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Choline chloride/urea as an effective plasticizer for production of cellulose films

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ABSTRACT

Recently, choline chloride/urea (ChCl/urea), a typical deep eutectic solvent (DES), has been found to possess various applications in organic synthesis, electrochemistry, and nanomaterial preparation. Herein we reported the first attempt to plasticize regenerated cellulose film (RCF) using ChCl/urea as an effective plasticizer. Meanwhile, RCFs plasticized with glycerol and sorbitol were also prepared for comparison. The plasticized RCFs were investigated by Fourier transform infrared (FT-IR) spectroscopy, wide-angle X-ray diffraction (XRD), atomic force microscopy (AFM), and mechanical testing. Transparent and soft RCFs could be successfully prepared in the presence of ChCl/urea, and high elongation at break (34.88%) suggested a significant plasticizing efficiency. No new crystal and phase separation occurred to ChCl/urea plasticized RCFs. The thermal stability of ChCl/urea plasticized RCF was lowered. These results indicated that ChCl/urea was an effective plasticizer for producing cellulose films.

1. Introduction

In recent years, DESs, which have similar properties to ionic liquids (ILs) but are much cheaper and more "green" than ILs, have attracted considerable attention (Abbott, Boothby, Capper, Davies, & Rasheed, 2004). A DES is generally composed of two or three cheap and safe components that are capable of self-association through hydrogen bond interactions, forming a eutectic mixture with a melting point lower than that of each individual component. DESs are generally formed by mixing a quaternary ammonium or phosphonium salt with a hydrogen bond donor agent, for instances, acids, alcohols, amines or carbohydrates (Abbott, Capper, Davies, Rasheed, & Tambyrajah, 2003; Choi et al., 2011; Kareem, Mjalli, Hashim, & AlNashef, 2010). Most of DESs have the solvent characteristics similar to ILs, such as low volatility, wide liquid range, water-compatibility, non-flammability, nontoxicity, biocompatibility, and biodegradability. Furthermore, they show the ability to customize their physical properties by choosing the right constituents in terms of chemical nature, relative composition or water content (Choi et al., 2011).

ChCl/urea is the most widely investigated DES. The chemical structures of ChCl and urea were shown in Scheme 1. Abbott et al. (Abbott et al., 2003) first found that the mixture of ChCl and urea showed a deep eutectic effect at a molar ratio of ChCl to urea of 1:2, and its melting point (12 °C) is much lower than that of individual component. ChCl/urea has exhibited excellent performances in various areas such as catalysis (Ilgen et al., 2009; Singh, Lobo, & Shankarling, 2010; Sonawane, Phadtare, Borse, Jagtap, & Shankarling, 2010), organic synthesis (Azizi, Batebi, Bagherpour, & Ghafuri, 2012), electrochemistry (Steichen, Thomassey, Siebentritt, & Dale, 2011; Yang, Guo, Birbilis, Wu, & Ding, 2011; Yue, Jia, Yao, Sun, & Jing, 2012), nanoparticle preparation (Chirea et al., 2011; Dong, Hsu, Wong, & Lu, 2010; Liao, Jiang, Zhou, Chen, & Sun, 2008), and carbon material production (Carriazo, Gutiérrez, Ferrer, & Monte, 2010).

Recently, Abbott et al. (Abbott, Ballantyne, Conde, Ryder, & Wise, 2012) found that ChCl/urea could significantly plasticize corn starch to produce a soft and flexible plastic with mechanical properties similar to oil-derived plastics. Ramesh et al. (Ramesh, Shanti, & Morris, 2012) reported that the addition of ChCl/urea into corn starch could enhance the room temperature ionic conductivity by increasing the amorphous elastomeric phase in corn starch (CS): lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) matrix. That was, the presence of ChCl/urea led to the breakage of hydrogen bond in the hydroxyl functional group (—OH) in CS: LiTFSI

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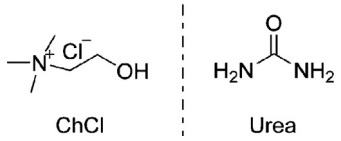

Scheme 1. Chemical structures of ChCl and urea, respectively.

polymer backbone. Furthermore, flexible agarose films were also successfully prepared with ChCl/urea (Shamsuri & Daik, 2012). The pristine agarose film with ChCl/urea was rather smooth and exhibited higher optical transparency as compared with that one without plasticizer. Therefore, ChCl/urea would be a novel plasticizer for biopolymers. In this work, we made the first attempt to investigate the plasticization of ChCl/urea for cellulose film.

