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Structure and properties of novel regenerated cellulose fibers prepared in NaOH complex solution

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ABSTRACT

Novel spinning solution, prepared by dissolving hydroxyethyl cellulose (HEC) owning a low molar substitution (*MS*) into NaOH/urea/thiouea aqueous solution with a specific weight ratio of 8:8:6.5, was employed to fabricate a new type of regenerated fibers by wet-spun method. The structure and properties of the resultant HEC fibers were characterized by ^{13}C NMR, FTIR, synchrotron WAXS, SEM, and tensile tester. The results showed that HEC fibers exhibited structure identical with HEC because of the physical dissolution and coagulation processes, but quite different from native cellulose due to partial breakage of hydrogen bonds and crystal transformation from cellulose I to cellulose II during cellulose modification. The resultant HEC fibers with relatively dense and homogenous structure displayed good moisture related properties and stayed stable in alkali solution with low concentration. Moreover, the novel fibers owned good dry mechanical properties in spit of their slightly poor wet mechanical properties comparable to viscose rayon, showing great potential in substituting the traditional viscose fibers.

1. Introduction

Cellulose, the most abundant renewable resource, is mainly used for the production of regenerated materials (fibers, films, sponges and so forth) and for the synthesis of cellulose derivatives (ethers and esters) (Klemm, Heublein, Fink, & Bohn, 2005). In particular, regenerated cellulose products, inheriting excellent merits from cellulose including biodegradability, biocompatibility and multitude of chemical derivations (Heinze & Liebert, 2001; Klemm et al., 2006), arouse fervent popular devotion and enthusiasm. Nevertheless, on account of the large amounts of network connecting hydrogen bonds and partially crystal structure, cellulose is hard to melt or dissolve in common solvent, which enormously hampered its development. Fortunately, the processing handicap could be overcome through chemical modification and caused significant changes in solubility of cellulose by introducing appropriate chemical entities (Abderahmane, El Barkany, Hassan, & Abdel-Karim, 2011; Heinze, 1998).

Currently, the most important large-scale technical route to produce regenerated cellulose fibers is the viscose process, which improves solubility of cellulose in sodium hydroxide (NaOH) by generating a metastable intermediate product cellulose xanthogenate. The process has ripened technically but is accompanied by environmental deleterious byproducts (CS_2, H_2S, heavy metals) (Fink, Weigel, Purz, & Ganster, 2001). Another new spinning process of producing cellulose fibers based on synthesizing a cellulose derivative is the CarbaCell process (Halidan & Wumanjiang, 2009; Yin et al., 2007; Yin, Shen, & Icafpm, 2009). However, the industrial application of CarbaCell process has been restricted until it resolves the problems of excessive energy consumption, high cost and organic byproducts in synthetic process. Therefore, more attentions have been paid to develop new ways to produce regenerated cellulose fibers avoiding complicated processing route and hazardous byproducts.

Recently, cellulose derivative hydroxyethyl cellulose (HEC) with low molar substitution (*MS*), as an alkali-soluble cellulose compound, was demonstrated to be an efficient alternative to the viscose process for yielding regenerated fibers in a non-polluting, cheap and short production cycle. HEC is one of the most widely studied nonionic cellulose ethers prepared by reaction of ethylene oxide (EO) with alkali-cellulose in a heterogeneous process. The resulting polymer consists of glycosyl units substituted in position 2, 3 or 6 with a hydroxyethyl group. HEC powders with various

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MS could be obtained by adjusting reagent quantities and reaction conditions. Different from commercial HEC with high *MS* of about 2.5, which has been employed in extensive utilizations (Erkselius & Karlsson, 2005; Guo, Skinner, Harcum, & Barnum, 1998; Sun, Sun, Wei, Liu, & Zhang, 2007), HEC with low *MS* is rarely mentioned, although it is actually a promising substitute for the traditional viscose process. With the introduction of slight hydroxyethyl groups, cellulose becomes soluble and shapeable in alkaline solution to produce films or fibers.

In our previous studies (Zhang, Li, Yu, & Gu, 2009; Zhang, Li, Yu, & Hsieh, 2010a), NaOH/urea/thiourea aqueous solution system was proved to dissolve cellulose rapidly and directly. In this work, it is planned to take advantage of the environmentally benign green solvent to obtain HEC spinning dope with high concentration. An initial exploration was made to prepare wet-spun regenerated fibers with the HEC spinning dope using a pilot machine, and then a series of techniques were used to clarify the structure and properties of HEC fibers. It provides a promising and meaningful pathway to develop the production of novel regenerated cellulose fibers.

2. Experimental

2.1. Materials

Cellulose powders (*DP* = 1000) were kindly supplied by Xiangtai Cellulose Corporation (Hubei Province, China). All chemical reagents of analytical grade were purchased from commercial resources in China and used without further purification. Viscose rayon, kindly supplied by Shandong Helon Co., Ltd., China, was manufactured with a conventional wet-spinning process.

