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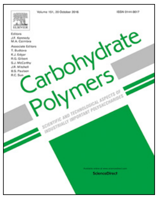

Regeneration of cellulose dissolved in ionic liquid using laser-heated melt-electrospinning

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ABSTRACT

A “green” and highly efficient route was proposed to fabricate ultrafine cellulose fibers. The processing steps include cellulose dissolution, gel preparation, melt-electrospinning and fiber coagulation. High DP cellulose can be easily dissolved in 1-butyl-3-methylimidazolium chloride (BmimCl) when the blend was stirred at 110 °C for 2 h. The maximum solubility can reach up to 16.7 wt%. A homogeneous ternary cellulose/BmimCl/ethanol or cellulose/BmimCl/water gel was made by the methods of crystallization and casting for the purpose of fixing the shape of the cellulose/BmimCl solution. After laser-heating and electrospinning, multiple jets were ejected from the gel tip and then frozen on a super cold target. Pure cellulose fibers without beads and blocks were achieved after coagulation. The results of WAXD and FTIR indicated that the regenerated cellulose fibers were amorphous and chemically stable. More importantly, this approach can be applied to other polysaccharides for the preparation of ultrafine fibers.

1. Introduction

Cellulose is the most abundant renewable resource on the earth. Cellulose-based products have been applied in many important fields in the forms of fibers, films, composites, and textiles. Native cellulose is insoluble in most common organic solvents due to the ordered networks of strong hydrogen bonding and the interactions of van der Waals' force. An ideal solvent to dissolve cellulose should meet the criteria of high solubility, rapid dissolution, low toxicity, and insensitive to side-reactions (Seoud, Koschella, Fidale, Dorn, & Heinze, 2007). Several non-derivatizing solvents were developed since the 1930s such as *N*-methylmorpholine-*N*-oxide (NMMO, for Lyocell process), lithium chloride / *N,N*-dimethylacetamide (LiCl/DMAc), and dimethylsulfoxide / tetrabutylammonium fluoride (DMSO/TBAF) (Pinkert, Marsh, & Pang, 2010). Although these solvents have been established for mass production or chemical analysis, the problems of toxicity, flammability, and poor recyclability are still to be resolved.

Among new potential solvents, ionic liquids (ILs) were regarded as the “Alkahest” during the past two decades, since ILs can dissolve most native polysaccharides (cellulose, chitin, starch, etc.) and proteins (silk, wool, collagen, etc.) (Meli, Miao, Dordick, & Linhardt, 2010). In addition, ILs are also regarded as “green” solvents due to their unique characteristics such as low vapor pressure, noninflammability and chemically stable, which are benefit for recycling (Laus et al., 2005). Swatloski and co-workers first succeeded in dissolving cellulose with 1-butyl-3-methylimidazolium chloride, and the maximum solubility can reach up to 25 wt% by using microwave heating (Swatloski, Spear, Holbrey, & Rogers, 2002). Since then, multiple ILs made up of different cations and anions were synthesized with the objective dissolving native cellulose more efficiently. A consensus has been reached that ILs with the ions of imidazolium, pyridinium, formate, acetate and chloride have a high cellulose-dissolution capacity (Pinkert et al., 2010). 1-butyl-3-methylimidazolium chloride (BmimCl) and 1-allyl-3-methylimidazolium chloride (AmimCl), in particular, are the two most popular ILs in the known commercial products. The cellulose-dissolving conditions of BmimCl and AmimCl have been carefully studied as well (Pinkert, Marsh, Pang, & Staiger, 2009). Unlike the common solvents, cellulose may decompose in ILs due to the breakdown of the β-1,4-glycosidic bonds (Zhang, Wu, Zhang, & He, 2005).