Cellulose, the most abundant polysaccharide on the earth, is an ideal alternative to petroleum-based polymers for various applications (Lucia & Rojas, 2007), such as fiber, film, and food packaging (Turner, Spear, Holbrey, & Rogers, 2004; Qi, Chang, & Zhang, 2009). Among these research activities, cellulose-based films have received ever increasing interest. Although some works have been carried out to prepare cellulose-based biodegradable films, the stiff characteristic due to the extensive hydrogen bonds among cellulose chains is still a key problem that restricts their uses in a wide range of applications (Huq et al., 2012; Takegawa, Murakami, Kaneko, & Kadokawa, 2010). Hence, to enhance film forming performance and obtain soft cellulose film, it is necessary to reduce the strong hydrogen bonds. Plasticization is a very simple but useful method to improve the properties of polymers. The additions of glycerol, sorbitol and glycols as plasticizers have been widely applied for cellulosic materials production (Liu, Pang, Zhang, Wu, & Sun, 2013; Xiao, Zhang, Zhang, Lu, & Zhang, 2003).

Being inspired by the above works, the present work was undertaken to evaluate the potential application of ChCl/urea as an inexpensive and environment-friendly plasticizer for cellulose film. The structure and physical properties of the plasticized films were characterized by FT-IR, XRD, TGA, AFM, and tensile testing. For the first time it was shown that ChCl/urea exhibited good plasticizing effect for cellulose film.

2. Experiments

2.1. Materials

Cotton linter with a particle size of 200 mesh was provided by Ruifeng cellulose Co., Ltd (Shandong, China). The content of α-cellulose was 98 wt% and the ash content was less than 0.1 wt%. The viscosity average degree of polymerization of cotton linter measured in CUEN solution was 780 anhydroglucose units on average. Cotton linter was dried in a vaccum oven for 24 h at 50 °C, and then stored in a desiccator. ChCl (98%) was purchased from Beijing lark technology Co., Ltd (Beijing, China) and 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) was purchased from Shanghai chengjie chemical Co., Ltd. Sorbitol, glycerol and urea were all analytical reagents and used as received without further purification.

2.2. Preparation of regenerated cellulose films

The fabrication scheme of RCFs with or without plasticizer was illustrated in Fig. S1. In a typical procedure, RCF was prepared as followed. [BMIM]Cl (30.00 g) was first melted in an oil bath at 100 °C for 1 h, and then cotton linter (1.00 g) was dissolved in [BMIM]Cl at 100 °C with magnetic stirring until cotton linter was completely dissolved to give a clear and viscous solution (about 5 h). Polarized light microscopy (OLYMPUS BX-51) was used to assess the dissolution extent of cotton linter. Then the dissolved cellulose solution was cast on a plastic plate and dipped in deionized water to obtain transparent cellulose gel. The gel was washed with deionized water to remove [BMIM]Cl ($AgNO_3$ solution as indicator). ChCl/urea (molar ratio of 1:2) solutions with various molar ratios of ChCl/urea to H_2O (from 0.01:1 to 0.06:1) were prepared by adding desired amount urea and ChCl into deionized water. The cellulose gels were soaked into the as-prepared ChCl/urea aqueous solutions for 12 h, followed by drying the gels in an oven at 55 °C for 24 h to obtain ChCl/urea plasticized cellulose films. The corresponding cellulose films were named as ChCl/$urea_{0.01}$, ChCl/$urea_{0.02}$, ChCl/$urea_{0.04}$, and ChCl/$urea_{0.06}$ (0.01, 0.02, 0.04, and 0.06 represent the molar ratio of ChCl/urea to H_2O) according to the concentrations of ChCl/urea in the soaking solutions. The reference sample without ChCl/urea was also prepared in the similar way mentioned above. Meanwhile, cellulose films with glycerol, sorbitol, urea, and ChCl alone were also prepared for comparison and coded as $G_{0.01}$, $G_{0.04}$, $S_{0.01}$, $S_{0.04}$, $Urea_{0.04}$, and $ChCl_{0.04}$, respectively, according to the concentrations of substance in the soaking solutions (G represents glycerol and S represents sorbitol; 0.01 and 0.04 represent the molar ratio of plasticizer to H_2O of 0.01:1 and 0.04:1). The contents of plasticizers in cellulose films were calculated as follow. After being weighed, plasticized cellulose films were dialyzed for one week to completely remove plasticizer, which was followed by drying at 105 °C for 4 h. Plasticizer content (c_p) was calculated from the difference between initial (m_I) and final (m_F) weights of cellulose films, using the following formula: $c_p = (m_I - m_F)/m_I$. Before characterization, all films were kept in a conditioning room (50% relative humidity and 24 °C) for 24 h. What's more, those cellulose films were stored for two months in order to identify the stability of plasticizers in films.

