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Structure and properties of regenerated cellulose fibers from different technology processes

Guansen Jiang[a], Weifeng Huang[a], Lin Li[b], Xiao Wang[a], Fengjian Pang[b], Yumei Zhang[a,*], Huaping Wang[a]

[a] State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, Shanghai 201620, China
[b] Shandong Helon Co., Ltd, Shandong 261000, China

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ABSTRACT

The crystalline and microstructure of the regenerated cellulose fibers prepared from different solvents and technology processes were investigated by synchrotron wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS). WAXD results indicated that the crystal orientation, crystallinity of Lyocell and IL-cell fibers were higher than those of Viscose and Newdal fibers. The size of micro-voids located in the cross-section of regenerated cellulose fibers was analyzed based on the results of SAXS. And the technology process had little effect on the radius of the micro-voids. The micro-voids in Viscose and Newdal fibers have longer length (L) and greater misorientation (B_Φ) than that in Lyocell and IL-cell fibers. This reveals that the average void volumes of Viscose and Newdal fibers were larger. Furthermore, the regenerated cellulose fibers from dry-jet-wet-spinning process exhibited completely a higher E-modulus, tenacity than the fibers spun by wet-spinning method did.

1. Introduction

Polymers from renewable resources have attracted much attention because of their biodegradability and potential to replace petrochemicals in many fields. Cellulose as a linear polysaccharide exhibited outstanding properties and wide applications, and became the most abundant renewable polymeric material.

However, processing of cellulose is difficult in general as this natural polymer does not melt or solve in usual solvents due to its inter- and intra-hydrogen bond, partially crystalline structure. Moreover, the traditional Viscose technologies to produce cellulose-regenerated materials caused serious environmental burdens. Therefore, new processing approaches have long been scrutinized to avoid complicated processing routes and hazardous byproducts (Fink, Weigel, Purz, & Ganster, 2001).

It is found that cellulose can swell and dissolve in several solvents, such as N-methylmorpholine-N-oxide (NMMO) (Fink et al., 2001), dimethyl sulfoxide (DMSO)/paraformaldehyde (PF), N, N-dimethylacetamide (DMAc)/lithium chloride (LiCl) and alkali solutions (Roy, Budtova, & Navard, 2003) and ionic liquids (ILs) (Swatloski, Spear, Holbrey, & Rogers, 2002). Among those solvents mentioned above, only the use of NMMO/H_2O in its process of commercialization has made technical breakthroughs and lead to a new man-made cellulose fibers with the generic name, Lyocell (Fink et al., 2001).

Swatloski et al. (2002) first reported that ILs could be used as another direct solvent for cellulose without derivatization, which disclosed another new solvent for cellulose following NMMO/H_2O. Since then, numbers of ILs dissolving cellulose have been found (Fukaya, Hayashi, Wada, & Ohno, 2008; Fukaya, Sugimoto, & Ohno, 2006; Zhang, Wu, Zhang, & He, 2005). The dissolving ability and mechanism, the solution properties and the processing ability related to cellulose and ILs have been reported (Kosan, Michels, & Meister, 2008; Kosan, Schwikal, & Meister, 2010; Moulthrop, Swatloski, Moyna, & Rogers, 2005; Remsing, Swatloski, Rogers, & Moyna, 2006; Youngs, Hardacre, & Holbrey, 2007; Youngs et al., 2006; Zhang et al., 2005, 2010). Besides, the cellulose could also be dissolved in ILs with other material formed the composite (Kadokawa, Murakami, Takegawa, & Kaneko, 2009; Murakami, Kaneko, & Kadokawa, 2007; Takegawa, Murakami, Kaneko, & Kadokawa, 2010; Zhang et al., 2007). As the unique advantage of ionic liquid in environment and specific chemical–physical properties, the potential industrial applications of ILs were developed.

The preparation of regenerated cellulose fibers through direct dissolution not only overcome the tedious technology for producing conventional Viscose fibers, but also exhibited a series of unique performance (Kosan et al., 2008). The mechanical properties of

* Corresponding author. Tel.: +86 021 67792957; fax: +86 021 67792855.
E-mail addresses: jgs115@126.com (G. Jiang), yellow11bee@163.com (W. Huang), lilin3285@163.com (L. Li), wxmelora@163.com (X. Wang), pangfj@163169.net (F. Pang), zhangym@dhu.edu.cn (Y. Zhang), wanghp@dhu.edu.cn (H. Wang).

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regenerated cellulose fibers vary according to processing technologies (Kosan et al., 2008). Compared with the Viscose fibers (Fink et al., 2001), for example, the regenerated cellulose fibers prepared from the direct dissolution technology showed larger tenacity and modulus and lower elongation. It is known that the mechanical properties depend on the micro-morphology structure which is influenced by the processing technology. Although the mechanical properties of regenerated cellulose fibers from different technology have been reported, the details of the relationship between the properties and structure need further research.

In this article, the regenerated cellulose fibers were prepared from the traditional and modified Viscose technology, NMMO and ILs technology, respectively. The morphology and structure of the regenerated cellulose fibers, including the surface and cross-section morphology, the orientation of the chain, the crystalline structure and the micro-voids, are discussed to explain the relationship between the structure and mechanical properties of the cellulose fibers.

2. Experimental

2.1. Materials

The Viscose, Newdal, Lyocell and IL-cell fibers were spun from different technology processes, which include the traditional and modified Viscose process, NMMO and ILs process.

Viscose (Helon®, Shandong Helon Co. Ltd., China), was spun with a conventional wet-spinning process from cellulose pulp (degree of polymerization (*DP*): 450–550, Shandong Helon Co. Ltd., China).

