cellulose films, fibers, beads and few as homogeneous reaction media for the preparation of cellulose derivatives had been

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successfully investigated. These solvents possess several undesired properties, like uncontrollable side reactions, limited dissolving capability, high toxicity and thermal instability. Therefore, there is still a strong demand for new "green" cellulose solvents for making cellulose-based materials under homogeneous conditions (Gericke, Schlufter, Liebert, Heinze, & Budtova, 2009; Pang, Liu, Zhang, Wu, & Sun, 2013).

Recently, room temperature ionic liquids (ILs) as new "green" solvents has been widespread concerned in the public due to their various advantages such as eco-friendly, good chemical and thermal stability, lower hydrophobicity, low flammability, low melting point and ease of recycling (Peng, Ren, & Sun, 2010). Furthermore, it had also been reported that ionic liquids exhibited outstanding dissolving capability for cellulose (Liu et al., 2013). The application of cellulose was fueled by the discovery of ILs as proper cellulose solvents. It had been proved that the unique properties of ILs can be permitted transform of cellulose into a broad variety of new, eco-friendly materials for numerous commercial purposes such as bio-plastics, and also into high value products (Liebert et al., 2010). The fabrication of chitin/cellulose composite films using ionic liquids of 1-butyl-3-methylimidazolium chloride (BmimCl) and 1-allyl-3-methylimidazolium bromide (AmimBr) as solvents had been investigated by Takegawa, Murakami, Kaneko, and Kadokawa (2010). The results showed that BmimCl was good solvent for the regeneration of microcrystalline cellulose, the obtained cellulose films were transparent and flexible. Moreover, with the increase in the proportion of chitin and cellulose, the mechanical properties of the films were significantly improved. In addition, the microcrystalline cellulose (PMCC)/nanocrystalline cellulose (NCC) composite films with a significant enhancement in thermal stability and mechanical properties was also studied by Ma, Zhou, Li, and Ou (2011). Furthermore, different film materials possessed various properties had been successfully prepared and investigated in previous reports(Peng, Ren, Zhong, & Sun 2011; Zhong, Peng, Yang, Cao, & Sun, 2013; Hameed, Guo, Tay, & Kazarian, 2011).

At present, extensive work has been done to study the commercial potential of celluloses-based materials using different ionic liquids. However, the exploitation of cellulose-based materials using different kinds of biomass as raw materials in ionic liquid has not been reported yet. In this study, in order to compare the structure and properties of cellulose films prepared from different kinds of cellulose, four kinds of cellulose including pine, cotton, bamboo cellulose and microcrystalline cellulose (MCC) were chosen as raw materials to elaborate eco-friendly cellulose films with ionic liquid 1-ethyl-3-methylimidazolium acetate (EmimAc) as solvent. In order to evaluate the desirability of their applications in the packaging and functional materials fields, the morphology, surface and mechanical properties of different kinds of cellulose regenerated films were comparatively characterized by SEM and AFM, contact angle measurement and tensile stress. This work presents a facile approach to environmentally friendly prepare high-strength cellulose films with different kinds of cellulose as raw materials.

2. Materials and methods

2.1. Materials

In order to compare the film properties obtained from different cellulose raw materials, four kinds of cellulose raw materials including cotton linter, microcrystalline cellulose and raw cellulose materials from pine and bamboo were used in this study. Cotton linters were kindly supplied by Silver Hawk Fiber Corporation (Shandong province, China). Microcrystalline cellulose (MCC) was purchased from Sinopharm Chemical Reagent Corporation Limited. The raw cellulose materials from pine and bamboo were obtained by delignification followed by removal of hemicelluloses, and the procedures were consistent with the literature described by Liu, Sun, Zhang, and Ren (2007). Ionic liquid, 1-ethyl-3-methylimidazolium acetate (EmimAc), with purity ≥95%, was purchased from Lanzhou Institute of Chemical Physics. All chemicals were analytical grade reagents and used as received without further purification.

2.2. Preparation of regenerated cellulose films

Cellulose regenerated films were prepared according to the following procedure. The mixtures (around 5 wt.%) were prepared by dissolving the different kinds of cellulose samples (5 g) in EmimAc (100 g) under magnetic stirring at 80 °C for 0.5 h. The mixtures were then degassed by being kept standing at 80 °C for 1 h. After that, the cellulose films were fabricated by casting the homogeneous mixture on glass plate. The obtained cellulose films were soaked in deionized water and washed thoroughly to remove ionic liquid. Finally, the cellulose films were dried in atmosphere for 48 h and stored in moisture controlled desiccators.