2.2. Preparation of HEC samples

2.2.1. Synthesis of HEC

Cellulose powders pre-dried in the vacuum were immersed in 21 wt% NaOH aqueous solution with vigorous stirring at ambient temperature. Alkaline cellulose gained through squeezing was placed in a homemade 2 L stainless steel autoclave equipped with a vacuum and a mechanical stirrer. Certain amount of liquid EO was added into the vacuum autoclave simultaneously. The mixture was stirred at 40 °C for 100 min to make the gasified EO fully react with alkaline cellulose powders. The etherification reaction ended after the pressure inside the autoclave nearly return to the initial value. The as-product was neutralized with acetic acid, repeatedly rinsed with distilled water, and then dried under vacuum. The mass ratio of EO to alkaline cellulose was kept from 1:10 to 4:10, and the resultant 4 samples with different *MS* were named as HEC-1, HEC-2, HEC-3 and HEC-4.

2.2.2. Preparation of HEC spinning solutions

A certain amount of dried HEC-2 powders were immersed into the 8 wt% NaOH/8 wt% urea/6.5 wt% thiourea aqueous solution precooled to −10 °C. Transparent HEC solution with a concentration of 9 wt% was obtained after vigorously stirring at 0 °C for 2 h. It is difficult for original cellulose to dissolve in NaOH complex solutions at such a concentration (Cai & Zhang, 2005; Isogai & Atalla, 1998; Zhang, Li, Yu, & Hsieh, 2010a).

2.2.3. Preparation of HEC fibers

After centrifuged at 5000 rpm for 30 min to remove the air bubble, the HEC solution was transferred to a spinning tank. A simple pilot scale wet-spinning apparatus reported in our previous work (Zhang & Luo, 2011) was used to prepare regenerated cellulose fibers. A pressure of 0.1 MPa was applied to the spinning solution to extrude it through a spinneret filling with 24 orifices (0.1 mm in diameter). The spinneret cylinder was immersed directly into the coagulation bath composed of 12 wt% H_2SO_4 and 10 wt% Na_2SO_4 at 20 °C. The apparent jet stretch ratio (the ratio of the take-up velocity to the dope extrusion velocity) was 70%. The fibers were subsequently washed until the pH value of the fibers was about 7, and further drawing-up was conducted where the post-drawing ratio was adjusted to be 110%. The fibers were gradually dried by a heating roller (surface temperature 80 °C) and winded on a spool.

2.3. Characterization

2.3.1. MS determination of HEC samples

MS was determined by the gas–liquid chromatography (GLC) method (Alvarez-Lorenzo, Lorenzo-Ferreira, Gomez-Amoza, Souto, & Concheiro, 1999; Wu, Shao, Zhang, & Wang, 2009). HEC was reacted with hydroiodic acid, producing 1 mol of ethyl iodide per mole of hydroxyethyl substituent, and these products were then extracted from the reaction mixture with o-xylene and quantified by GLC using toluene as internal reference. The GLC was performed on a GC-7800 chromatograph (Labthink, China).

2.3.2. Solubility determination of HEC samples

The solubility of different HEC samples was evaluated by putting them dispersed into water at 25 °C and 8 wt% NaOH aqueous solution at 0 °C, respectively. The swelling and dissolving processes of HEC samples in them were qualitatively assessed by XPR-500 polarized optical microscopy (POM, Caikang Optical instrument Co., Ltd., Shanghai, China) equipped with a digital camera.

HEC-1 and HEC-2 samples were dissolved in 8 wt% NaOH aqueous solution and 8 wt% NaOH/8 wt% urea/6.5 wt% thiourea aqueous solution at 0 °C, respectively, and solutions with various concentration were prepared. The maximum concentration of HEC entirely dissolved in both solvents was considered as the solubility.

2.3.3. Nuclear magnetic resonance (^{13}C NMR) measurement

Solutions with concentration of 6 wt% for ^{13}C NMR (Bruker AV 400, Switzerland, magnetic field 9.4 T) measurements were prepared by dispersing the required amount of cellulose powders, HEC and regenerated fibers into the solvent (8 wt% NaOH/8 wt% urea/6.5 wt% thiourea/77.5 wt% D_2O) at −10 °C with vigorous stirring in a 5 ml tube, respectively. The solvent and solution were injected into NMR tubes using syringes and the measurements were carried out at room temperature.

2.3.4. Fourier transformed infrared spectroscopy (FTIR) measurement

The FTIR spectra were recorded on an attenuated total reflection Fourier transform infrared (ATR-FTIR) instrument (Nicolet Nexus 670, Thermo Fisher, USA) in the range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1}.

2.3.5. Synchrotron wide angle X-ray scattering (WAXS) measurement

The crystal structures of cellulose powders, HEC powders and regenerated fibers were investigated by the WAXS measurements carried out at 16B1 Beamline station in Shanghai Synchrotron Radiation Facility (SSRF) with a wavelength of 0.124 nm. A CCD X-ray detector (MAR CCD-165) was used at a distance of 90 mm from the sample and a typical image acquisition time was 100 s. The diffraction patterns of samples were processed with software package FIT2D in order to correct the air scattering and obtain the integrated intensity profiles. The crystallinity of samples was quantified from the integrated diffraction intensity profiles.

