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Chemical modification of cellulose by in situ reactive extrusion in ionic liquid

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ABSTRACT

In order to prepare the spinning solution of cellulose with high concentration in environmentally friendly solvent, cellulose was chemically modified by in situ reactive extrusion with several chemicals, such as urea, phthalic anhydride (PA), maleic anhydride (MA) and butyl glycidyl ether (BGE) and with ionic liquid namely 1-N-butyl-3-methylimidazolium chloride (BMIMCl) as reaction medium. These four modifiers all in situ grafted onto cellulose and the modification effectiveness was found to decrease in the sequence, MA > PA > BGE > urea. The formation of side chain on cellulose backbone destroyed the regularity of cellulose chains and the hydrogen bond network efficiently. The concentration of modified cellulose in spinning solution can be up to 14–25%, comparing with 9% for unmodified cellulose in BMIMCl. The high solid content results in high efficiency and less energy consumption of fiber production and solvent recycle.

1. Introduction

Cellulose is one of the most abundant organic raw materials and wildly used in composite materials, textiles, drug delivery systems and personal care products, owing to its good hygroscopicity, dyeability and drapability. However, the presence of three hydroxyl groups in each glucose residue of cellulose results in strong hydrogen-bonding interactions and high crystallinity, so cellulose only can dissolve in particular solvent such as $NaOH/CS_2$, $Cu(NH_3)_4(OH)_2$, N-methyl morpholine Oxide (NMMO), N,N-dimethylacetamide (DMAc)/LiCl (Heinze & Liebert, 2001; Ishii, Tatsumi, & Matsumoto, 2003; Kunze & Fink, 2005; Rosenau, Potthast, Sixta, & Kosma, 2001).

Viscose fiber and copper ammonia fiber are the first two commercial manmade fibers that were developed over 100 years ago. The conventional viscose and cupro processes use $NaOH/CS_2$ and $Cu(NH_3)_4(OH)_2$ as solvents, respectively, and generate several environmentally hazardous byproducts unfortunately, including toxic gas and heavy metals. In recent decades, many other cellulose solvents have been developed to reduce the processing steps as well as to minimize the hazardous byproducts. The $NMMO/H_2O$ and DMAc/LiCl systems are the most representative and mature technology to attain high concentration solutions. The highly polar solvents can form new hydrogen bonding network with cellulose molecules and disrupt the hydrogen bonding of cellulose itself, leading to the dissolution of cellulose. Lyocell fiber is commercialized by using $NMMO/H_2O$ as a direct solvent and displays high strength and high fibrillation tendency in the wet state. However, the $NMMO/H_2O$ system requires high temperature for dissolution and antioxidants to avoid side reactions of solvent, resulting in degradation of cellulose and high costs. The DMAc/LiCl system has better stability and higher dissolve ability than $NMMO/H_2O$, but it requires pre-swelling by sequential solvent exchange and heating and has difficulty in recovering of the solvent. The formation of cellulose carbamate (CC) by transformation of cellulose with urea is another economical attempt without pollution, but the CC process still has many issues that need to be overcome, including the minimization of several side reactions and reduction of undesired byproducts.

Recently, ionic liquids (ILs) which contain strong hydrogen-bond acceptors such as Cl^-, Br^- or SCN^- have been successfully used to dissolve and process cellulose (Barthel & Heinze, 2006; Heinze, Schwikal, & Barthel, 2005; Wendler, Kosan, Krieg, & Meister, 2009). These small hydrogen bond acceptors are assumed to be responsible for interrupting the extensive intermolecular and intramolecular hydrogen bonding of cellulose (Edgar, Heinze, & Liebert, 2009; Wu, Zhang, Zhang, He, Ren, & Guo, 2004, Liu & Sun, 2008). In general, ILs are thermally stable over a wide range of temperature and appropriate reaction media for the homogeneous modification of cellulose. The dissolution process is usually occurred under heat, pressure or radiation in the batch reactor or

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flask (Birgit, Christoph, & Frank, 2008; Brown, Laborie, & Zhang, 2012). For example, cellulose concentration of 25 wt% in 1-butyl-3-methylimidazolium chloride (BMIMCl) can be achieved using microwave heating (Swatloski, Spear, Holbrey, & Rogers, 2002); but the concentration of cellulose in BMIMCl is only about 10–15 wt% with continuous heating and stirring for several hours (Galas, Pyc, & Romanowska, 1997).