2.3. Characterization

The degrees polymerization (DP) of all the cellulose raw materials and regenerated cellulose films were measured by TAPPI test method using copper ethylenediamine (CED) as a solvent and a capillary viscometer to give an indication of the average degree of polymerization of the cellulose materials. The viscosities determined as centipoises (cP) were converted to degree of polymerization (DP) based on the following formula:

$$DP^{0.905} = 0.75 \times [954 \times \log(X) - 325],$$

where X = TAPPI viscosity in cP.

Film thickness was studied with a micrometer (Lorentzen & Wettre, precision 1 μm). The thickness of six different locations on film was detected, and the average values were used in the calculation of the mechanical test.

The morphology of cellulose films were studied by scanning electron microscopy analysis (SEM). The regenerated cellulose film samples were coated with gold palladium in a sputter coater (E-1010, Hitachi, Japan), and then were observed with a scanning electron microscope (S-3400N, Hitachi, Japan) at acceleration voltages of 10 kV.

Atomic force microscopy (AFM) (SPM-9600, Shimadzu) was used to study the nano-morphology of film surface. Small pieces of films were glued onto metal disks and attached to a magnetic sample holder located on the top of the scanner tube. Phase images were recorded under ambient air conditions. All of the images were recorded in contact mode in air using silicon cantilevers.

Infrared spectra of cellulose film samples were recorded with a Fourier transform IR spectrometer (FT-IR TENSOR27, Germany) in ATR mode. The scan range was 400–4000 cm^{-1}, and the resolution rate was 2 cm^{-1}.

The surface free energies of the cellulose films were measured by the contact angles analysis (Krüss DSA100 Germany). The measurements were performed at room temperature by the sessile drop method using a goniometer equipped with a high-speed camera (OCA 20, Data physics Ltd., Germany).

Crystallinity of the regenerated cellulose film samples was determined by X-ray diffraction method using XRD-6000 instrument (Shimidzu, Japan). The X-ray diffractograms were recorded in reflection mode in the angular range of 5–40° (2θ) with a scanning speed of 5°/min.

Thermal analysis was determined by using thermogravimetric analysis (TGA) and differential thermal analysis (DTA) on a simultaneous thermal analyzer (SDT Q600 TGA/DSC, TA Instrument). The

samples weighing around 10 mg were detected from room temperature to 600 °C under nitrogen flow with a heating rate 10 °C/min.

The tensile strength of the regenerated cellulose films were measured by using a tensile testing machine (Zwick Universal testing machine Z005) fitted with a 200 N load cell with the crosshead speed of 0.5 mm/min, The samples were cut in the rectangular specimens with a width of 20 mm and length of 60 mm, and the initial distance between the grips was 20 mm. Eight specimens of each formulation were tested, and the average values were calculated. The measurements were performed under room temperature.

3. Results and discussion

3.1. Morphology of cellulose films

In order to determine the morphology of the cellulose films, the samples were analyzed by scanning electron microscopy (SEM) and atomic force microscopy (AFM), and the SEM and AFM micrographs of the regenerated films prepared with cellulose raw materials from pine, cotton, bamboo cellulose and MCC (sample a, b, c, d) are shown in Figs. 1 and 2. The SEM images indicated that all of the cellulose films displayed a homogeneous and smooth surface, which indicated the complete dissolution of different kinds of cellulose in ionic liquids. In addition, small nodules and contours were observed in all the cellulose film samples in the SEM images, which was resulted from strong hydrogen bonds of cellulose (Zhong et al., 2013). In comparison, the cellulose film prepared by cotton linters (sample b) displayed a more homogeneous and smoother morphology as compared with other samples, which served as good evidence for complete dissolution of cotton linters in ionic liquids. The homogeneous and smoother morphology indicated a higher molecular orientation degree of cotton film obtained by the regenerated process.

In addition, the higher resolution AFM images in Fig. 2 were also taken to determine the structure roughness of cellulose films. The micrographs disclosed that all the films displayed a typical granular morphology. Furthermore, it was observed that the roughness of the cellulose film prepared by cotton linter (sample b) was significantly lower than other cellulose films, which was consistent with the results from SEM. This probably due to the extremely high cellulose content in cotton linter. It has been reported that, the cellulose content of cotton is 88–96%, however, the initial cellulose contents in pine and bamboo are around 50% (Yang, Qiu, Ren, & Li, 2011). Although the cellulose materials from pine and bamboo were obtained by delignification followed by removal of hemicelluloses, they should contain some residual lignin and hemicelluloses, which resulted in higher roughness surface structure of pine and bamboo cellulose film samples.