2.3. Characterizations

2.3.1. AFM analysis

In AFM scanning, two to four locations on each sample were tested. Topographic (height) and phase images were recorded under ambient air condition. All of the images were recorded in tapping mode in air using silicon cantilevers with a resonance frequency between 250 and 300 kHz.

2.3.2. Thermal analysis

TGA of film was performed on a simultaneous thermal analyzer (Pyris Diamond TG/DSC-200, US). A total of 5.0–10.0 mg of sample was placed in an aluminum pan, and heated from ambient temperature to 600 °C at a rate of 10 °C min^{-1} in a nitrogen atmosphere with a flush rate of 25 mL min^{-1}.

2.3.3. XRD analysis

XRD plots of film specimens were created with a Bruker D8 advance diffractometer equipped with a Cu Kα source monochromatized by a Ni filter (λ = 0.15418 nm). The equatorial profiles of the diffraction patterns were captured in an increment of 0.04° for 2θ values and the diffraction angle was ranged from 5° to 50°. The sealed tube X-ray generator system was operated at an acceleration voltage of 45 kV and a current of 25 mA. All samples were tested without being grinded.

2.3.4. FT-IR spectra

ATR-FTIR spectra were recorded on a Vector 33 infrared spectrum instrument (Bruker Corporation, Germany). The scan range was 500–4000 cm^{-1}, and the resolution rate was 1 cm^{-1}.

Table 1
RCFs and their film-forming performances.

Entry[a]	Molar ratio[b]	Plasticizer content (%)	Film formation (at beginning)	Film formation (after storage)
ChCl/urea$_0$	0	0	Corrugated, stiff	No change
ChCl/urea$_{0.01}$	0.01:1	30.29	Plain, soft, transparent	No change
ChCl/urea$_{0.02}$	0.02:1	53.25	Plain, soft, transparent	No change
ChCl/urea$_{0.04}$	0.04:1	58.04	Plain, soft, transparent	No change
ChCl/urea$_{0.06}$	0.06:1	62.07	Plain, soft, transparent	No change
Urea$_{0.04}$	0.04:1	–	Opaque, stiff	No change
ChCl$_{0.04}$	0.04:1	–	Transparent, contractive	No change
G$_{0.01}$	0.01:1	6.70	Plain, soft	No change
G$_{0.04}$	0.04:1	–	Plain, soft	No change
S$_{0.01}$	0.01:1	56.88	Plain, soft	No change
S$_{0.04}$	0.04:1	–	Plain, soft	Rough, stiff

[a] Molar ratio of ChCl to urea = 2:1.
[b] Representing molar ratio of plasticizer to H_2O in dipping aqueous solution.

2.3.5. Tensile strength testing

The tensile strengths of films were measured in a tensile testing machine (Universal testing machine 5565, Instron) fitted with a 100 N load cell. The samples were cut into rectangular specimens with a width of 15 mm and a length of 70 mm. The separation rate of the grips was kept constant at 4 mm min^{-1}. The stress–strain curve was recorded for each sample. The measurements were performed at 24 °C and 50% RH, and mechanical tensile data of each sample present in this paper was averaged over six specimens.

3. Results and discussion

3.1. Film formation performance

In recent years, biodegradable cellulose-based films have attracted considerable attention (Turner et al., 2004; Qi et al., 2009). However, the production of plain and soft cellulose films is still a big challenge due to considerable hydrogen bonds among cellulose chains, restricting their uses in a wide range of applications. Plasticizer can increase the free volume between polymer chains by reducing the number of active centers available for rigid polymer–polymer contacts. Till now, several plasticizers, such as glycerol, glycol, sorbitol, carboxymethyl cellulose (CMC), α-monoglycerides, have been studied to produce soft cellulose films with enhanced chemical and physical properties (Pang, Liu, Zhang, Wu, & Sun, 2013; Xiao et al., 2003). In this work, ChCl/urea was used as a plasticizer to produce RCFs. The performances of various RCFs and plasticizers content in RCFs were shown in Table 1 and Fig. 1.

