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Crystalline characteristics of cellulose fiber and film regenerated from ionic liquid solution

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ABSTRACT

Regenerated cellulose fiber, fiber extrudate, and film were produced from cellulose solution prepared with raw pulp and ionic liquid solvent 1-butyl-3-methylimidazolium chloride ([BMIM]Cl). Spinning setting was based on a dry-jet and wet-spun approach including extrusion, coagulation, drawing, drying, and winding. Crystallization of the experimental fiber, fiber extrudate, and film was evaluated using a technique of wide angle X-ray diffraction (WAXD). Crystallinity index, crystallite size, and crystal orientation factor were calculated and compared among these samples. Influence of die shape, die dimension, and drawing speed on the regenerated cellulose crystallinity was discussed. The study indicated that the pulp cellulose was a Cellulose I type structure. The cellulose regeneration from the [BMIM]Cl solution completed a transformation from this intermediate phase to a final Cellulose II phase. The die shape and dimension and drawing speed were all important factors affecting the crystallinity of regenerated cellulose fiber and film.

1. Introduction

Current rayon production capacity accounts for approximately 5% of the world man-made fiber production. It is predicted that global rayon production and demand will grow at an increasing rate of 3.8% per year from 2009 to 2014 (Blagoev, Bizzari, & Inoguchi, 2011). Although rayon fiber is still a major regenerated cellulose fiber commercially available for many end uses, its manufacturing approach is making a significant environment impact because of heavy use of strong acids and bases and high consumption of water and energy. Recent cellulose research has paid much attention to ionic liquids that can be ideal green solvents for dissolving raw cellulose in the production of regenerated cellulose fiber (Gutowski et al., 2003; Hesse-Ertelt, Heinze, Kosan, Schwikal, & Meister, 2010; Kosan, Dorn, Meister, & Heinze, 2010a; Rogers, Holbrey, Spear, & Swatloski, 2002; Swatloski, Holbrey, Weston, & Rogers, 2006; Swatloski, Spear, Holbrey, & Rogers, 2002; Wang, Gurau, & Rogers, 2012). Ionic liquids are a type of organic salts having a liquid phase below boiling temperature. Their cationic component determines chemical stability, while their anionic part plays an important role in chemical reaction (Fukaya, Sugimoto, & Ohno, 2006; Greaves & Drummond, 2013; Hu et al., 2013; Kosan, Michels, & Meister, 2008; Wang, Gurau, Kelley, Myerson, & Rogers, 2013). Compared to the widely used rayon technology and Tencel®/Lyocell® technology (Fink, Weigel, & Purz, 2001; Hayhurst & Banks, 2005; Kosan, Dorn, & Meister, 2010; Liu & Hu, 2006; Wendler, Graneß, Büttner, Mechtler, & Heinze, 2006; Wendler, Graneß, & Heinze, 2005), it is found that the use of ionic liquids for making cellulose solutions renders several advantages such as lower dissolving temperature (below 100 °C) and vapor pressure, lower to zero toxicity, better thermal stability, no hydrolysis, and easy solvent recovery (Hermanutz, Gaehr, Uerdingen, Meister, & Kosan, 2008; Zhao et al., 2012; Zhu et al., 2006). These technical attractions drive a lot of research investigation.

Fabrication of regenerated cellulose fiber using the ionic liquid solvent 1-butyl-3-methyllimidazolium chloride ([BMIM]Cl) was first reported in Michels and Kosan's (2005) work. They found that a transformation of cellulose I to cellulose II occurred after [BMIM]Cl dissolution and cellulose precipitation in water bath, as previously observed in lyocell spinning that uses *N*-methylmorpholine-*N*-oxide monohydrate (NMMO) for cellulose dissolution. This result was also mentioned in the work of Cai, Zhang, Guo, Shao, and Hu (2010). Similar work on using [BMIM]Cl to dissolve bagasse cellulose for fiber spinning was reported (Jiang, Sun, Hao, & Chen, 2011). Regenerated cellulose fiber was also produced from cellulose solutions prepared by the ionic liquids 1-ethyl-3-methylimidazolium acetate ([EMIM]Ac) and 1-ethyl-3-methylimidazolium diethyl phosphates ([EMIM]DEP) (Ingildeev,

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Effenberger, Bredereck, & Hermanutz, 2013), for a comparison with the cellulose fiber regenerated from NMMO solution. Kosan et al. conducted a comparative study on the four ionic liquids, [BMIM]Cl, 1-*N*-butyl-3-methylimidazolium acetate ([BMIM]Ac), 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl), and [EMIM]Ac, for the dissolution and regeneration of cellulose (Kosan et al., 2008). In a study reported recently, [EMIM]Ac solvent was applied to the preparation of cellulose solution mixed with polysaccharide particles (Wendler et al., 2010).

Overall, the research efforts mentioned above were focused mainly on solute solubility, solution viscosity, fiber spinning process, fiber tensile strength, and fiber crystallinity. To deal with ionic liquids, understanding how they work for dissolving cellulose polymer would be critical to both researchers and fiber manufacturers. Further research is needed to continue the investigation on ionic liquids in terms of their efficiency for cellulose dissolution, mechanism of cellulose crystallization during fiber coagulation, and processability for cellulose fiber spinning, so that the rayon industry would be able to produce regenerated cellulose fiber using ionic liquids as an eco-friendly new solvent system. This paper presents a study on the materials of regenerated cellulose fiber and film fabricated from a [BMIM]Cl solution. A major purpose of this work was to examine influences of spinning conditions on cellulose crystallization taken place during fiber/film precipitation in water bath.