Due to high cost, low yield and the difficulty in recovering of the solvent, the industrial production of cellulose with a solvent method is restricted. With the increased awareness of the environmental protection and the increased material demands of citizens, more and more attention is paid to the chemical modification of cellulose along with the green solvent to decrease the intermolecular force of cellulose (French, Rajasekaran, & Condon, 2001; Heinze & Koschella, 2005; Zhao et al., 2007). According to its molecular structure, cellulose is an active chemical. Through the reaction with the hydroxyl groups of cellulose, the functional groups are introduced into cellulose molecules to break the hydrogenbonding network of cellulose, decrease cellulose crystallinity and improve cellulose solubility (Dahou, Ghemati, Oudia, & Aliouche, 2010; Kamel, Ali, Jahangir, Shah, & El-Gendy, 2008; Narita, Tabata, & Yoshida, 2007; Odian, 2004).

In this work, a co-rotating twin-screw extruder was used to conduct the reactive extrusion processing by in situ derivatization of cellulose in the presence of BMIMCl and different modifiers including urea, phthalic anhydride (PA), maleic anhydride (MA) or butyl glycidyl ether (BGE). We attempt to use the high shear stress of extruder to improve the dissolving efficiency of cellulose in BMIMCl as well as the modification effect of modifiers. The objective of this work was to increase the polymer concentration in BMIMCl by cellulose activation through in situ derivatization. The derivatization effect of cellulose with four different modifiers was compared by the investigation of the molecular structure, crystal structure, thermal property and rheological property modified cellulose.

2. Experimental

2.1. Materials

Cotton cellulose was supplied by Jiangsu Longma green fiber industry Co., Ltd. BMIMCl was purchased from Shanghai Chengjie Chemical industry Co., Ltd. Urea (T_m = 132.7 °C), PA (T_m = 131.2 °C), MA (T_m = 52.8 °C) and BGE (T_b = 151.5 °C) were from Sinopharm Chemical Reagent Co., Ltd.

2.2. Extrusion

Cellulose powder was dried under vacuum at 70 °C for 24 h. With BMIMCl as reaction medium, cellulose was mixed with urea, PA, MA and BGE using a blender (Model 31BL92, Waring Products Limited, New Hartford, CT) for several seconds, respectively. Four cellulose/BMIMCl/modifier mixtures were extruded at a constant ratio (20 wt%/60 wt%/20 wt%). The extrusion process experiments were implemented on a co-rotating twin-screw extruder (L/D = 48, D = 35 mm). The barrel temperatures of the extruder for these mixtures except cellulose/BMIMCl/BGE from zone 1 to zone 9 were 100, 110, 120, 130, 140, 140, 150, 150 and 150 °C. The die temperature was 140 °C. The screw rotation speed was 50 rpm and the retention time during extrusion was 10 min. Besides, the mixture of cellulose/BMIMCl (25 wt%/75 wt%) was also extruded at the same condition. Due to the low boiling point of BGE, the barrel temperatures of the extruder for cellulose/BMIMCl/BGE from zone1 to zone 9 were set to 80, 80, 90, 100, 110, 110, 120, 120 and 120 °C, and the die temperature was 110 °C. After reactive extrusion, modified cellulose were washed with distilled water and alcohol successively and then extracted with acetone for 24 h to remove BMIMCl and unreacted modifier. Finally, the modified cellulose were washed with distilled water again and dried at 60 °C for 24 h in a vacuum oven, which were named as cellulose-g-urea, cellulose-g-PA, cellulose-g-MA, cellulose-g-BGE and regenerated cellulose, respectively.

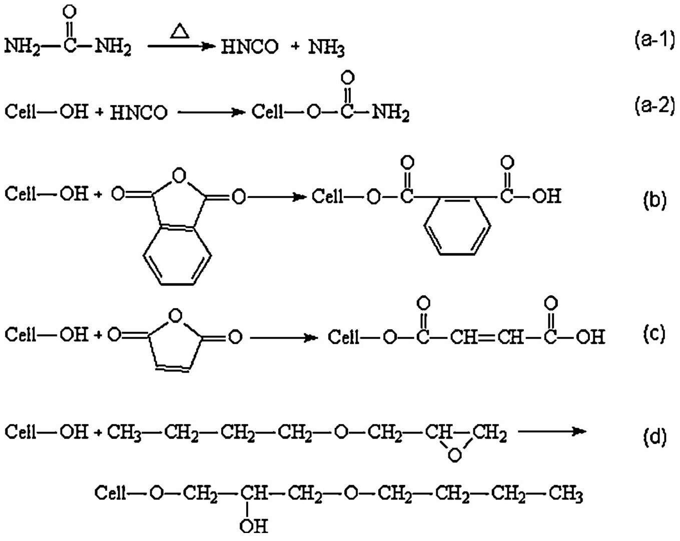

Fig. 1. The reaction mechanisms for (a) cellulose with urea, (b) cellulose with PA, (c) cellulose with MA, (d) cellulose with BGE.