Newdal (Newdal®, Shandong Helon Co. Ltd., China) is the high wet modulus fiber, supplied by Shandong Helon Co. Ltd., China, which was spun with a modified Viscose process from cellulose pulp (*DP*: 600–900, Shandong Helon Co. Ltd., China).

Lyocell (Tencel®, Lenzing Group, Austria), was spun with a dry-jet-wet-spinning process from cellulose pulp (*DP*: 500–900, Lenzing Group, Austria) with NMMO as solvent.

IL-cell, prepared in Shandong Helon Co. Ltd., China, was spun with a dry-jet-wet-spinning process from cellulose pulp (*DP*: 500–800, Shandong Helon Co. Ltd., China) with 1-N-butyl-3-methylimidazolium chloride ([BMIM]Cl) as solvent and water as coagulating bath.

2.2. Measurements

Wide-angle X-ray diffraction (WAXD) experiments were carried out at the Beam line (U7B) in the National Synchrotron Radiation Laboratory (NSRL) with a wavelength of 0.154 nm. A bundle of cellulose fibers were placed in a sample holder with the fiber direction perpendicular to the X-ray beam. The distance between the image plate (Mar 345) and the sample for WAXD was 213.5 mm. A typical image acquisition time was 180 s.

The 2D WAXD pattern was processed with the software package FIT2D (Hammersley, 1987–1997) to correct for air scattering.

The crystal orientation along the fiber axis was calculated by the Herman's orientation parameter (f_c) (Klug & Alexamder, 1954):

$$f_c = \frac{(3\langle\cos^2\varphi_{c,Z}\rangle - 1)}{2} \quad (1)$$

The orientation parameter $\langle\cos^2\varphi_{c,Z}\rangle$ was determined according to the Wilchinsky Model (1959) and crystal symmetry of regenerated cellulose fibers (Kolpak & Blackwell, 1976) with the characteristic reflections in equatorial, (1 1 0), (0 2 0) and ($\bar{1}$ 1 0). For the reflections ($h\,k\,l$), the orientation parameter $\langle\cos^2\varphi_{h\,k\,l}\rangle$ can be calculated from equation (Klug & Alexamder, 1954):

$$\langle\cos^2\varphi_{h\,k\,l}\rangle = \frac{\int_0^{\pi/2} I(\varphi_{h\,k\,l})\cos^2\varphi_{h\,k\,l}\sin\varphi_{h\,k\,l}d\varphi_{h\,k\,l}}{\int_0^{\pi/2} I(\varphi_{h\,k\,l})\sin\varphi_{h\,k\,l}d\varphi_{h\,k\,l}} \quad (2)$$

where $\varphi_{h\,k\,l}$ represents the azimuthal angle and $I(\varphi_{h\,k\,l})$ is the intensity along the ($h\,k\,l$) reflection.

The orientation parameter $\langle\cos^2\varphi_{h\,k\,l}\rangle$ of regenerated cellulose was evaluated from WAXD 2D detector images according to the method reported in the literature (Gindl, Martinschitz, Boesecke, & Keckes, 2006).

The crystallinity of regenerated cellulose was quantified from the WAXD pattern using the following procedures. On the basis of the 2D WAXD patterns of powder samples, which were corrected for air scattering, the integrated diffraction intensity profile was calculated. And from the curve-fitting process of this profile, the data were analyzed with Peak fit software (version 4.12, Seasolve Co., San Jose, CA). Then, the crystallinity was calculated according to Eq. (3):

$$W_{c,x} = \frac{I_c}{I_c + I_a} \times 100\% \quad (3)$$

where $W_{c,x}$ is the crystallinity, I_c and I_a are the total crystal peak area of the crystalline and the amorphous phases, respectively.

The average crystallite size $L_{h\,k\,l}$ perpendicular to the reflection planes ($h\,k\,l$) was determined according to the Scherrer's equation:

$$L_{h\,k\,l} = \frac{K\lambda}{B_{h\,k\,l}\cos\theta} \quad (4)$$

where λ is the wavelength of the X-rays, θ is half of the diffraction angle (2θ), $B_{h\,k\,l}$ is the half-width of reflection plane ($h\,k\,l$) and K is a constant that is commonly assigned a value of 0.9.

Birefringence measurements of fibers were carried out on an Olympus Co. (Tokyo, Japan) XP51 optical polarized light microscope with the aid of an Olympus CTB Berek compensator. Moreover the birefringence of regenerated cellulose fibers were calculated from the empirical equation as follows:

$$\Delta n = \frac{\theta\lambda}{180^\circ d} \quad (5)$$

where $\lambda = 0.589 \times 10^{-9}$ m; θ is the compensatory angle (°); d is the diameter of cellulose filament.

SAXS profiles were obtained at Beamline (16B1) in Shanghai Synchrotron Radiation Facility (SSRF). The wavelength used was 0.124 nm. A CCD X-ray detector (MAR CCD 165) was employed at a distance of 5053 mm from the sample. Tendon of ox (L = 65.0 nm) was used for calibration. A method of ionization chamber reading was used to subtract the background scattering from the air pathway and instrumentation. The corresponding profiles were normalized to beam intensity and corrected relative to an empty sample cell background. A typical image acquisition time was 40 s. The images were carried out using the software package FIT2D (Hammersley, 1987–1997).

For the regenerated cellulose fibers, it is known for us that the contribution for SAXS is mainly from the micro-voids due to the solution spinning process (Chen et al., 2006, 2007; Crawshaw & Cameron, 2000; Moss, Butler, Müller, & Cameron, 2002; Statton, 1956; Vickers, Briggs, Ibbett, Payne, & Smith, 2001). As the schematic diagram for the drawn cellulose fibers is illustrated in Fig. 2, the needle-shaped micro-voids and aligned parallel to the fiber direction caused a streak along the equator in SAXS. The radius of micro-voids with circles cross section can be described by Guinier