As shown in Table 1, the content of plasticizer in cellulose film increased with the increase of the concentration of ChCl/urea aqueous solution, and the maximum plasticizer content could be up to 62.07%, indicating that RCFs showed good absorption properties for ChCl/urea. It was noted that identification of the ratio of ChCl to urea in these films was difficult, because ChCl and urea were hard to withdraw from films separately. Additionally, the plasticizer contents of G$_{0.01}$ and S$_{0.01}$ were 6.70 and 56.88%, respectively. The results showed that the absorption capability of RCF for sorbitol was much higher than glycerol and ChCl/urea (ChCl/urea$_{0.01}$ = 30.29%), even when the molecular weights of glycerol (92.09) and sorbitol (182.18) were taken into account. Table 1 also presented the performances of various cellulose films, which was intuitively showed in Fig. 1. As shown in Fig. 1a, RCF without plasticizer (ChCl/urea$_0$, Fig. 1a) was plicated and stiff. The inset in Fig. 1a intuitively showed the rigid characteristic of RCF without plasticizer. It was found that RCF plasticized with glycerol was soft and smooth (Fig. 1b), and similar RCF could also be prepared by sorbitol plasticization (image not shown). However, after being stored for two months, sorbitol plasticized RCF became very haze and brittle (Fig. 1c), which may be due to sorbitol crystallizing in the film. Similar phenomenon also occurred to starch films

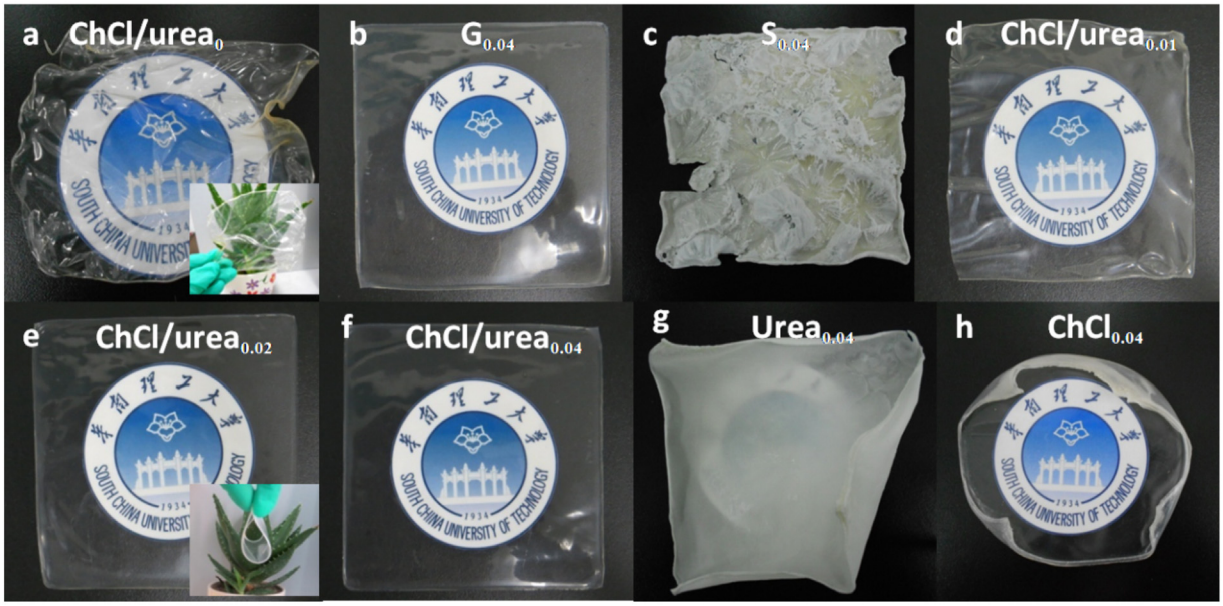

Fig. 1. Optical images of (a) reference film and RCFs with plasticizers: (b) G$_{0.04}$, (c) S$_{0.04}$, (d) ChCl/urea$_{0.01}$, (e) ChCl/urea$_{0.02}$, (f) ChCl/urea$_{0.04}$, (g) Urea$_{0.04}$, and (h) ChCl$_{0.04}$.