2.3.6. Scanning electron microscope (SEM) measurement

Morphologies of the regenerated HEC fibers were researched by SEM (Hitachi S-6000, Japan). The samples were fractured in

liquid nitrogen to reveal the cross sections for SEM measurement. All the samples were sputtered with gold and then observed and photographed.

2.3.7. Evaluation of water retention value (WRV)

1.0 g of samples was soaked into distilled water for 2 h at ambient temperature, and then centrifuged at a relative centrifugal force (RCF) of 1000 × *g* for 20 min, after which the weight of the wet fibers was measured as W_0. Subsequently, the sample was dried at 105 °C until their mass kept constant, and reweighed to be W_1. The water retention value (WRV) was calculated from Eq. (1):

$$\text{WRV}\ (\%) = \frac{W_0 - W_1}{W_1} \times 100 \quad (1)$$

2.3.8. Evaluation of moisture regain

Moisture regain of HEC fibers was determined with the method described in standard ATSM D1348. About 1.0 g of HEC fibers or viscose rayon, conditioned in a standard atmosphere of 65% RH at 20 °C for a minimum of 24 h, were weighed (W_a), dried in an oven at 105 °C for 4 h and reweighed (W_b). Moisture regain was determined by the following equation (Eq. (2)):

$$\text{Moisture regain}\ (\%) = \frac{W_a - W_b}{W_b} \times 100 \quad (2)$$

2.3.9. Stability of HEC fibers in alkali solution

Weight loss of cellulose fibers during the treatment of alkali was determined. 1.0 g of fibers was conditioned at 65% RH and 20 °C for 24 h and weighed (W_1). The HEC fibers or viscose rayon were immersed in 1 wt% and 8 wt% NaOH aqueous solution at 20 °C for 24 h with a bath ratio of 1:10 (w/w), respectively. After filtration, the insoluble fiber fractions were isolated and poured into 5 wt% H_2SO_4 for neutralization, subsequently washed with water and acetone, and dried at 105 °C to constant weight. Then the fibers were conditioned at 65% RH and 20 °C for 24 h again and reweighed (W_2). The solubility of cellulose fibers was calculated from Eq. (3)

$$\text{Solubility}\ (\%) = \frac{W_1 - W_2}{W_1} \times 100 \quad (3)$$

2.3.10. Tensile test of HEC fibers

Tensile strength of the HEC fibers and viscose rayon were measured on a universal tensile tester (XQ-1, Donghua University, China) according to the standard method ASTM D3822-01. The fiber samples were preconditioned for 1 day so that they would reach the standard atmospheric equilibrium of 65% relative humidity (RH) at 20 °C. A gauge length of 20 mm was employed and the tensile speed was 20 mm/min. The statistical results came from 30 measurements for each specimen.

Table 1
Solubility of HEC with different *MS* in NaOH aqueous solution and water.

Sample	Mass ratio of EO to cellulose	*MS*	8 wt% NaOH solution	water
Cellulose	0	0	×	×
HEC-1	1:10	0.19	●	×
HEC-2	2:10	0.30	●	×
HEC-3	3:10	0.54	●	■
HEC-4	4:10	0.81	●	●

×: hard to dissolve in this solvent; ●: entirely or partially dissolve in this solvent; ■: dramatically swell, unsuitable for spinning.

3. Results and discussion

3.1. Determination of MS and solvent for HEC spinning dope

HEC, prepared by reaction of EO with alkali-cellulose in a heterogeneous process, evidently improves its solubility due to the reduced density of hydrogen bonds and then the partial destroying of crystal structure during the modification process. HEC at various *MS* levels can be produced through adjusting the mass ratio of EO to cellulose in reaction, each of which displays different properties including solubility and fiber formation. The solubility of HEC with different *MS* in 8 wt% NaOH aqueous solution and water was presented in Table 1. It was clear that the HEC solubility increased rapidly with increasing the *MS* of HEC. However, the continuous rising in *MS* brought about excessive swelling or even partial dissolution in water, which may hamper the steady spinning progress. For example, HEC-3 and HEC-4 samples with *MS* values more than 0.30 had excellent solubility in NaOH aqueous solution. The as-spun fibers prepared by spinning solution of HEC with higher *MS* value were inclined to be dramatically swollen in water bath, which was proved unsuitable for continuous spinning.

Furthermore, the solubility of HEC samples was evaluated by maximum concentration of HEC entirely dissolved in NaOH or NaOH/urea/thiourea solution. The results showed that HEC-1 and HEC-2 had the maximum concentration of 5 wt% and 8 wt% in NaOH solvent, while the corresponding maximum concentrations of 7 wt% and 13 wt% in NaOH/urea/thiourea solvent were found to the two pulps. Obviously, NaOH/urea/thiourea aqueous system was more powerful in dissolving HEC than NaOH aqueous solution, and the reason may be attributed to the combined actions of NaOH, urea and thiourea (Jin, Zha, & Gu, 2007). In the complex solvent, NaOH breaks the intermolecular hydrogen bonding of HEC macromolecules, while urea and thiourea acted as a layer outside that prevents the association of HEC macromolecules and leads to the dispersion of HEC chains in NaOH complex solvent. Fig. 1 showed the POM photographs of HEC-2 dissolved in the two alkali solvent systems at the concentration of 9 wt% at the same dissolving