2. Materials and methods

2.1. Solution preparation and fiber/film spinning

Raw materials used in the study were commercial grade southern pine pulp with a DP of 1900 and [BMIM]Cl solvent (purity > 95%) purchased from Sigma-Aldrich Corp., USA. The fabrication of regenerated cellulose fiber/film involved two steps: dissolution of cellulose in [BMIM]Cl to make spinning dope and extrusion of the spinning dope to form regenerated cellulose fiber and film. Experimental procedure used in this study was the same as that described in the previous publication (Jiang et al., 2011). In brief, the cellulose solution with 6 wt% cellulose concentrations was prepared by adding ground wood pulp into [BMIM]Cl solvent for dissolving under controlled heating and vacuuming. The obtained cellulose solution was fed into a desk-top screwless extruder for extruding the solution into a water bath where cellulose fiber/film was precipitated when the ionic liquid was washed away by tap water. Rotor speed of the extruder was controlled within 169 – 221 rpm. Spin header was heated to 100 °C for spinning with a 30-mm air gap above the spin bath. Regenerated cellulose fiber was drawn at a spin-draw ratio between 10 and 30, dried when passing through a tube with 80–100 °C hot air flow, and finally wound onto a spool using a winding device with a winding speed ranging from 80 to 225 mm/s. The experimental fiber ran a second-time washing and drying under the same dry setting.

2.2. Characterization of fiber/film crystallinity

To investigate the degree of crystallinity, crystal size, and crystallite orientation of the regenerated cellulose fiber and film, the technique of wide angle X-ray diffraction (WAXD) was used. X-ray diffraction patterns of pulp board, cellulose fiber, and film were measured by the WAXD instrument RAPID II (Rigaku Americas Corporation). The instrument has a curved imaging plate area detector which is able to collect the complete Debye rings of samples measured in transmission. A bundle of cellulose fibers were mounted vertically on the gonimeter. During measurements, the fiber sample rotated at a constant speed of one degree per second. Since fiber samples were mounted vertically and rotated constantly (or rotationally symmetric), the φ setting has little effect on the diffraction patterns. For pulp board and cellulose film, a strip of sample cut along the machine direction was mounted vertically on the gonimeter. The position of sample was fixed with a surface perpendicular to the X-ray direction during measurement. All the tests lasted for 90 min. Blank tests were run under the same conditions as fiber and film X-ray diffraction. The 2-D images of blank tests were removed from the 2-D images of fiber and film X-ray diffraction to reduce the effect of background diffraction. The meridional reflections of fiber have a maximum intensity at the Bragg angle. Based on the amount of the meridional reflection, which have a maximum intensity, different percent crystallinities of cellulose samples would be determined. The experimental X-ray diffraction patterns were simulated by the following mathematical model (Ruland, 1961; Vonk, 1973; Hindeleh & Johnson, 1974; Jing, Zhang, & Wu, 2002):

$$Y = \sum_{i=1}^{n} Q_i + R \tag{1}$$

where

$$Q_i = f_i G_i + (1 - f_i) C_i$$

$$R = a + bx + cx^2 + dx^3$$

In the above equations, Y is the total diffraction intensity of all crystalline and non-crystalline parts; Q_i is individual diffraction intensity from each crystal part; G_i and C_i are Gaussian and Lorentz functions, respectively; f_i is a fractional parameter; n is the number of total diffraction peaks; R is the intensity of amorphous halo from non-crystalline part; and a, b, c, and d are four constants. All the parameters in the model above were determined using a least squares regression method (curve fitting) which was implemented by the MATLAB curve fitting program. The parameters for crystalline peaks of Cellulose I and II were used as the initial input parameters of the model in Eq. (1).

The fiber/film crystallinity index (CI) could be calculated by a ratio between sum of area under each crystalline peak and area under the experimental diffraction curve:

$$CI = \frac{\text{sum of area under each crustalline peak } (Q_i)}{\text{area under experimental diffraction curve}} \tag{2}$$

In this analysis of crystallinity index, an assumption was made that the amorphous contribution is the only contribution to the X-ray diffraction peak broadening. Other factors such as crystallite size which might contribute to the peak broadening were not considered a contributor to the diffraction peak broadening (Garvey, Parker, & Simon, 2005).

The cellulose uniaxial crystallite orientation along fiber axis is determined by the Herman's crystal orientation factor f_c defined as:

$$f_c = 1 - \frac{3}{2}\left(\frac{\int_0^{\pi/2} I(\varphi)\sin^3\varphi d\varphi}{\int_0^{\pi/2} I(\varphi)\sin\varphi d\varphi}\right) \tag{3}$$

where $I(\varphi)$ is intensity of scattered diffraction and φ is azimuthal angle (Krassig, 1996). For cellulose film, a biaxial orientation factors should be used. It was reported that the crystalline orientation of polymer films is closely related to that in the polymer fibers. We would only calculate the uniaxial orientation factor of fibers in this study.

The crystallite size L is calculated by the Scherrer equation:

$$L = \frac{k\lambda}{\beta \cos\theta} \tag{4}$$

where k is a geometrical Scherrer constant ($k = 0.94$); λ is the X-ray wave length (for Cu radiation $\lambda = 1.54$ Å); β is the intensity of full