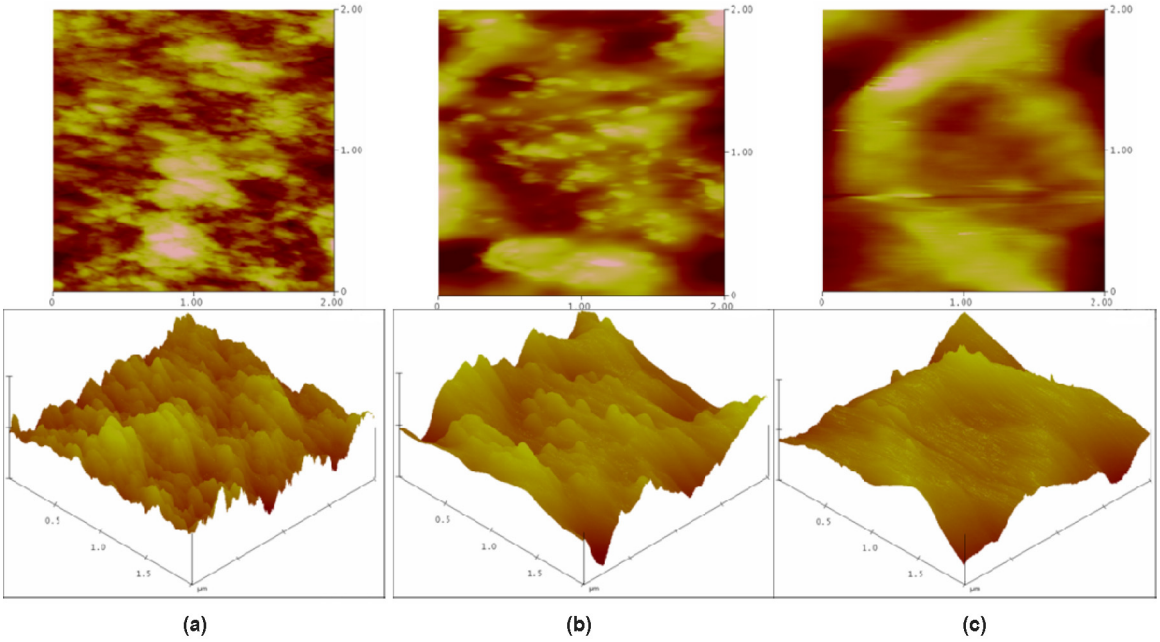

Fig. 2. AFM images of RCFs: (a) reference sample, (b) ChCl/urea$_{0.02}$, and (c) ChCl/urea$_{0.04}$.

plasticized with ≥50% sorbitol (Krogars et al., 2003). ChCl/urea mixture showed pretty good plasticizing effect for cellulose film. At low concentration (ChCl/urea$_{0.01}$, Fig. 1d), RCF was transparent and soft, and showed only a little shrinkage, which was in sharp contrast to pure RCF (ChCl/urea$_0$). At a higher concentration (ChCl/urea$_{0.04}$, Fig. 1e, f), RCF was softer and smoother, and no shrinkage could be observed. The results indicated that urea combined with ChCl had excellent plasticizing effect for cellulose. Furthermore, ChCl/urea plasticized RCFs showed little change after being stored for two months (image not shown), suggesting that the compatibility of cellulose and ChCl/urea was pretty good. However, RCF plasticized with urea alone (Urea$_{0.04}$, Fig. 1g) showed poor film forming performance, as indicated by its optical opacity and brittleness. Although RCF plasticized with ChCl alone (Fig. 1h) was transparent, shrinkage still occurred, suggesting that urea or ChCl alone showed poor plasticizing effect for cellulose film. Thus the excellent plasticizing effect must be associated with the synergetic effect of the two components. Therefore, ChCl/urea as a novel plasticizer is comparable to traditional plasticizers, such as glycerol and sorbitol.

3.2. Morphology of film surface

AFM images with high resolution were recorded to obtain the surface structural information of RCFs, and the representative images were shown in Fig. 2. The surface of the reference sample without plasticizer was composed of large amounts of nanonodules, and these nodules were tightly connected with each other, forming a rough surface. Similar phenomenon also occurred to RCF prepared from ionic liquid (Liu et al., 2013). These spheres may represent the high-aggregation region of cellulose chains (Pradhan, Choudhary, & Samantaray, 2008; Singh, Kim, & Rhee, 2008). Compared with the reference film, the surface of ChCl/urea plasticized RCF showed fewer nodules, and showed smoother surface morphology (Fig. 2b). With the increase in the content of ChCl/urea in cellulose films, the number of nodules was further reduced and finally almost all nodules disappeared (Fig. 2c).

The nodules on the film surface may result from cellulose macromolecule aggregation due to strong hydrogen bonds among cellulose chains. Cl^- anion of ChCl may tend to detach hydrogen atom that initially bonds with oxygen atom in —OH functional group in cellulose chain, while the choline cation may interact with the oxygen atom (Sankri et al., 2010). Urea molecule, as hydrogen donator, may interact mainly with Cl^- anions through N—H···Cl hydrogen bond, forming a complex (Sun, Li, Wu, & Li, 2013), and choline chloride acts as a bridge between the urea and sugar moieties (Abbott et al., 2012). As a result, the hydrogen bonds were greatly reduced and the aggregation of cellulose chains became much weak. Therefore, the nodules on the surface of ChCl/urea plasticized RCFs significantly decreased, exhibiting ChCl/urea good plasticizing effect on cellulose films.