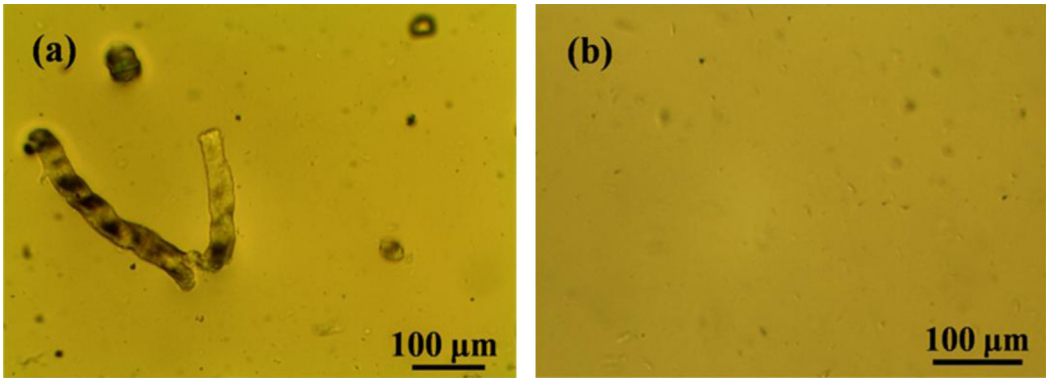

Fig. 1. POM photographs of HEC-2 dissolved in (a) NaOH aqueous solution and (b) NaOH/urea/thiourea aqueous solution at the concentration of 9 wt%.

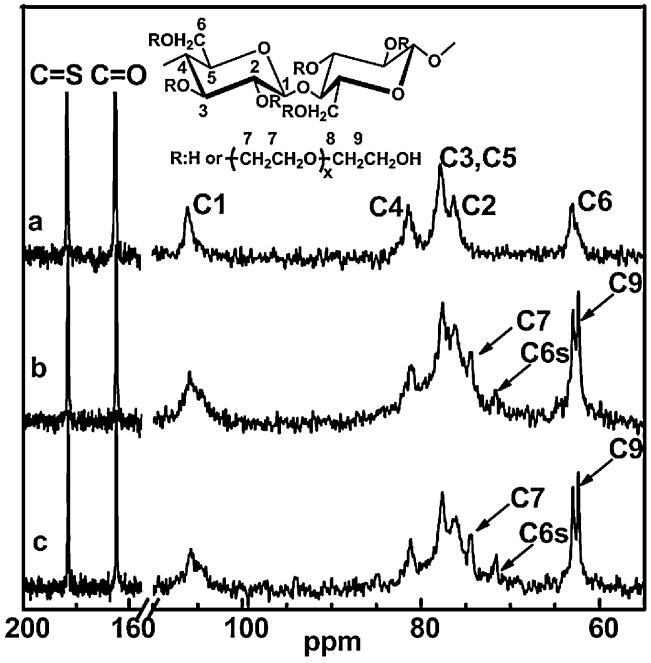

Fig. 2. Liquid ^{13}C NMR spectra of (a) cellulose, (b) HEC and (c) regenerated HEC fibers in NaOH/urea/thiourea/D_2O solution.

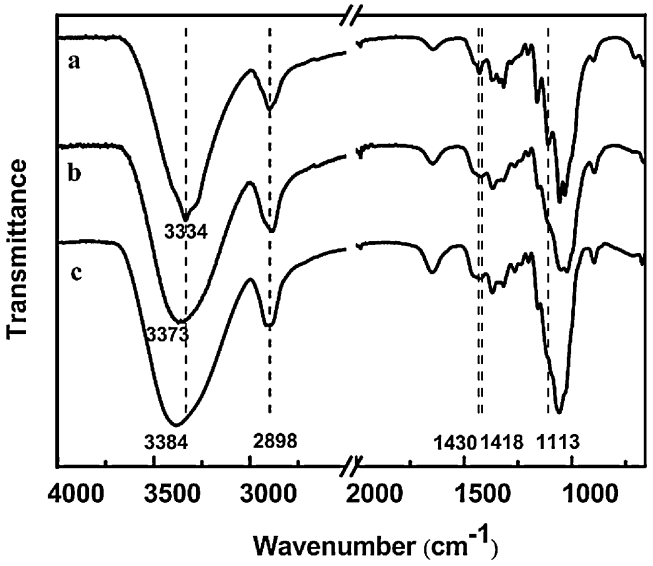

Fig. 3. FTIR spectra of (a) cellulose, (b) HEC and (c) regenerated HEC fibers.

time, in support of the better dissolving capacity of the novel NaOH/urea/thiourea aqueous solution. It could be found that there were undissolved swollen HEC fragments existing in NaOH solution, while almost nothing left in the NaOH/urea/thiourea solution. In view of the high solubility and good spinnability, the optimal spinning solution was prepared by dissolving HEC-2 with a *MS* of 0.30 into 8 wt% NaOH/8 wt% urea/6.5 wt% thiourea aqueous solution.