2.3. Characterizations

Solubility test was evaluated by dissolution method. After 100 g BMIMCl solvent was heated to 100 °C, an appropriate amount of cellulose samples was added into it with vigorous stirring for 10 min at 100 °C to obtain a transparent cellulose solution. The remaining undissolved fractions were washed using water and acetone, respectively, and then dried at 60 °C for 24 h in a vacuum oven.

Fourier-transform infrared (FTIR) spectroscopy with an attenuated total reflectance (ATR) accessory was performed on a Nicolet Nexus 670 + Raman Module at a resolution of 2 cm^{-1} in the transmission mode.

Cross-polarisation magic angle spinning carbon-13 solid-state nuclear magnetic resonance spectra (CP/MAS ^{13}C-NMR) was performed on Bruker DSX-400 spectrometer under a static field strength of 2.3 T (100 MHZ 1 H) at 25 °C.

Differential scanning calorimeter (DSC) was performed on Netzsch DSC PC 200 at heating rates of 10 °C/min.

Thermal gravimetric analysis (TGA) was performed using a simultaneous thermal analyzer at heating rates of 5 °C/min in air atmosphere.

Rheological characterization was carried out using a HAAKE RheoStress 600 Rotational Rheometer with a 20 mm parallel plate under nitrogen atmosphere.

3. Results and discussions

3.1. Grafting reactions

The hydroxyl groups at C-2, C-3 and C-6 of cellulose are reactive, which can react with many functional groups such as amino, anhydride and epoxy groups. The mechanisms of these reactions between cellulose and urea, PA, MA and BGE are described in Fig. 1, respectively.

Table 1
Characterization of original cellulose and modified cellulose used in this work.

Samples	DP	DS[a]	Polymer concentration in the BMIMCl (%)
Original cellulose	580		9.0
Cellulose-g-urea	522	0.24	14.3
Cellulose-g-PA	493	0.29	18.2
Cellulose-g-MA	445	0.61	25.0
Cellulose-g-BGE	501		16.7

[a] DS value of cellulose-g-BGE cannot be obtained from NMR data because the signal of ether for cellulose-g-BGE at about 62 ppm is overlapped by the C-6 signal of cellulose.

The degree of polymerization (DP) and the degree of substitution (DS) values of cellulose are both important feature influencing their properties. DP was measured viscosimetrically in copper ethylenediamine solution (CuEn) and the obtained intrinsic viscosities converted into the respective values of DP by Eq. (1) (Grobe, 1989).

$$\overline{\mathrm{DP}}^{0.905} = 0.75[\eta]_{\mathrm{CuEn}}\,(\mathrm{cm}^3\,\mathrm{g}^{-1}) \qquad (1)$$

DS was calculated from a ratio of the integrals of NMR peaks by Eq. (2) (Raymond, Morin, & Marchessault, 1993).

$$\mathrm{DS} = \frac{n_{\mathrm{CE}} \times I_{\mathrm{CA}}}{n_{\mathrm{CA}} \times I_{\mathrm{CE}}} \qquad (2)$$

where I_{CA} and I_{CE} are the integration of peaks of corresponding carbonyl carbons and cellulose carbons, respectively. n_{AC} and n_{CE} are the number of carbon atoms in the corresponding carbonyl group and in cellulose.

The solubility of cellulose samples in BMIMCl was calculated by Eq. (3).

$$C = \frac{w_1 - w_2}{100} \qquad (3)$$

where C is the concentration of cellulose samples in BMIMCl, w_1 is the weight of original cellulose samples, and w_2 is the weight of undissolved fractions.

The DP, DS and the concentration of cellulose samples are shown in Table 1. Owing to the short retention time during extrusion, the DS value of modified cellulose is obvious less than that of modified cellulose prepared in a batch reactor for 2–4 h. Therefore, cellulose samples do not undergo severe depolymerization after reactive extrusion and it is good to retain the inherent properties of cellulose. Due to the strong shear stress of twin-screw extruder, the dissolving efficiency of cellulose in [BMIM]Cl is improved obviously and the hydrogen bond network of cellulose is destroyed rapidly. Meanwhile, the movement of modifiers to the cellulose chains is promoted by the chemical effect of BMIMCl and the physical effect of the shear force, so the number of hydroxyl groups of modified cellulose decreased and the concentration of modified cellulose in spinning solution is higher than that of original cellulose, which is benefit to improve the production efficiency, fiber quality and fiber stability. In comparison with other modified cellulose, cellulose-g-MA has lower DP, higher DS and solubility. This is probably related to the structure of MA that has less steric hindrance, higher activity and polarity, so MA can easily move to the surface of cellulose, even can migrate into the interior of cellulose and consequently have more contact opportunity with hydroxyl groups of cellulose. Through the chemical modification with MA, the intermolecular interaction of cellulose was decreased effectively and Cl atom was easy to penetrate into the interior of cellulose-g-MA to form weak hydrogen bond with H atom of cellulose-g-MA. Thus, the hydrogen-bonding interactions in the cellulose-g-MA were weakened and more cellulose-g-MA was dissolved in BMIMCl finally.