3.3. FT-IR characterization

The FT-IR spectra of various RCFs were shown in Fig. 3. The absorption bands of reference sample at around 3369, 2920, 1116,

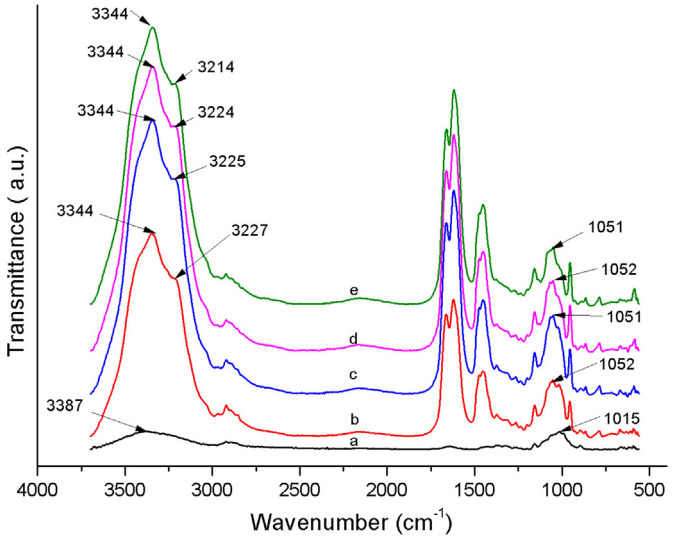

Fig. 3. FT-IR spectra of RCFs: (a) reference sample, (b) ChCl/urea$_{0.01}$, (c) ChCl/urea$_{0.02}$, (d) ChCl/urea$_{0.04}$, and (e) ChCl/urea$_{0.06}$.

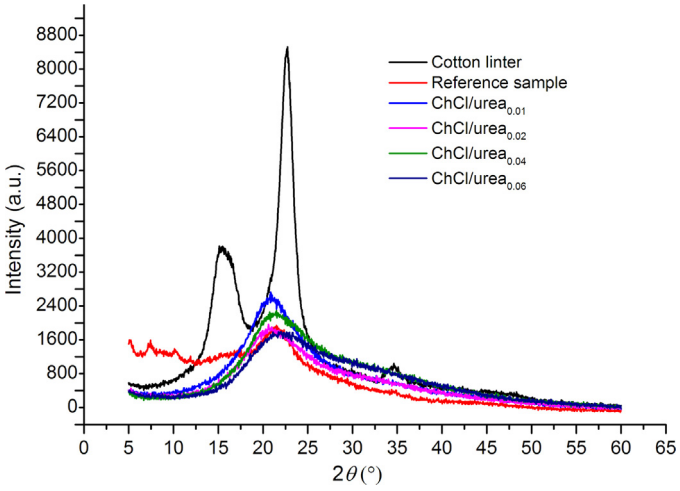

Fig. 4. XRD patterns of RCFs.

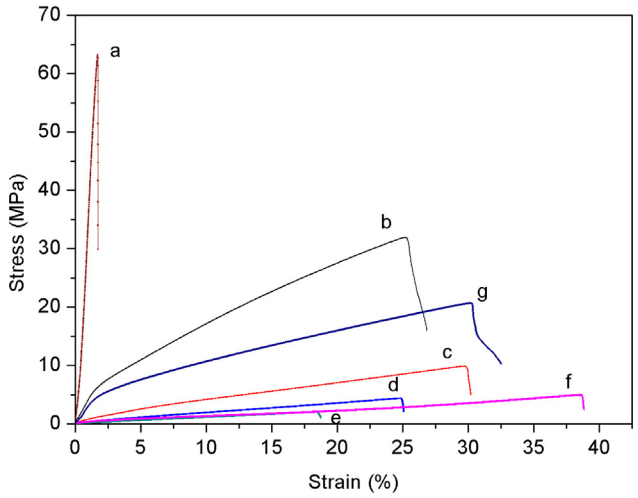

Fig. 5. Stress–strain curves of RFCs: (a) reference sample, (b) ChCl/urea$_{0.01}$, (c) ChCl/urea$_{0.02}$, (d) ChCl/urea$_{0.04}$, (e) ChCl/urea$_{0.06}$, (f) G$_{0.01}$, and (g) S$_{0.01}$.