It is worth mentioning that no irreversible gelation behavior was observed in the 9 wt% HEC spinning dope by means of the dynamic rheology measurement, which has never been achieved when high concentration cellulose dissolved in alkali solvent systems (Cai & Zhang, 2006; Ruan, Lue, & Zhang, 2008; Weng, Zhang, Ruan, Shi, & Xu, 2004; Zhang, Li, & Yu, 2011). It is undoubtedly indicated that the novel HEC solution performs a superior thermal stability, which will be discussed intensively in our future paper.

3.2. Characterization of regenerated HEC fibers

3.2.1. Structures of HEC regenerated fibers

Fig. 2 displayed the liquid ^{13}C NMR spectra of cellulose, HEC and regenerated HEC fibers in 8 wt% NaOH/8 wt% urea/6.5 wt% thiourea/77.5 wt% D_2O solution. There were no obvious differences between spectra of regenerated fibers and HEC, demonstrating the absence of chemical reactions with HEC during dissolution and coagulation process. A few changes emerged in the spectra of etherified samples, contributing to the successful introduction of hydroxyethyl groups into cellulose chains. It could be obviously found from the latter two spectra that the signals at 62–63 ppm were split into two peaks. The left peak was assigned to unsubstituted C6 based on the chemical shift of the corresponding carbon in cellulose, whereas the other one was assigned to C9 at the end of side chains (DeMember, Taylor, Trummer, Rubin, & Chiklis, 1977). Another new peak occurred at 74.35 ppm was attributed to C7 of hydroxyethyl groups.

As the resonance of the carbon attached to an etherified hydroxyl group would be shifted downfield by 8–11 ppm as compared to that of the carbon bearing an unsubstituted hydroxyl group (Kimura, Shigemura, Kubo, & Maru, 1985), the new peak at 71.73 ppm in the spectrum was assigned to C6s (the substituted C6 bearing hydroxyethyl groups). The peak was weak owing to the relative low *MS* of the sample. Irrespective of substitution, the chemical shifts of C1, C3 and C5, and C4 for HEC and HEC fibers solution were considered to be similar to those for cellulose, because low degree of etherification induced minor influence on chemical shifts of carbon signals in the anhydroglucose unit (AGU) (Kimura, Azuma, & Gray, 1993). However, the signals corresponding to unsubstituted C2 were shifted slightly from 75.28 ppm to 76.08 ppm, which was considered to be influenced by the overlap with C8. The signals of C2 and C3 bearing etherified hydroxyl groups (C2s and C3s) were missing in the spectra of Fig. 2b and c, in good agreements with the previous report (Nelson & O'Connor, 1964) that most of the side chains were readily attached to the C6-position where the hydroxyl groups showed the highest reactivity for heterogeneous hydroxyethylation due to favorable steric accessibility.

Fig. 3 presented the FTIR spectra of cellulose, HEC and regenerated HEC fibers. The stretching vibration of strong hydrogen bonded hydroxyl groups at around 3720–3000 cm^{-1} was commonly observed for all the spectra. For comparison with cellulose, the absorption peak of the band was shifted distinctly from 3334 cm^{-1} to a higher wave-number 3384 cm^{-1} after hydroxyethylation treatment, as a result of the decrease of intra- and intermolecular bonds. The 1430 cm^{-1} band assigned as symmetric —CH_2 bending vibration was changed to 1418 cm^{-1} accompanied by a considerable decrease in absorbance intensity, indicating the alteration of the conformation of CH_2OH at C6 from the "*tg*" to the "gt" form (Oh et al., 2005). The band at 1113 cm^{-1} appeared only as a shoulder in the latter two spectra but looked strong in the cellulose spectrum, which was also affected by the variation of hydrogen bonding during crystal transformation (Nelson & O'Connor, 1964). Furthermore, it was clearly found that there existed good agreements between the spectra of HEC and HEC fibers, as another powerful evidence to support the direct dissolution of HEC occurred in NaOH/urea/thiourea aqueous solution as well as the physical regeneration process of regenerated HEC fibers.

The WAXS patterns were quite different among the cellulose, HEC and regenerated HEC fibers as shown in Fig. 4. The original cellulose displayed the cellulose I structure, while the other two etherified samples displayed the typical cellulose II structure with one broad reflection of (1 1 0)/(0 2 0) lattice plane at around