3.2. Crystallinity of cellulose films

The crystallinity of different kinds of cellulose and the corresponding cellulose film samples were determined by X-ray analysis. The XRD patterns of different cellulose from pine, cotton, bamboo, MCC and the corresponding cellulose films (images A, B, C, D) are shown in Fig. 3. The XRD patterns illustrated the diffraction patterns of the samples, whereas the corresponding calculated crystallinity and DP values are listed in Table 1. The X-ray patterns of the different cellulose (solid line) showed typical diffraction cellulose I angles (2θ) around at 14.8°, 16.8° and 22.6°, which were assigned to crystallographic plane reflections planes of (−1 1 0), (1 1 0) and (2 0 0), respectively (Isogai, Usuda, Kato, Uryu, & Atalla, 1989). The diffractograms revealed a relatively ordered structure with narrow peak at 22.6° (2 0 0) and a diffuse peak between 14.8 and 16.8° (−1 1 0 and 1 1 0). The sharper diffraction peak at 22.6°

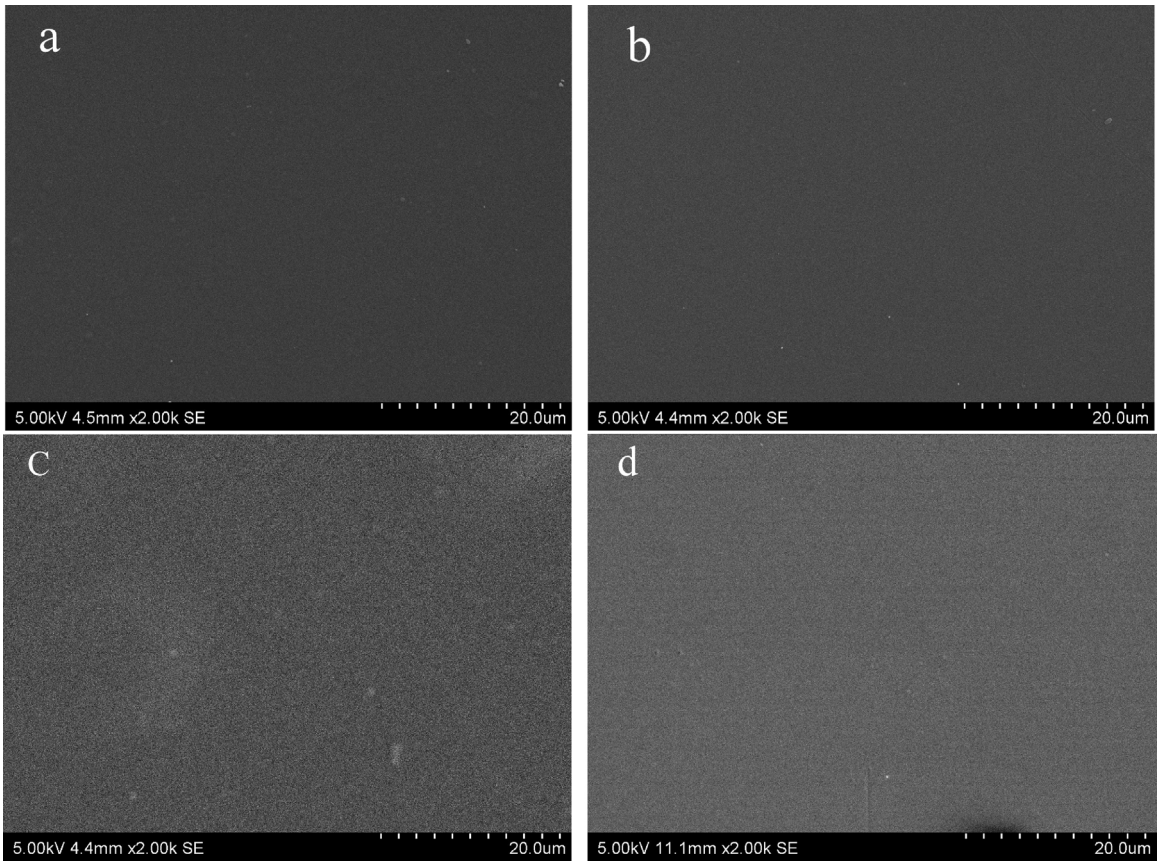

Fig. 1. SEM micrographs of cellulose films: (a) pine; (b) cotton; (c) bamboo; (d) MCC.