1000, and 900 cm^{-1} are the characteristic absorptions of cellulose (Jin et al., 2009; Lateef, Grimes, Kewcharoenwong, & Feinberg, 2009; Murakami, Kaneko, & Kadokawa, 2007). Compared with the reference sample, new absorption bands at around 3200, 1661, 1620, and 735 cm^{-1} appeared in the spectra of ChCl/urea plasticized RCFs, which are the characteristic bands of ChCl/urea, namely, the N—H stretching vibration of amide group, amide C=O stretching vibration, amide N—H scissoring vibration, and C—N$^+$ symmetric stretching vibration (Park, Oh, & Choi, 2013; Shamsuri and Daik, 2012). Noticeably, the bands of the O—H stretching of alcohol group and the N—H stretching vibration of amide group shifted to lower wavenumbers in the presence of ChCl/urea, which can be attributed to the formation of the intermolecular hydrogen bonds between ChCl/urea and cellulose. It can also be seen that the bond of C—O stretching of cellulose shifted toward higher wavenumber with the incorporation of ChCl/urea, which was due to the decrease in internal hydrogen bonds among cellulose (Shamsuri and Daik, 2012). Since amide groups of urea could form stable hydrogen bonding with both the chloride anions in choline chloride and the hydroxyl groups in the polysaccharide molecules (Abbott et al., 2003; Ma & Yu, 2004), it can be deduced that hydrogen bonds exist between hydroxyl groups of cellulose and amide groups of ChCl/urea.

3.4. XRD analysis

The crystal structures of RCFs with or without ChCl/urea were shown in Fig. 4. The diffraction pattern of original cellulose (Fig. 4a) showed typical cellulose I structure. A sharp peak at $2\theta = 22.7^\circ$ originates from cellulose crystalline plane (2 0 0) (Zhao et al., 2006) and diffraction peaks at $2\theta = 15.5^\circ$ and 34.6° correspond to cellulose crystalline plane (1 0 1) and (0 0 4) (Duchemin, Mathew, & Oksman, 2009), respectively. By dissolution of cellulose and subsequent regeneration, cellulose I can be transformed into cellulose II (Cheng et al., 2011). The spectrum of the reference film showed peaks at $2\theta = 12^\circ$ corresponding to the plane with Miller indices of (−1 1 0) and 21.0°, which may be attributed to the overlap peak of the two diffraction planes of (1 1 0) and (0 2 0) (French & Cintrón, 2013). It was interesting that all spectra of RCFs plasticized with ChCl/urea showed only one peak at $2\theta = 21.0^\circ$, indicating lower crystallinities. This can be explained by the fact that the formation of intermolecular hydrogen bonds between ChCl/urea and cellulose weakened the hydrogen bonds among cellulose molecules, and the result was that the macromolecule chains move more easily, which consequently effected the crystallinity of cellulose.

Table 2
Mechanical testing results of RCFs.

Sample	Tensile stress (MPa)	Tensile strain at break (%)	Elastic modulus (MPa)
ChCl/ureax_0	60.83 ± 7.02	2.22 ± 0.42	414.20 ± 76.61
ChCl/urea$_{0.01}$	31.34 ± 2.65	25.92 ± 0.25	185.24 ± 38.90
ChCl/urea$_{0.02}$	9.68 ± 0.49	29.23 ± 0.96	44.17 ± 5.22
ChCl/urea$_{0.04}$	4.40 ± 0.05	25.83 ± 1.44	18.50 ± 1.94
ChCl/urea$_{0.06}$	4.14 ± 0.37	34.88 ± 0.11	14.80 ± 1.57
G$_{0.01}$	28.89 ± 0.88	36.78 ± 1.36	129.73 ± 4.91
S$_{0.01}$	22.52 ± 2.94	30.21 ± 3.86	150.53 ± 18.95

3.5. Mechanical testing

Fig. 5 showed the stress–strain curves of RCFs and the results of tensile testing were shown in Table 2. The reference sample exhibited a tensile strength up to 60.83 MPa, while the elongation at break was only 2.22%. The result indicated the stiff characteristic of pure cellulose film, which was exactly consistent with the results obtained from Fig. 1a. However, once plasticizer was incorporated, the elongations at break of RCFs significantly increased, ranging from 25.83 to 36.78%, depending on the concentration and type of plasticizer. The tensile stress of G$_{0.01}$ and S$_{0.01}$ decreased to 28.89 and 22.52 MPa, whereas their elongations increased to 36.78 and 30.21%, indicating a significant plasticizing effect. ChCl/urea also showed its good plasticizing effect for RCF, as indicated by the significant increase in elongation ranging from 25.92 to 34.88%. Although the tensile strength of RCF decreased with the increase of the content of ChCl/urea, 31.34 MPa could be achieved with 25.92% of elongation, showing the potential of ChCl/urea as a novel plasticizer for cellulose films. The plasticizing effect can be attributed to the formation of intermolecular hydrogen bonds between plasticizer and cellulose, resulting in cellulose chains moving more easily (Xiao et al., 2003). The effect led to the increase in elongation and decrease in tensile strength significantly. This was supported by the FT-IR spectra and XRD analysis as previously described.