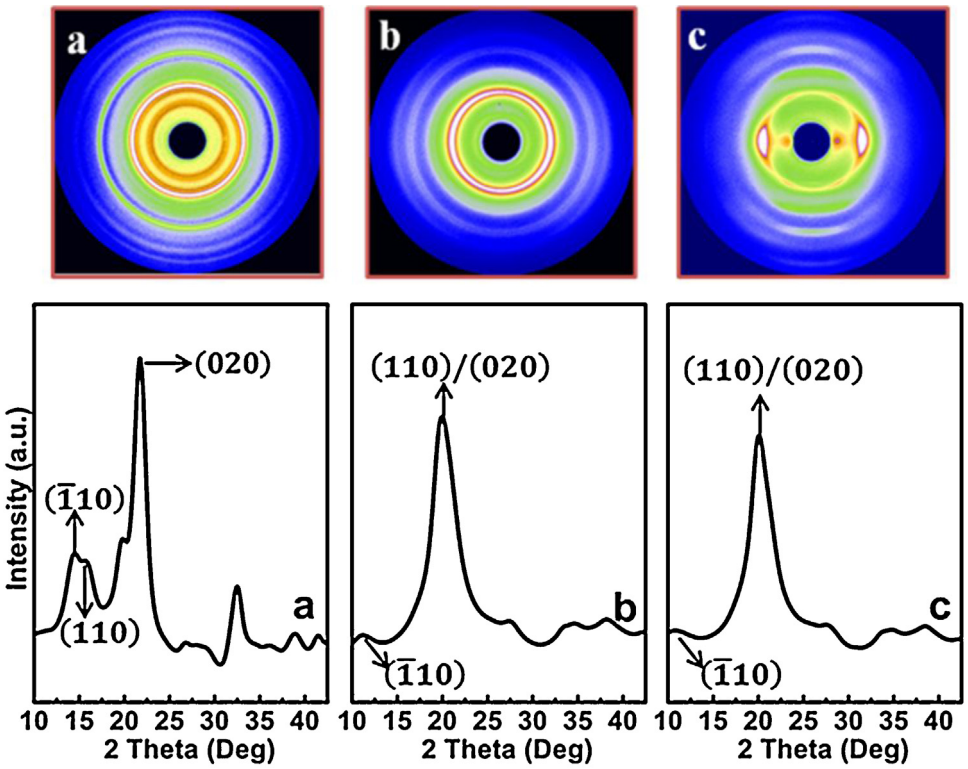

Fig. 4. WAXS patterns and their integrated profiles of (a) cellulose, (b) HEC and (c) regenerated HEC fibers.

20° as well as another weak peak at about 11° (Langan, Sukumar, Nishiyama, & Chanzy, 2005). Compared to cellulose and HEC powders that exhibited typical amorphous patterns, the reflection of HEC fibers appeared as broad arcs with $(\bar{1}\,1\,0)$ and $(1\,1\,0)/(0\,2\,0)$ planes on the equator. This indicates the existence of relatively low crystal orientation, which may be aroused by the lack of effective drawing.

Moreover, the transformation of crystal structure could be clearly found according to Fig. 4. During the modification, cellulose was first fully exposed to alkali solution accompanying with increased reactivity of cellulose toward chemical modification and structural transformation from cellulose I to cellulose II. The subsequent introduction of hydroxyethyl groups could not change the characteristics of cellulose II due to the low *MS*, but further reduced the structural regularity attributing to the random distribution and various chain lengths of the substituents embedding into the cellulose bone chains. It was confirmed from the increased *d*-spacing of the $(\bar{1}\,1\,0)$ planes and the distinct decline of crystallinity from cellulose (68.42%) to HEC (47.81%). The crystallinity of HEC regenerated fibers was 42.2%, slightly lower than that of HEC, verifying that no noticeable degradation in HEC molecular chains occurred during its dissolution and coagulation processes. Table 2 listed the crystallinity of HEC fibers as well as other well-known regenerated fibers. It was clearly seen that the novel fibers showed higher crystallinity than common viscose rayon, but close to that of Lyocell and Cuprammonium fibers (Mao, Zhang, Cai, Zhou, & Kondo, 2008).

3.2.2. Morphologies of HEC regenerated fibers

Fig. 5 shows the SEM photographs of the longitudinal and cross-sectional shapes of regenerated HEC fibers prepared by a laboratory wet-spinning apparatus. The longitudinal surface of HEC fibers was generally smooth except for a few microscopic cracks, indicating that the regeneration process of HEC was not quite uniform. Moreover, the cross-section of the novel HEC fibers regenerated from acid coagulating bath was fused into a relatively dense and homogeneous structure, displaying a true circle, markedly different from the lobulate shape of the viscose ray with obvious skin-corn structure, but similar to those of cuprammonium rayon and Lyocell fibers (Woodings, 2001). This could be interpreted by the fact that the novel fibers were regenerated directly from HEC dope in a quasi-gel state formed mainly by physical cross-linking through hydrogen bonds between molecule chains without an asymmetrical chemical reaction on the fibers (Cai et al., 2004; Zhang, Li, & Yu, 2010b). In addition, the appropriate coagulation conditions provided the as-spun fibers with a soft and deformable surface layer formed at the very beginning of coagulation, which was also helpful to the sub-rounded, cross-sectional shape. Porous structure with small voids usually found in wet-spun fibers as a result of phase separation accompanied by volume changes. However, as seen in Fig. 5d, there were no apparent small voids found in the prepared HEC fibers, which may be sealed in a drying operation as the coagulated structure was flexible enough.