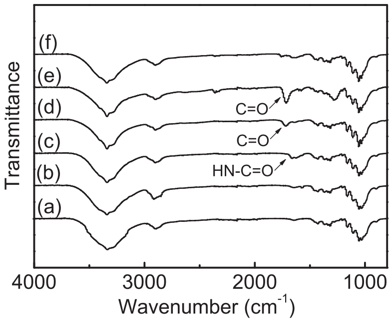

Fig. 2. FTIR spectra of (a) original cellulose, (b) regenerated cellulose, (c) cellulose-g-urea, (d) cellulose-g-PA, (e) cellulose-g-MA, (f) cellulose-g-BGE.

3.2. FTIR analysis

Fig. 2 shows the FTIR spectra for cellulose samples. In comparison with unmodified cellulose, cellulose-g-urea displays a new peak of ester absorption of the amide group at 1680 cm^{-1}, and new peaks appears at 1720 cm^{-1} for the cellulose-g-PA and cellulose-g-MA, which is related to the absorption of the ester band of the carbonyl group. However, the C—O—C signal for cellulose-g-BGE might be overlapped by the cellulose′s own characteristic absorption peak. Compared to other modified cellulose, the ester absorption of cellulose-g-MA is the most obvious. It implies that MA has higher reactivity with cellulose than other modifiers, which is consistent with the DS results.

Fig. 3 shows the FTIR spectra of hydrogen bonded O—H stretching vibrations. Hydrogen bond of cellulose can be divided into the intramolecular hydrogen bond of 2-OH···O-6 at 3410 cm^{-1}, the intramolecular hydrogen bond of 3-OH···O-5 at 3340 cm^{-1}, and the intermolecular hydrogen bond of 6-OH···O-3′ at 3280 cm^{-1} (Schwanninger, Rodrigues, Pereira, & Hinterstoisser, 2004). The intensity of the peak at 3280 cm^{-1} in the modified cellulose reduced obviously, indicating that more intermolecular hydrogen bond is destructed compared to the intramolecular hydrogen bond. In general, the relative reactivity of hydroxyl groups can be expressed as OH-C6 > OH-C2 > OH-C3 (Krassig, 1993). Therefore, the peak at 3410 cm^{-1} in the modified cellulose displayed lower intensity compared to the peak at 3340 cm^{-1} and the higher reactive of anhydride groups with cellulose leads to an obvious decrease in the band at 3410 cm^{-1} for cellulose-g-PA and cellulose-g-MA.

3.3. ^{13}C NMR analysis

The ^{13}C NMR spectra of cellulose samples are shown in Fig. 4. A new peak appears at 174.3 ppm in the spectrum of cellulose-g-urea, which is related to the absorption of carbonyl band of amide groups. The carbon chemical shift of carbonyl groups for cellulose-g-PA and cellulose-g-MA were 171.0 ppm and 169.7 ppm, respectively. Moreover, the C-1 carbon resonance of modified cellulose split into two peaks owing to the neighboring substituent at the C-2 and C-3 position.

In the spectra of cellulose, the most valuable peak is C-4. The two characteristic peaks of C-4 correspond to the amorphous region signal at 80–86 ppm and the crystalline region signal at 86–92 ppm, respectively (Klemm, Philpp, Heinze, Heinze, & Wagenknecht, 1998). The crystallinity (χ_c) of cellulose can be calculated by the relative intensity of crystallized C-4 as Eq. (4).

$$\chi_c = \frac{S_c}{S_c + S_a} \times 100\% \qquad (4)$$

where S_c and S_a are the area of the crystalline and amorphous regions of C-4, respectively.

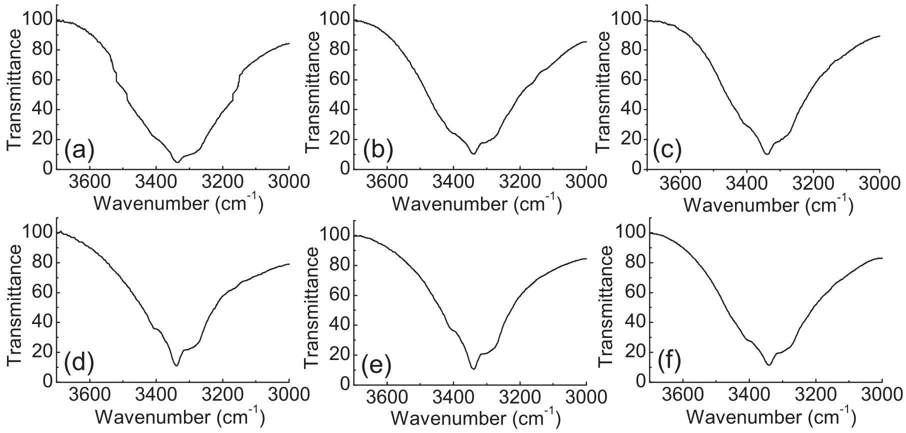

Fig. 3. FTIR spectra of hydrogen bonded OH stretching for (a) original cellulose, (b) regenerated cellulose, (c) cellulose-g-urea, (d) cellulose-g-PA, (e) cellulose-g-MA, (f) cellulose-g-BGE.

