



# 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.

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## 1. Introduction

Cellulose is one of the most abundant organic raw materials and widely 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<sub>2</sub>, Cu(NH<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>, 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<sub>2</sub> and Cu(NH<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub> 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<sub>2</sub>O 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<sub>2</sub>O as a direct solvent and displays high strength and high fibrillation tendency in the wet state. However, the NMMO/H<sub>2</sub>O 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<sub>2</sub>O, 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<sup>-</sup>, Br<sup>-</sup> or SCN<sup>-</sup> 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 ( $T_m = 132.7^\circ\text{C}$ ), PA ( $T_m = 131.2^\circ\text{C}$ ), MA ( $T_m = 52.8^\circ\text{C}$ ) and BGE ( $T_b = 151.5^\circ\text{C}$ ) were from Sinopharm Chemical Reagent Co., Ltd.

### 2.2. Extrusion

Cellulose powder was dried under vacuum at  $70^\circ\text{C}$  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  $150^\circ\text{C}$ . The die temperature was  $140^\circ\text{C}$ . 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 zone 1 to zone 9 were set to 80, 80, 90, 100, 110, 110, 120, 120 and  $120^\circ\text{C}$ , and the die temperature was  $110^\circ\text{C}$ . After reactive extrusion, modified cellulose were washed with distilled water and alcohol successively

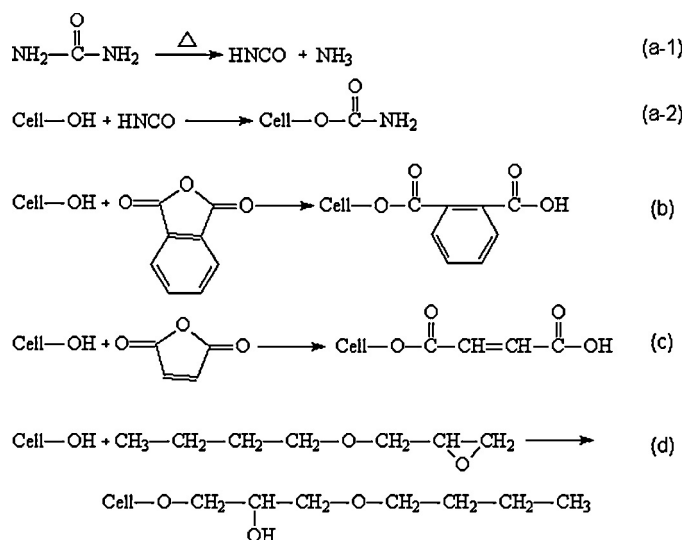


Fig. 1. The reaction mechanisms for (a) cellulose with urea, (b) cellulose with PA, (c) cellulose with MA, (d) cellulose with BGE.

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  $60^\circ\text{C}$  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.

### 2.3. Characterizations

Solubility test was evaluated by dissolution method. After 100 g BMIMCl solvent was heated to  $100^\circ\text{C}$ , an appropriate amount of cellulose samples was added into it with vigorous stirring for 10 min at  $100^\circ\text{C}$  to obtain a transparent cellulose solution. The remaining undissolved fractions were washed using water and acetone, respectively, and then dried at  $60^\circ\text{C}$  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  $2\text{ cm}^{-1}$  in the transmission mode.

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

Differential scanning calorimeter (DSC) was performed on Netzsch DSC PC 200 at heating rates of  $10^\circ\text{C}/\text{min}$ .

Thermal gravimetric analysis (TGA) was performed using a simultaneous thermal analyzer at heating rates of  $5^\circ\text{C}/\text{min}$  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.

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