The cellulose, which was dissolved in IL, was often processed into films by using casting. IL as a solvent can be washed off by distilled water or by ethanol (Turner, Spear, Holbrey, & Rogers, 2004). The quality of the cellulose film largely depends on the processing parameters of thickness and concentration (Zhang et al., 2005). Kadokawa

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et al first reported a gelation method to fix the shape of the cellulose/IL mixture (Kadokawa, Murakami, & Kaneko, 2008). In comparison with film casting, the cellulose fibers prepared from cellulose/ILs spinning dope is much more complicated. Various ILs were tried to fabricate dry-wet-spun cellulose fibers, whose mechanical properties were very close to the mechanical properties of the Lyocell fibers (Cai, Zhang, Guo, Shao, & Hu, 2010; Hauru, Hummel, Nieminen, Michud, & Sixta, 2016; Kosan, Michels, & Meister, 2007). However, for electrospinning, the high viscous spinning dopes easily stuck at the needle. The addition of organic co-solvents, namely organic electrolyte solutions (OESs), can efficiently reduce the viscosities of the spinning dopes (Clough, 2017). Xu et al studied the spinnability of electrospun cellulose fibers by using the AmimCl/DMSO as an OES (Xu et al., 2008). As a result, the Rayleigh instability was suppressed and the stability of jet whipping was enhanced with the addition of the DMSO (Xu et al., 2008). Later, Ahn et al studied the effects of dimethylformamide and dimethylacetamide as the co-solvents on the properties of the electrospun cellulose fibers (Ahn et al., 2012). Nonetheless, the OESs, to some extent, still contain the hazardous organic solvents and the cost of recycling would increase as well. 1-ethyl-3-methylimidazolium acetate, a low viscous IL, was selected to dissolve cellulose in 8 wt% (Freire et al., 2011). As a result, nanosized cellulose fibers with smooth surface were produced (Freire et al., 2011). In addition, the electrospinning equipped with a heater, called melt-electrospinning, is another choice to minimize the viscosity of spinning dopes. The technique has been extensively developed by the research groups of Joo (Zhmayev, Cho, & Joo, 2011; Cho, Zhmayev, & Joo, 2011; Zhmayev, Cho, & Joo, 2010), Ogata (Ogata, Lu et al., 2007; Ogata, Shimada, Yamaguchi, Nakane, & Ogihara, 2007; Ogata, Yamaguchi et al., 2007), Yang (Li et al., 2014; Liu, Zhao, Zhang, Zhang, & Yang, 2012), and Dalton (Brown, Dalton, & Hutmacher, 2016; Dalton, Grafahrend, Klinkhammer, Klee, & Möller, 2007; Hrynevich et al., 2018; Ruijter et al., 2018). Quan et al processed cellulose-IL spinning dopes through melt-electrospinning, but with this method beads and blocks cannot be eliminated (Quan, Kang, & Chin, 2010).

The main objective of this paper is to fabricate ultrafine cellulose fibers through an eco-friendly and highly efficient method. To this end, the effects of dissolving parameters on DP and thermal properties of the regenerated cellulose will be studied first; the methods of cellulose gelation will then be discussed; afterwards, the morphology, the crystalline structure and the chemical reaction of the cellulose fibers will be evaluated by SEM, WAXD and FTIR.

2. Experimental

2.1. Materials

Raw cellulose (DP = 1053, W-400 G, Nippon Paper Industries Co., Ltd., Tokyo); 1-butyl-3-methylimidazolium chloride (BmimCl, melting temp. = 70 °C, Sigma Aldrich); Lithium chloride (LiCl, anhydrous, Nacalai Tesque, Inc., Kyoto); *N,N*-Dimethylacetamide (DMAc, Nacalai Tesque, Inc., Kyoto).

All the materials were used as received without further purification.

2.2. Experimental routes

Scheme 1 shows the route to fabricate cellulose fibers. This route mainly consists of four steps.

(I) **Dissolution of cellulose.**

The raw cellulose was dried at 70 °C for two days before using. The ionic liquid, BmimCl, was stored in a vacuum box to keep it dry. Certain proportions of cellulose and BmimCl were mixed under nitrogen atmosphere. To facilitate the dissolving process, the mixture was vigorously stirred at 110 °C for at least two hours. A clear and homogeneous solution was obtained when the cellulose was completely dissolved.