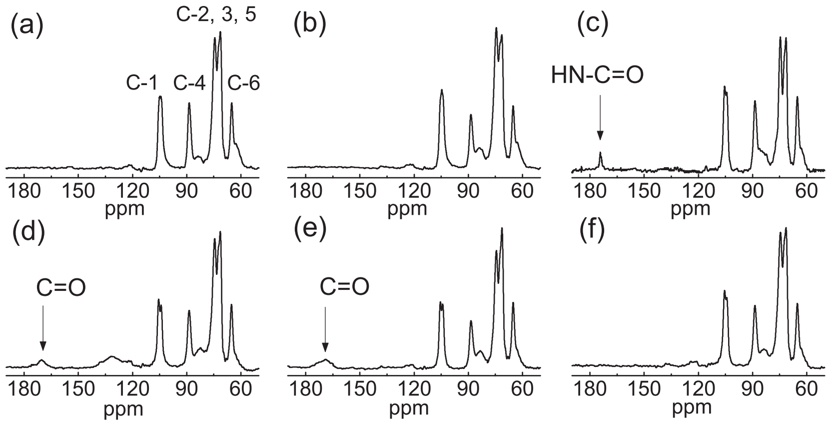

Fig. 4. ^{13}C NMR spectra of (a) original cellulose, (b) regenerated cellulose, (c) cellulose-g-urea, (d) cellulose-g-PA, (e) cellulose-g-MA, (f) cellulose-g-BGE.

Table 2
Crystallinity of original cellulose, regenerated cellulose and modified cellulose.

Samples	X_c (%)
Original cellulose	62.7
Regenerated cellulose	58.3
Cellulose-g-urea	50.5
Cellulose-g-PA	46.4
Cellulose-g-MA	38.9
Cellulose-g-BGE	44.8

The crystallinity of cellulose samples is reported in Table 2. The formation of side chain on the backbone of cellulose increases the difficulty for cellulose chains to organize and aggregate, so the crystallinity of modified cellulose is decreased and the crystallinity of cellulose-g-MA is much lower than that of other modified cellulose. It indicated that cellulose-g-MA contains more side chains which prevented microfibril from approaching one another and affected the crystallization behavior of cellulose. The increased amorphous region in cellulose-g-MA could offer more spaces to accommodate MA molecules and facilitate the grafting reaction.

3.4. Thermalgravimetric analysis

TGA and DTG curves obtained for cellulose samples are presented in Fig. 5. Original cellulose powder presents one decomposition peak with maximum at 345.7 °C while DTG peak of the regenerated cellulose becomes wider and shifts to lower temperature. This is expected as the molecular chain of cellulose

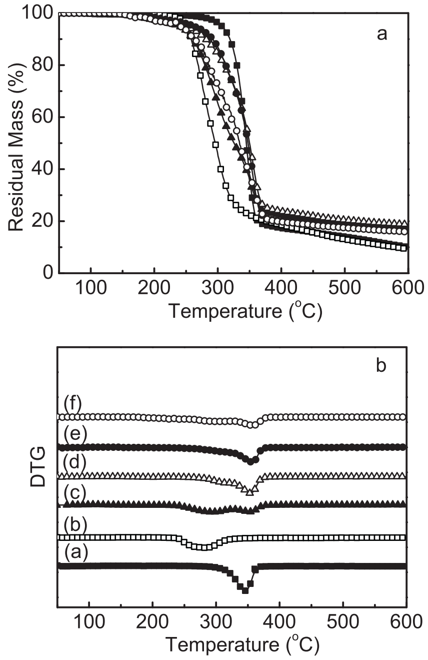

Fig. 5. **a** TGA and **b** DTG curves of (a) original cellulose, (b) regenerated cellulose, (c) cellulose-g-urea, (d) cellulose-g-PA, (e) cellulose-g-MA, (f) cellulose-g-BGE.