3.6. Thermal properties

The effect of ChCl/urea on the thermal stability of RCFs was investigated by thermal degradation, and the TG and DTA curves of urea, ChCl, and RCFs with different contents of ChCl/urea were shown in Fig. 6. It can be observed that there was only one sharp peak at about 322 °C appearing in the DTA curve of the

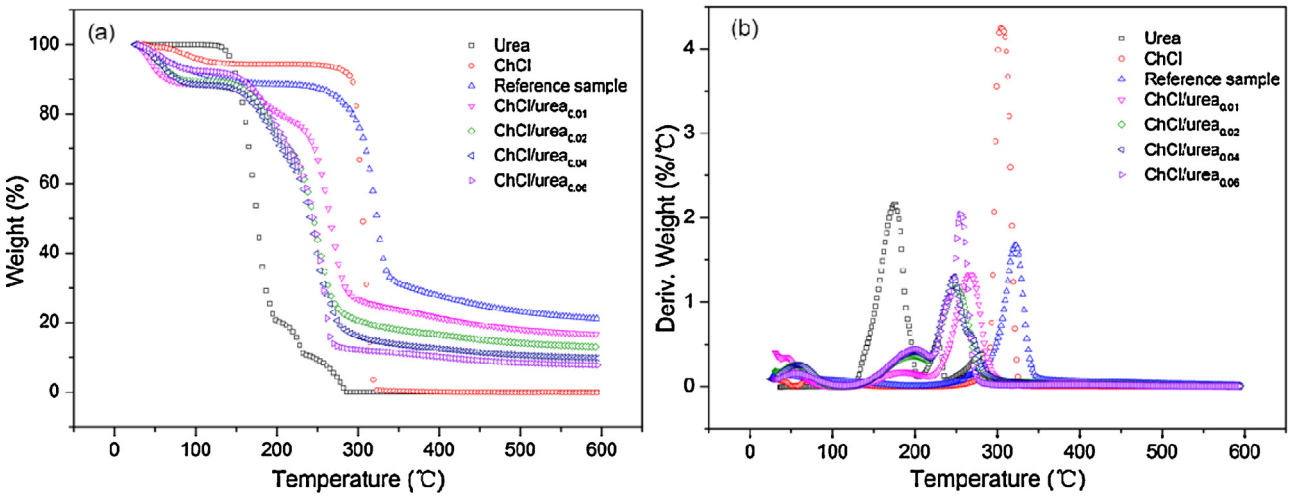

Fig. 6. TGA (a) and DTA (b) of urea, ChCl, and RCFs with different contents of ChCl/urea.

reference sample, which was associated with the degradation of cellulose, while three pyrolysis peaks appeared in the DTA curves of RCFs plasticized with ChCl/urea. The first degradation peak around 90 °C was associated with the volatilization of water. The second weight loss (shoulder peak) occurring at about 200 °C was mainly attributed to the thermal decomposition of urea segment, because the initial degradation temperature of pure urea was low, occurring at 134 °C, as shown in Fig. 6(a). Since the degradation temperature of ChCl (270–325 °C) was very close to cellulose (250–350 °C), the third peak at about 300 °C should be assigned to the thermal decomposition of cellulose chains and ChCl. Therefore, the lower degradation temperature of ChCl/urea plasticized RFC was attributed to the presence of ChCl/urea.

4. Conclusions

This work showed that ChCl/urea was an efficient plasticizer for RCF, and allowed to produce flexible and transparent cellulose films. ChCl/urea showed good compatibility with cellulose, and no chemical reaction and crystallization occurred between the plasticizer and cellulose. By incorporating ChCl/urea, the film forming performance of cellulose was significantly improved by disrupting the strong inter- and intra-hydrogen bonds, resulting in the increase in elongation and decrease in tensile strength of RCF. The addition of ChCl/urea could also lower the thermal stability of RCFs due to the reduction of hydrogen bonds. These results indicated that ChCl/urea was comparable to glycerol and sorbitol, and could be used as a potential plasticizer for RCF.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2014.08.113.

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