3.2.3. Moisture related properties of HEC fibers

Moisture related properties of regenerated cellulose fibers are of great importance as they have a significant influence on their processing and application. Water retention and moisture regain, as indicators to investigate the interaction between liquid or gaseous water and HEC fibers, were listed in Table 2. It was found that both the WRV and moisture regain of HEC fibers seemed to be affected by etherification. HEC fibers possessed WRV of 146% and moisture regain of 14.5%, which distinctly exceeded those of other regenerated cellulose fibers. This manifested that a more powerful bonding between water molecules and HEC molecules appeared due to the strong attraction of hydroxyethyl groups to H_2O molecules. The aggregation structure of the fibers also had a significant influence on moisture related properties (Kreze & Malej, 2003). For the novel HEC fibers, the large portion of amorphous structure and a relatively loosen crystal structure caused by etherification together with void

Table 2
Physical properties of the novel HEC fibers.

Sample	HEC fibers		Viscose rayon	Lyocell fibers	Cuprammonium fibers
Crystallinity (%)	42.2		30.0	42.0	43.0
Cross-section	Round/ova		Lobate	Round/oval	Round/oval
	Homogeneous		Core/skin	Homogeneous	Homogeneous
Tensile strength (cN/dtex)	1.8–2.1	Dry	1.9–2.2	4.0–4.4	1.5–2.0
	0.7–1.0	Wet	1.1–1.2	3.6–3.8	0.9–1.2
Elongation at break (%)	10–20	Dry	20–25	14–16	7–24
	15–25	Wet	25–30	16–18	16–43
WRV (%)	146		92	100	65–70
Moisture regain (%)	14.5		12.5	10.5	12.5
Solubility in NaOH solution at 20 °C (%)	78.9	8 wt%	51.6	–	–
	4.2	1 wt%	3.0	–	–
Reference	This work		This work	Woodings (2001)	Woodings (2001)

structure formed in phase separation process would contribute to the excellent moisture related properties.

3.2.4. Stability of HEC fibers in alkali solution

The introduced hydroxyethyl groups provided cellulose with excellent solubility in alkali solution, which meant the HEC fibers were less stable in alkali environment since HEC cannot convert back to cellulose during coagulation process as viscose rayon did. Table 2 presented the solubility of HEC fibers in NaOH solution at 20 °C. Most of HEC fibers were dissolved when immersed in 8 wt% NaOH solution for 24 h, while only part of viscose rayon could be dissolved under the same conditions. Fortunately, when HEC fibers and viscose rayon were dispersed into 1 wt% NaOH solution whose concentration was much higher than alkali environments in general usage, the solubility of HEC fibers reduced evidently, just slightly higher than that of viscose rayon, indicating that the HEC fibers were available in practical application.

3.2.5. Tensile properties of HEC fibers

The parameters of tensile properties for the novel HEC fibers with other commercial regenerated fibers were summarized in Table 2, and the stress–strain curves of HEC fibers in dry and wet state were illustrated in Fig. 6. The HEC fibers spun via the preliminary pilot plant possessed dry tensile strength and elongation at break close to commercial viscose rayon, although the orientation of the novel fibers was not full enough. It was well convinced that the fiber orientation as well as crystal structure would be significantly improved after further optimization of the spinning process with special attention on the coagulation conditions and drawing processes. It must be emphasized here that the concentration of HEC spinning dope applied has the potential to increase in view of the results from dissolution, which can endow the fibers with better tensile properties due to the more uniform and denser fiber structure (Laszkiewicz, Wcislo, & Cuculo, 1992). Therefore, it is desirable to produce the novel HEC fibers with excellent dry mechanical properties the same as or even greater than that of viscose rayon.

Moreover, it can be seen that the wet tensile strength of novel HEC fibers was in the range of 0.7–1.0 cN/dtex, lower than that of viscose rayon, which was closely related with the moisture related properties of HEC fibers. When the HEC fibers were immersed in water, H_2O molecules could not only penetrate into amorphous areas of HEC fibers but also part of crystalline areas because the distance between crystal planes increased due to the replacement of the hydroxyl groups in HEC crystals with hydroxyethyl groups. The