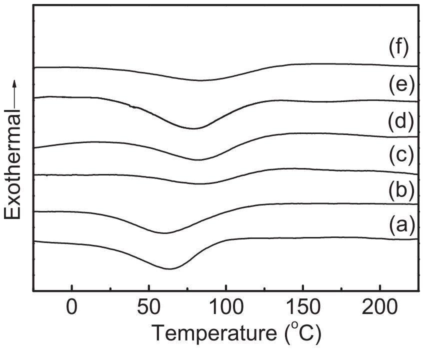

Fig. 6. DSC plots of (a) original cellulose, (b) regenerated cellulose, (c) cellulose-g-urea, (d) cellulose-g-PA, (e) cellulose-g-MA, (f) cellulose-g-BGE.

was interrupted after dissolved in BMIMCl, so the polymerization degree and the thermal stability of regenerated cellulose was reduced. However, the modified cellulose presents two decomposition steps: the first step of weight loss from 250 to 310 °C is similar with the regenerated cellulose and the second step of weight loss from 310 to 370 °C is similar with the original cellulose. The first peak of DTG curves is related to the decomposition of ungrafted cellulose, while the second peak of DTG curves can be assigned to the decomposition of grafted cellulose. As shown in Fig. 5, the first peak of cellulose-g-MA almost disappeared, indicating that most cellulose was reacted with MA to form grafted cellulose. The DTG peak for grafted cellulose in modified cellulose occurs at about 354 °C, which is 10 °C higher than that of original cellulose, indicating that the side chains on the cellulose improved the thermal stability of cellulose.

3.5. Thermal behavior

Polymers with hydrophilic groups absorb water easily such as cellulose, so some water will associated with cellulose powder inevitably even in the dry state. In the past, some workers have examined that the dehydration of cellulose usually take place in the temperature range of 10–90 °C (Hatakeyama & Hatakeyama, 1998; Hatakeyama & Quinn, 1994). We studied the dehydration process of cellulose using DSC method, as shown in Fig. 6. Original cellulose shows a broad endothermic peak in the temperature range of 10–110 °C with a maximum at 63 °C, which is consistent with the literatures mentioned above. After modification, the endothermic peaks shift to higher temperature. On the one hand, the increase of steric hindrance increases the difficulty in water structure breakage around modified cellulose, which increases the dehydration temperature. On the other hand, the formation of side chain decreases the hydrogen bond interactions between cellulose ethers and water, which decrease the dehydration temperature. Evidently, the former is the main factor when comparing the dehydration of original cellulose with that of modified cellulose. However, the dehydration of cellulose-g-MA appeared at lower temperature than other modified cellulose. It indicated that the obvious reduction of intermolecular interactions of cellulose-g-MA decreased the hydrogen bonding between cellulose-g-MA and water. That is to say, the effect of the decreased intermolecular interactions on the dehydration of modified cellulose is more remarkable than that of the increased steric hindrance for the modified cellulose with different substitution.

3.6. Rheological properties

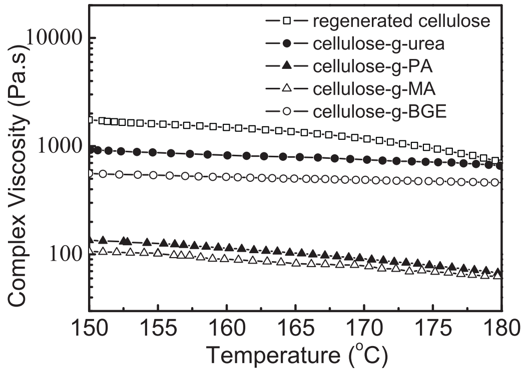

Fig. 7. Complex viscosity as a function of temperature at 11 Hz for regenerated cellulose and modified cellulose.

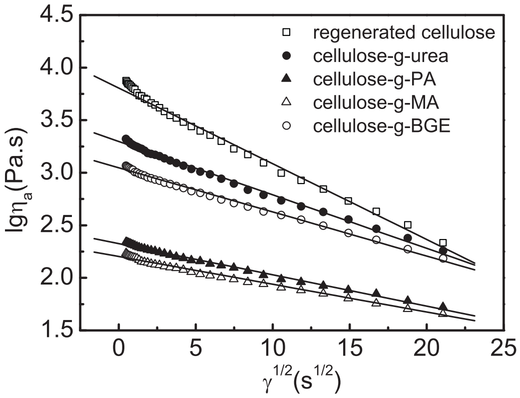

Fig. 8. $\lg \eta_a$ vs. $\gamma_{1/2}$ for regenerated cellulose and modified cellulose spinning dopes.

Table 3
Structural viscosity index of regenerated cellulose and modified cellulose.