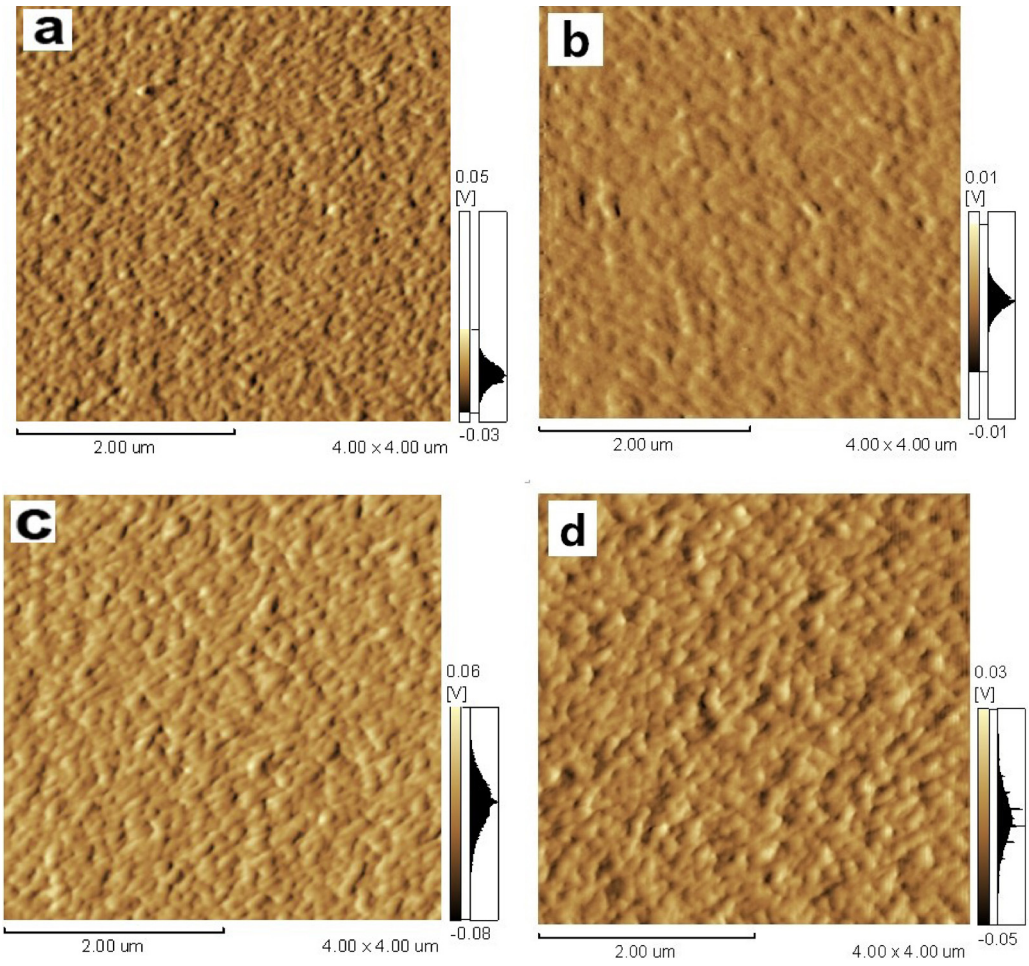

Fig. 2. AFM photos of cellulose films: (a) pine; (b) cotton; (c) bamboo; (d) MCC.

(2 0 0) indicated region of higher crystallinity as shown in Table 1 (Gupta, Uniyal, & Naithani, 2013). However, the patterns of the cellulose films (dash line in images A, B, C, D) showed a broad peak at approximately $2\theta = 12.5^\circ$, 20.1° with Miller indices of (−1 1 0), (1 1 0) (direction *c* of the unit cell is along the chain axis of the polymer), which characterized for the crystalline form of cellulose II (Han & Yan, 2010; Geng et al., 2014; Sun et al., 2010). These results indicated a crystal transition from cellulose I to cellulose II during the dissolution and regeneration process, the transition of the crystalline form probably caused by the easy association or aggregation of cellulose chains in ionic liquid solution or during the film formation (Peng et al., 2011). Furthermore, it was noted that the degree of crystallinity and DP of the cellulose films were greatly decreased compared to the corresponding cellulose materials (Table 1). This was probably due to the reason that the original crystalline structure and the β-glycosidic linkages between the sugar units had been partially destroyed or seriously modified during the dissolving and processing processes in ionic liquids, which resulted in the reduction of the crystallinity and DP values of the cellulose films (Feng & Chen, 2008). In addition, the inter- and intra-molecular hydrogen bonds of cellulose aggregated or reordered in the casting solution, resulting in crystalline structure of cellulose II. It has been demonstrated that the hydrogen bonds in cellulose II were also found between sheets, which meant that they formed a three-dimensional (3D) network (Langan, Nishiyama, & Chanzy, 1999). This meant that the regenerated cellulose films obtained a more stable structure due to the reorganization and rearrangement of hydrogen bonds between cellulose.