- **Preparation of cellulose/BmimCl gels.**

Since the cellulose/BmimCl solution was not solid at room temperature, two methods were carried out for gelation. For a low cellulose concentration (Conc. ≤ 9.1 wt%), the solution was pumped into a Teflon tube (inner diameter = 1.5 mm) and the tube ends were sealed for crystallization. The crystallized solution was then immersed in an ethanol bath for one minute. A portion of ethanol would permeate into the crystallized solution for gelation. At last, the free ethanol sticking on the rod was removed though a vacuum-drying process.

For high concentration (Conc. > 9.1 wt%), the viscous solution was casted on a heated poly(ethylene terephthalate) template with a thickness of 1 mm. The solution absorbed water as it was exposed to a humidity atmosphere (52%) for over 12 h, resulting in a liquid-to-gel phase transition. As a result, ternary cellulose/BmimCl/ethanol and cellulose/BmimCl/water gels are formed.

- **Laser-heated melt-electrospinning.**

The system was made up of a CO_2 laser (PIN-30R, Onizuca Glass Co., Ltd, $\lambda = 10.6\ \mu m$), a high voltage supply (Model-600 F, Pulse Electronic Engineering), a feeder, a holder, and a target. The voltage, the output power of laser, the feeding speed, and the nozzle-to-target distance were fixed at 18 kV, 10 W/cm^2, 93 μm/s and 5 cm, respectively. The metal target (90 × 90 mm) was filled with liquid nitrogen to freeze and collect the as-spun fibers. The temperature on the target surface can reach to -40 ± 3 °C.

- **Coagulation of cellulose fibers.**

After spinning, the as-spun fibers would put into an ethanol bath for coagulation. For a sufficient coagulation, the as-spun fibers were washed twice and the ratio of ethanol to cellulose was approx. 1 L to 1 g.

2.3. Characterizations

2.3.1. Scanning electron micrographs (SEMs)

The SEMs were taken by using a VE-7800 (KEYENCE) microscope at an electron voltage of 10 kV after samples were subjected to Au coating (IB-2, Eiko Engineering, Co., Ltd. Yamazaki, Japan) at a current of 7 mA for 3 min.

2.3.2. Wide angle X-ray diffractions (WAXDs)

The WAXDs were performed by using RINT-2500 (Rigaku, λ (Cu-Kα) = 1.5418 Å), operating at 50 mA and 40 kV. The crystallinities of cellulose I ($X_{c\text{-}I}$) and cellulose II ($X_{c\text{-}II}$) can be calculated from Eqs. (1) and (2) according to the Segal method (Segal, Creely, Martin, & Conrad, 1959):

$$X_{C-I} = \frac{I_{(200)} - I_{am}}{I_{(200)}} \times 100 \tag{1}$$

$$X_{C-II} = \frac{I_{(1\bar{1}0)} - I_{am}}{I_{(1\bar{1}0)}} \times 100 \tag{2}$$

where $I_{(200)}$ is the maximum intensity at 2θ = 22.5° for cellulose I; $I_{(1\bar{1}0)}$ is the maximum intensity at 2θ = 20.8° for cellulose II; I_{am} is the intensity at 2θ = 18° for cellulose I and 2θ = 16° for cellulose II.

2.3.3. Degree of polymerization (DP)

The intrinsic viscosity ($[\eta]$) was measured by using an Ubbelohde viscometer. The relationship between intrinsic viscosity and molecular weight (M_v) was estimated from the Mark-Houwink-Sakurada (MHS) equation (McCormick, Callais, & Hutchinson, 1985),

$$[\eta] = K\, M_v{}^{\alpha} \tag{3}$$

where $K = 1.278 \times 10^{-4}$ and $\alpha = 1.19$ for the solvents of DMAc/LiCl