Samples	$\Delta\eta$
Regenerated cellulose	7.2
Cellulose-g-urea	5.1
Cellulose-g-PA	3.0
Cellulose-g-MA	2.6
Cellulose-g-BGE	4.2

Fig. 7 shows the complex viscosity with temperature for modified cellulose spinning dopes respectively. Typical extrusion conditions experience 50–1000 s^{-1} shear rates (Giles, Wagner, & Mount, 2005), so the frequency sweep was set at 11 Hz, which is in the range of the shear rate during extrusion. It can be seen that the addition of modifier decreased the viscosity of modified cellulose and the addition of anhydride caused the most significant lowering of the viscosity. It indicated that the formation of side chain in cellulose-g-MA had better internal plasticization and stronger size exclusion effect, which increased the distance between cellulose molecules, so the gathering of cellulose chains during the extrusion was restricted and the interaction force between cellulose chains was decreased effectively. Although adding urea could reduce the number of hydrogen bonds between cellulose chains, urea and hydroxyl groups in cellulose molecules might form new hydrogen bonds, leading to an little decrease in viscosity.

The structural viscosity index ($\Delta\eta$) is a useful experimental parameter for the spinnability of spinning dope. The $\Delta\eta$ can be obtained by Eq. (5):

$$\Delta\eta = -\frac{d\lg \eta_a}{d\gamma^{1/2}} \times 100 \tag{5}$$

where η_a is apparent viscosity and γ is shear rate.

The $\lg \eta_a$ against $\gamma_{1/2}$ at 165 °C of modified cellulose spinning dopes are given in Fig. 8. The plots of $\lg \eta_a$ vs. $\gamma_{1/2}$ for cellulose samples exhibit good linear relationship. The values of $\Delta\eta$ can be obtained from the slopes of the straight lines, as shown in Table 3. $\Delta\eta$ values of modified cellulose were lower than regenerated cellulose and the $\Delta\eta$ of cellulose modified with anhydride was even lower, indicating the flowability and spinnability of cellulose-g-PA and cellulose-g-MA are much better.

4. Conclusions

In this study, a co-rotating twin-screw extruder was used to conduct the heterogeneous reactive extrusion by in situ modification of cellulose in the presence of BMIMCl as plasticizer and urea, PA, MA or BGE as modifier. Under high shear stress, the movement of modifier to cellulose chains was improved and the hydrogen-bonding interaction of cellulose was decreased. Compared to other modifiers, anhydride group has higher reaction activity with the hydroxyl group of cellulose, so the regularity of cellulose chains and the hydrogen bond between cellulose chains was destroyed effectively by the grafting reaction of cellulose with PA and MA. Moreover, the smaller molecular weight and less steric hindrance of MA favored the entrance of MA into the cellulose phase and increased the DS, so cellulose-g-MA exhibited lower crystallinity and better thermal stability than other modified cellulose and the spinning solution of cellulose-g-MA showed higher concentration and better spinnability. The in situ heterogeneous modification through reactive extrusion method may provide theoretical base for the industrial production of cellulose fiber with low energy consumption and high properties.

Acknowledgements

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References

Barthel, S., & Heinze, T. (2006). Acylation and carbanilation of cellulose in ionic liquids. *Green Chemistry*, *8*, 301–306. http://dx.doi.org/10.1039/b513157j

Birgit, K., Christoph, M., & Frank, M. (2008). Dissolution and forming of cellulose with ionic liquids. *Cellulose*, *15*, 59–66. http://dx.doi.org/10.1007/s10570-007-9160-x

Brown, E. E., Laborie, M. P. G., & Zhang, J. W. (2012). Glutaraldehyde treatment of bacterial cellulose/fibrin composites: Impact on morphology, tensile and viscoelastic properties. *Cellulose*, *19*, 127–137. http://dx.doi.org/10.1007/s10570-011-9617-9

Dahou, W., Ghemati, D., Oudia, A., & Aliouche, D. (2010). Preparation and biological characterization of cellulose graft copolymers. *Biochemical Engineering Journal*, *48*, 187–194. http://dx.doi.org/10.1016/j.bej.2009.10.006

Edgar, K., Heinze, T., & Liebert, T. (2009). *Cellulose solvents: For analysis, shaping and chemical modification*. Washington DC: American Chemical Society.

French, A. D., Rajasekaran, K., & Condon, B. (2001). Book review: Cellulose science and technology. *Cellulose*, *18*, 851–852. http://dx.doi.org/10.1007/s10570-011-9518-y

Galas, E., Pyc, R., & Romanowska, I. (1997). Hydrolysis and transformation of cellulose with *Aspergillus niger* IBT-90 enzymes. *Acta Biotechnologica*, *17*, 339–350. http://dx.doi.org/10.1002/abio.370170410

Grobe, A. (1989). *Polymer handbook*. New York: John Wiley & Sons.

Giles, H. F., Wagner, J. R., & Mount, E. M. (2005). *Extrusion: The definitive processing guide and handbook*. New York: William Andrew Publishing.