3.3. Hydrophilic analysis

Contact angle measurements with water were performed to provide information regarding the surface hydrophilicity of the cellulose films and the results are provided in Table 1. It can be seen that the contact angles of the film samples prepared from pine, cotton, bamboo cellulose and MCC (sample a, b, c, d) were 76.78°, 36.81°, 58.34° and 72.80°, respectively. In the hydrophilic analysis, the higher contact angle means a higher hydrophobic

Table 1
The DP values, crystallinity and contact angle of cellulose materials and cellulose films.

Samples	Cellulose materials		Cellulose films		
	DP	Crystallinity (%)	DP	Crystallinity (%)	Contact angle (θ)
Pine	819	49.02	559	39.58	76.78°
Cotton	831	54.01	570	34.04	36.81°
Bamboo	625	46.69	460	32.93	58.34°
MCC	240	51.36	145	40.58	72.80°

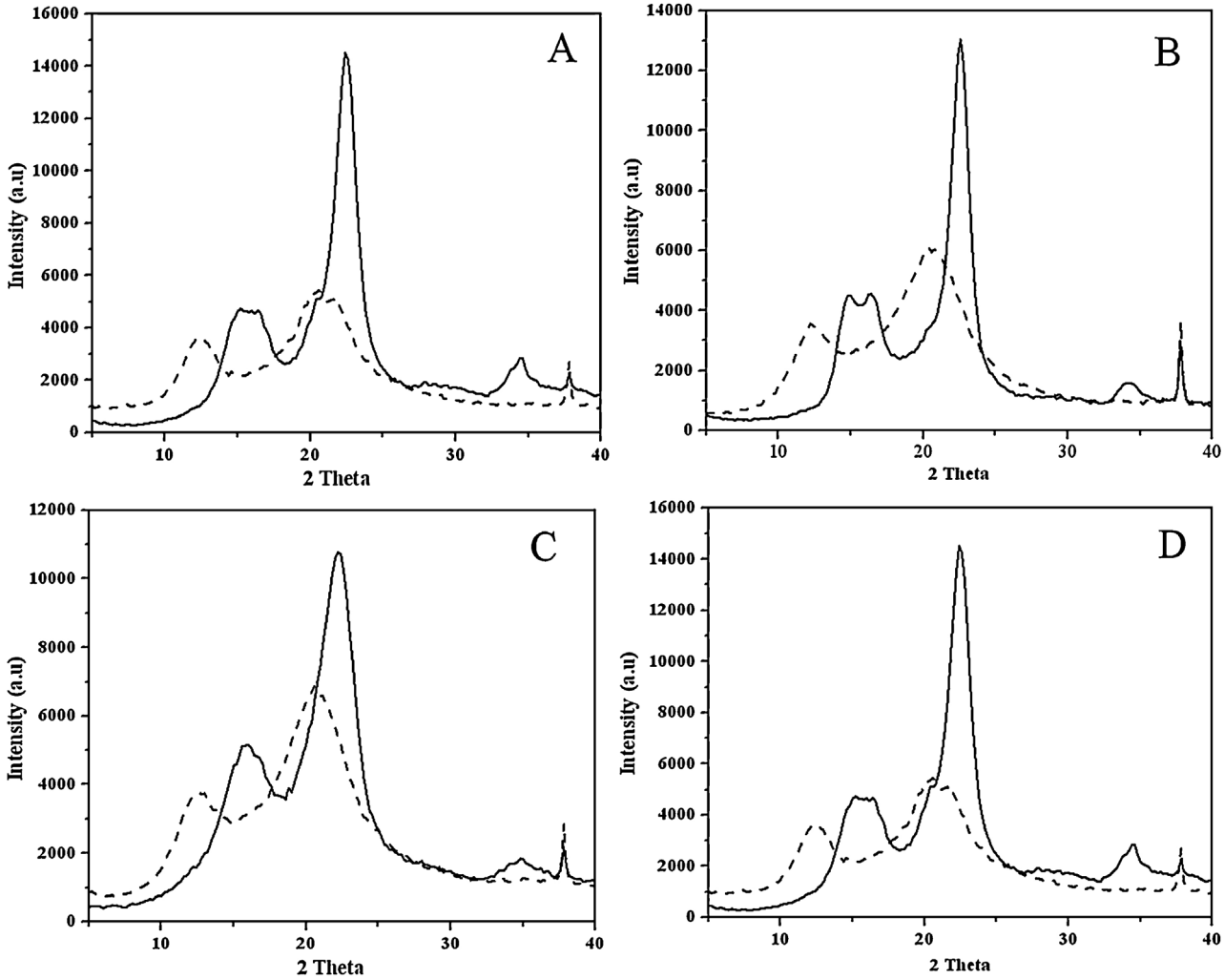

Fig. 3. XRD images of films: (a) pine; (b) cotton; (c) bamboo; (d) MCC (solid line: cellulose, dash line: cellulose film).