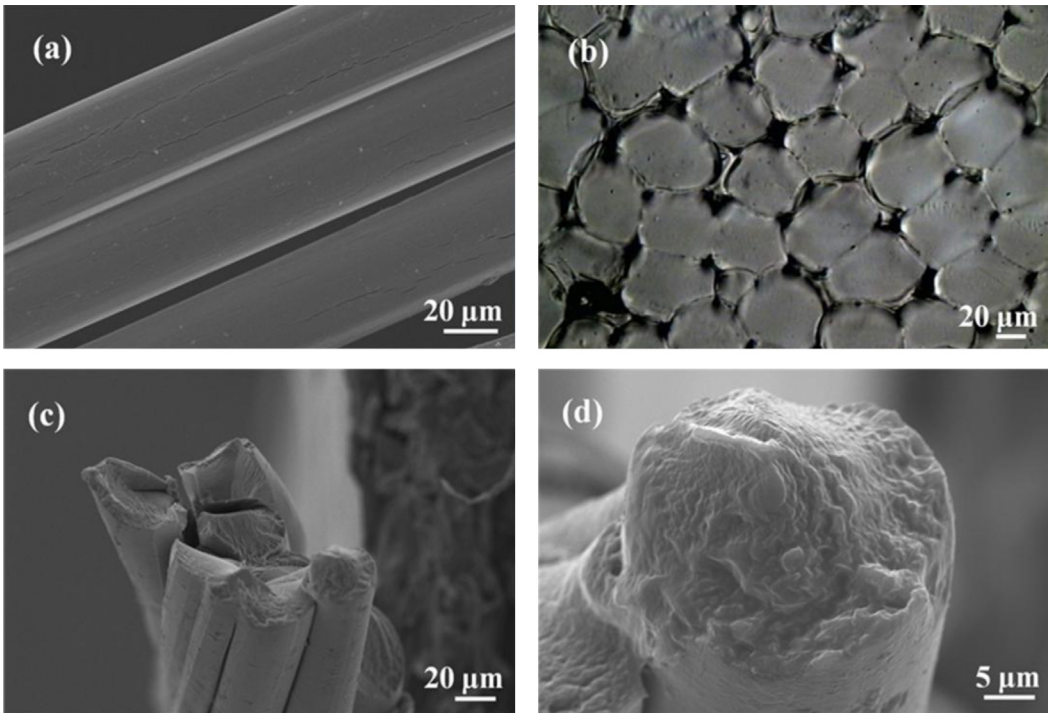

Fig. 5. SEM photographs of (a) longitudinal shape, (b)–(d) cross-section of HEC fibers.

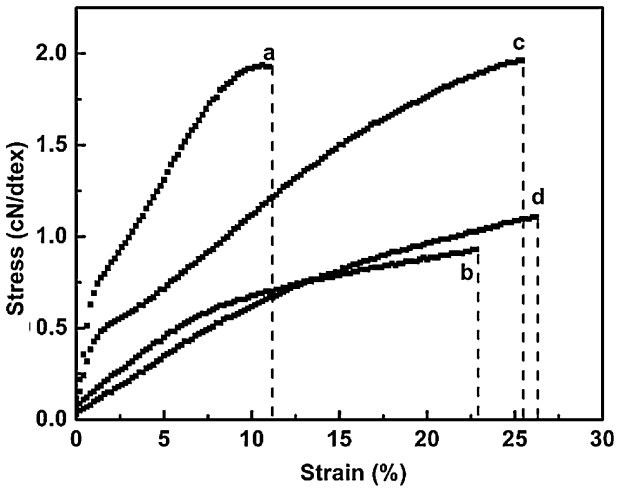

Fig. 6. Typical stress-strain curves for (a) HEC fibers at dry state, (b) HEC fibers at wet state, (c) viscose rayon at dry state, and (d) viscose rayon at wet state.

fiber macromolecules were pushed apart by the absorbed water and tended to be more dramatically swollen in water as a result of the modification by hydrophilic hydroxyethyl groups, resulting in weaker intermolecular interactions which made the fiber macromolecules unable to bear large tension.

The most efficient way to improve the wet mechanical properties was to decrease the *MS* of HEC applied for spinning under the premise of good solubility, which would be feasible with the help of green solvent NaOH/urea/thiourea solution. Sealing off the free hydroxyl groups of HEC molecular chains by reactions with crosslink agents would be another choice to improve the wet mechanical properties of HEC fibers, which was demonstrated to be effective in enhancing wet tensile strength of chitosan fibers (Knaul, Hudson, & Creber, 1999; Wei, Hudson, Mayer, & Kaplan, 1992), PVA fibers (Fujiwara, Shibayama, Chen, & Nomura, 1989) and viscose rayon (Li et al., 2008a; Li et al., 2008b). The presence of crosslink formed in a fiber structure was able to hold the molecules together in the network and strengthen the intermolecular interactions. Thus the crosslinked HEC fibers could bear more resistance to tension when encountering the water. Meanwhile, the moisture absorption properties of HEC fibers as well as the stability in alkali solution would be improved with these treatments, favorable to produce the fibers suitable for industrial manufacture and practical application in a more economical and eco-friendly way.

4. Conclusion

HEC with low *MS* was dissolved directly in NaOH/urea/thiourea aqueous solution, and corresponding regenerated fibers were prepared via a wet-spinning pilot machine. According to ^{13}C NMR data, the successful introduction of hydroxyethyl groups to the cellulose backbone was confirmed. Structural analysis from FTIR and X-ray studies demonstrated that major structural changes took place in the synthetic process of HEC, during which the crystal structure was partially destroyed and the crystal phase transition from cellulose I to cellulose II appeared and no noticeable change on HEC macromolecular structure occurred during its dissolution and coagulation processes. The as-produced HEC fibers stayed as stable as viscose rayon in alkali solution with low concentration. Regenerated HEC fibers exhibited an oval cross-section and a relatively dense structure, presenting excellent moisture absorption compared with other regenerated cellulose fibers. The mechanical properties of HEC fibers in the dry state were comparable to viscose rayon, while their wet tensile strength was relatively unsatisfactory. Continuous decreasing the *MS* of HEC applied, crosslinking treatments as well as optimization of spinning processes were selective to improve the mechanical properties of HEC fibers.

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