Hatakeyama, H., & Hatakeyama, T. (1998). Interaction between water and hydrophilic polymers. *Thermochimica Acta*, *308*, 3–22. http://dx.doi.org/10.1016/S0040-6031(97)00325-0

Hatakeyama, T., & Quinn, F. X. (1994). *Thermal analysis: Fundamentals and applications to polymer science*. New York: John Wiley & Sons.

Heinze, T., & Liebert, T. (2001). Unconventional methods in cellulose functionalization. *Progress in Polymer Science*, *26*, 1689–1762. http://dx.doi.org/10.1016/S0079-6700(01)00022-3

Heinze, T., & Koschella, A. (2005). Solvents applied in the field of cellulose chemistry—A mini review. *Polimeros*, *15*, 84–90. http://dx.doi.org/10.1590/S0104-14282005000200005

Heinze, T., Schwikal, K., & Barthel, S. (2005). Ionic liquids as reaction medium in cellulose functionalization. *Macromolecular Bioscience*, *5*, 520–525. http://dx.doi.org/10.1002/mabi.200500039

Ishii, D., Tatsumi, D., & Matsumoto, T. (2003). Effect of solvent exchange on the solid structure and dissolution behavior of cellulose. *Biomacromolecules*, *4*, 1238–1243. http://dx.doi.org/10.1021/bm034065g

Kamel, S., Ali, N., Jahangir, K., Shah, S. M., & El-Gendy, A. A. (2008). Pharmaceutical significance of cellulose: A review. *Express Polymer Letters*, *2*, 758–778. http://dx.doi.org/10.3144/expresspolymlett.2008.90

Klemm, D., Philpp, B., Heinze, T., Heinze, U., & Wagenknecht, W. (1998). . *Comprehensive cellulose chemistry: Fundamentals and analytical methods* (Vol. 1) Weinheim: Wiley-VCH Verlag GmbH.

Krassig, H. A. (1993). *Cellulose: Structure, accessibility and reactivity*. Yverdon: Gordon and Breach Science Publisher.

Kunze, J., & Fink, H. P. (2005). Structural changes and activation of cellulose by caustic soda solution with urea. *Macromolecular Symposia*, *223*, 175–187. http://dx.doi.org/10.1002/masy.200550512

Liu, S., & Sun, G. (2008). Radical graft functional modification of cellulose with allyl monomers: Chemistry and structure characterization. *Carbohydrate Polymers*, *71*, 614–625. http://dx.doi.org/10.1016/j.carbpol.2007.07.006

Narita, M., Tabata, M., & Yoshida, A. (2007). *Methods for preparing alkali cellulose and cellulose ether*. US 0149774A1.

Odian, G. (2004). *Principles of polymerization*. Hoboken: John Wiley & Sons.

Raymond, L., Morin, F. G., & Marchessault, R. H. (1993). Degree of deacetylation of chitosan using conductometric titration and solid-state NMR. *Carbohydrate Research*, *246*, 331–336. http://dx.doi.org/10.1016/0008-6215(93)84044-7

Rosenau, T., Potthast, A., Sixta, H., & Kosma, P. (2001). The chemistry of side reactions and byproduct formation in the system NMMO/cellulose (lyocell process). *Progress in Polymer Science*, *26*, 1763–1837. http://dx.doi.org/10.1016/S0079-6700(01)00023-5

Schwanninger, M., Rodrigues, J. C., Pereira, H., & Hinterstoisser, B. (2004). Effects of short-time vibratory ball milling on the shape of FT-IR spectra of wood and cellulose. *Vibrational Spectroscopy*, *36*, 23–40. http://dx.doi.org/10.1016/j.vibspec.2004.02.003

Swatloski, R. P., Spear, S. K., Holbrey, J. D., & Rogers, R. D. (2002). Dissolution of cellulose with ionic liquid. *Journal of the American Chemical Society*, *124*, 4974–4975. http://dx.doi.org/10.1021/ja025790m

Wendler, F., Kosan, B., Krieg, M., & Meister, F. (2009). Possibilities for the physical modification of cellulose shapes using ionic liquids. *Macromolecular Symposia*, *280*, 112–122. http://dx.doi.org/10.1002/masy.200950613

Wu, J., Zhang, J., Zhang, H., He, J., Ren, Q., & Guo, M. (2004). Homogeneous acetylation of cellulose in a new ionic liquid. *Biomacromolecules*, *5*, 266–268. http://dx.doi.org/10.1021/bm034398d

Zhao, H., Kwak, J. H., Wang, Y., Franz, J. A., White, J. M., & Holladay, J. E. (2007). Interactions between cellulose and N-methylmorpholine-N-oxide. *Carbohydrate Polymers*, *67*, 97–103. http://dx.doi.org/10.1016/j.carbpol.2006.04.019