of films ample. As shown in this result, the pine cellulose film sample have an high contact angle at 76.78°, which indicated that the pine cellulose film has a higher hydrophobicity than the other samples. On the contrary, the cotton cellulose film has the lowest hydrophobicity. This behavior was probably due to the crystallinity degree as well as the inter- and intra-molecular hydrogen bonding within the different kinds of cellulose which lowered the interfacial free energy, thereby preventing water to penetrate into the films, thus increasing the contact angle (Hameed et al., 2011; Eriksson, Notley, & Wågberg, 2007). This result was broadly consistent with the results from crystallinity values in Table 1.

3.4. FT-IR spectra analysis

FT-IR spectroscopy is a technique for investigating the intermolecular and intramolecular interactions in polymers (Wan et al., 2006). Fig. 4 presents FT-IR spectra of cellulose films prepared from pine, cotton, bamboo cellulose and MCC (Samples a, b, c and d). As shown in Fig. 4, all the FT-IR spectra of films exhibited the similar characteristic absorptions at 3356, 2893, 1578, 1419, 1369, 1315, 1261, 1200, 1157, 1022 and 895 cm^{-1}, which are associated with cellulose. The band at 3356 cm^{-1} is attributed to the O—H stretching vibration. The bands at 2896 cm^{-1} is assigned to CH-stretching and the peak at 1578 cm^{-1} is probably due to the bending mode of adsorbed water. A shoulder at 1157 cm^{-1} could be attributed to C—O—C pyranose ring skeletal vibrations in cellulose. The strong band at 1023 cm^{-1} is assigned to the characteristic C—O—C stretching (Jia et al., 2011). A small sharp band at 895 cm^{-1} is assigned to β-glucosidic linkages between the sugars units, indicating that the cellulose forming the backbone of the macromolecule are linked by β-form bonds (Gupta, Madan, & Bansal, 1987; Peng et al., 2011). The 1430, 1162, 1111 and 893 cm^{-1} absorption bands could be used to study the type of crystalline cell and the crystallinity changes because the crystalline cellulose I spectrum differed clearly in these bands from cellulose II and amorphous cellulose. As seen in Fig. 4, the characteristic bands of cellulose I at 1430, 1162 and 1111 cm^{-1} had not been found for all the cellulose film samples, which indicated a predominance of crystalline cellulose II. Furthermore, the band at 1420 cm^{-1} for film samples was a characteristic absorption of cellulose II and amorphous cellulose (Carrillo, Colom, Suňol, & Saurin, 2004). The band at 1315, 1200 and 1161 cm^{-1} are assigned to CH_2 wagging, OH in plane bending and C—O—C asymmetric stretching in cellulose II, respectively. This spectral behavior indicated an overwhelming presence of crystalline cellulose II. Therefore, it could be demonstrated that the cellulose film samples were mainly composed of crystalline cellulose II and amorphous cellulose with a negligible content of crystalline cellulose I.

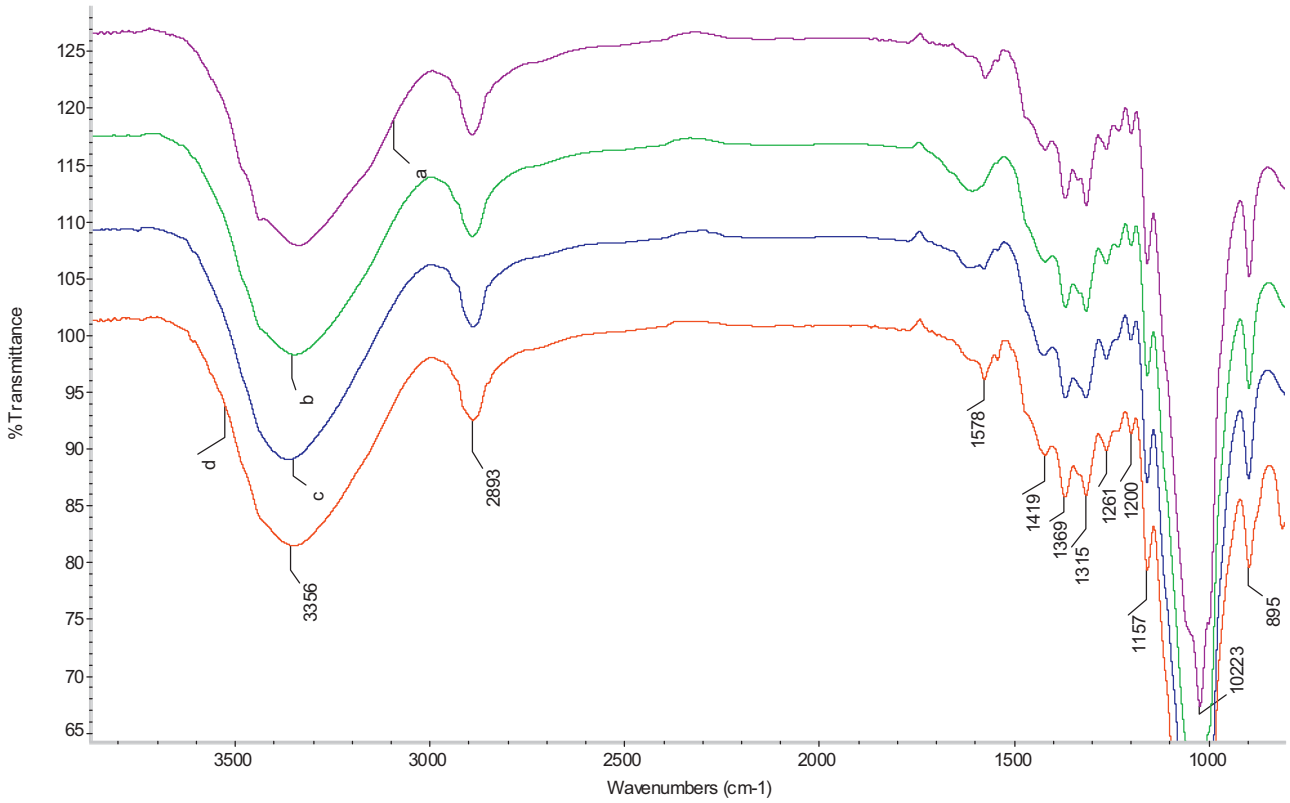

Fig. 4. FT-IR images of different films: (a) pine; (b) cotton; (c) bamboo; (d) MCC.

3.5. Thermal analysis

The TGA and DTA thermograms of cellulose films prepared from pine, cotton, bamboo cellulose and MCC (Samples a, b, c and d) are shown in Figs. 5 and 6. In the thermal study by TGA analysis (Fig. 5), the processes of water desorption and polymer degradation were observed. At low temperatures at approximately 50–100 °C, a slow pyrolysis process was detected. This process is attributed to the water desorption and caused by the hydrophilic behavior of cellulosic polymers. Moreover, the fast decomposition stages appear between 200 and 380 °C. In comparison, we could state that cellulose film sample prepared by cotton linters (sample b) possessed the highest thermal stability because the onset temperature of the decomposition process from cotton cellulose film was higher than that from the other films prepared by pine, bamboo and MCC cellulose. It has been shown that many of the physical and chemical properties of the cellulose are determined by its DP and the degree of crystallinity. The cellulose with higher DP possessed the higher resistance to thermal decomposition (Carrillo et al., 2004). Obviously, the thermal stability of regenerated cellulose films increased with the increase of the DP values, which meant that the thermal stability was mainly determined by DP values (Table 1). As shown from the DTA curves in Fig. 6, the pyrolysis of cellulose film sample prepared by MCC showed multiple well-resolved degradation peaks, which indicated that the MCC contained some relatively low molecular weight cellulose.

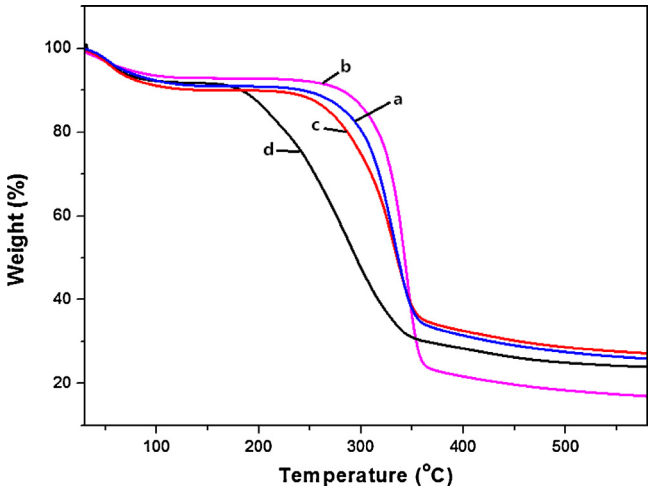

Fig. 5. TGA curves films: (a) pine; (b) cotton; (c) bamboo; (d) MCC.

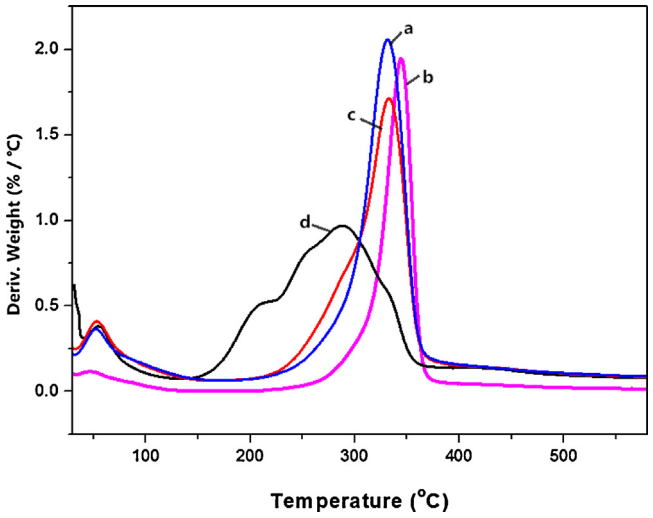

Fig. 6. DTA curves of films: (a) pine; (b) cotton; (c) bamboo; (d) MCC.

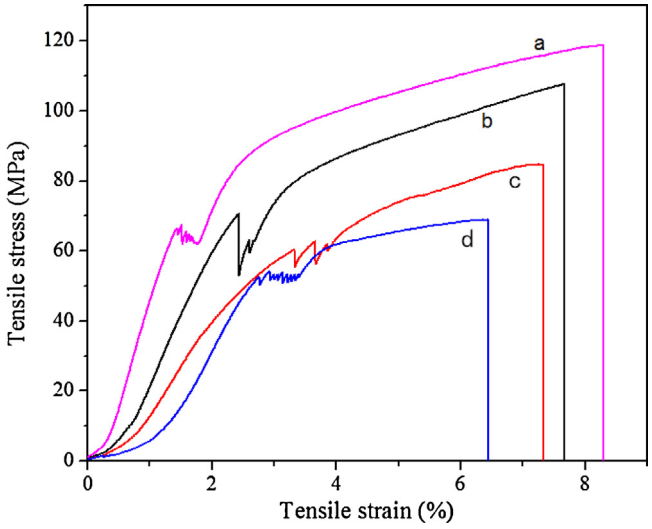

Fig. 7. Stress–strain curves of films: (a) pine; (b) cotton; (c) bamboo; (d) MCC.

3.6. Mechanical properties

Stress–strain curves for cellulose films prepared by pine, cotton, bamboo cellulose and MCC (samples a, b, c and d) at ambient temperature are shown in Fig. 7. As shown in Fig. 7, all the samples showed thermoplastic like behavior with stress increasing rapidly at small strains and more slowly after a yield point. It was noted that the pine cellulose film sample exhibited the most excellent tensile strength, which was suggested by the highest tensile stress (120 MPa). In comparison, the cellulose film made from MCC (curve d) was relatively weak, which was indicated by the maximum stress of 69 MPa. Cellulose is natural polymer, and its mechanical property was possibly determined by the synergistic effect of crystallinity and DP value. It has been illustrated that the mechanical strength of cellulose derivatives increases slightly with the increase of DP when it reaches the turning point (DP = 450) (Yang et al., 2011). This meant that the crystallinity values played a dominant role on the determination of cellulose film strength when the DP value of cellulose derivatives was more than 450. In addition, the biomolecular structure and functions are not only determined by H-bonding interactions but also stacking interactions between intrasheet and intersheet of cellulose layers, which are typically governed by van der Waals interactions, π–π interactions, and hydrophobic forces (Müller-Dethlefs & Hobza, 2000). Therefore, the highest tensile stress of cellulose film prepared from pine cellulose was mainly ascribed to higher DP and crystallinity values combined with hydrophobic forces.

4. Conclusion

In this paper, the regenerated cellulose films were successfully prepared using different cellulose (pine, cotton, bamboo, MCC) as raw materials and ionic liquid 1-ethyl-3-methylimidazolium acetate (EmimAc) as solvent. The FT-IR spectra and XRD showed the transition from cellulose I to II had occurred after the dissolution and regeneration process. Morphology analysis, by SEM and AFM, indicates that the cellulose film prepared by cotton cellulose displayed a more homogeneous and smoother morphology as compared with other samples, which served as good evidence for complete dissolution of cotton linters in ionic liquids. Furthermore, the thermal analysis showed that cotton cellulose film sample presented the highest thermal stability. In addition, the cellulose films prepared by pine cellulose displayed a better film formation and significant high tensile strength. In this study, cellulose films possessed notable properties were prepared from pine and cotton linter cellulose materials, which open a way for the utilization of these materials in further industrial application.

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