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# Solution blowing of submicron-scale cellulose fibers

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ABSTRACT

Solution blowing is an innovative process for spinning micro-/nano-fibers from polymer solutions using high-velocity gas flow as fiber forming driving force. Submicron-scale cellulose fibers were successfully solution blown by two improvement measures. First, cellulose solution was directly blown to fibers of 260–1900 nm in diameter by raising the air temperature along the spinning line which was proved to accelerate the evaporation of solvent and fiber forming. Second, coaxial solution blowing technique was established with cellulose solution and polyethylene oxide (PEO) solution used as core and shell liquids, respectively. The core–shell structures of the fibers were examined by SEM and TEM. Cellulose fibers with diameter between 160 nm and 960 nm were further obtained after removing PEO shell. X-ray diffraction studies showed that the two kinds of submicron-scale cellulose fibers are mostly amorphous.

## 1. Introduction

Recently, increasing attention has been paid to nature polymers because of their sustainability, eco-efficiency, industrial ecology, and renewable nature (Huang, Zhang, & Ramakrishna, 2003). Cellulose is an abundant and renewable resource found in most parts of the world, which makes it a cheap raw material for various applications, and it has a long history in fiber manufacturing (Frey, 2008). Since cellulose does not melt, earlier cellulose fibers were produced via wet spinning of cellulose xanthate to regenerate fibers in a sulfuric acid-containing coagulant (Tikhonovetskaya, Nabiev, & Burkhanova, 1998). After some effective solvents were found, the lyocell process of cellulose fibers was established by spinning its direct solutions in solvents such as N-methyl-morpholine-N-oxide/water (NMMO/$H_2O$), lithium chloride/N,N-dimethylacetamide (LiCl/DMAc) and others (Lu & Zhang, 2007).

Since electrospinning was established as a process for spinning fibers with submicron-scale diameter, a vast array of organic polymers as well as inorganic and hybrid nanofibers have been electrospun (Chen, Hou, Hu, Wendorff, & Greiner, 2009; Du & Hsieh, 2009; Greiner & Wendorff, 2007; Jian, Lu, & Zhu, 2006). There have also been several attempts to electrospin cellulose fibers using the solvents of LiCl/DMAc, NMMO/$H_2O$, ionic liquids, and trifluoroacetic acid (Kim, Kim, Kang, Marquez, & Joo, 2006; Kulpinski, 2005; Ohkawa, Hayashi, Nishida, Yamamoto, & Ducreux, 2009; Qi, Sui, Yuan, Wei, & Zhang, 2010; Quan, Kang, & Chin, 2010; Xu et al., 2008). And electrospun cellulose fibers are now finding use including electrical and biomedical applications (Baptista, Martins, & Fortunato, 2011; Ma, Burger, Hsiao, & Chu, 2011). However, most published works were carried out using experimental laboratory-scale set-ups equipped with a syringe needle, and the fibers were obtained in very low yields with 1.0–5.0 mL $h^{-1}$ solution flow rate (Son, Youk, & Park, 2004).

Melt blowing is a commercial one-step process for spinning polymer resin directly into ultrafine fibers with diameters down to 0.5–5 μm (Tang & Mukhopadhyay, 2006). In the process, a molten polymer is pressurized out through a fine capillary and then rapidly attenuated into fibers by the drawing force of high-velocity hot gas flow to collect on an open screen and form a nonwoven web (Ellison, Phatak, & Giles, 2007). Recently, melt blowing process was used with cellulose solution in NMMO/$H_2O$ to produce fine fibers in the micrometer range (Ebeling & Fink, 2006; Tang, Law, & Mukhopadhyay, 2001). The feasibility of this method comes from the fact that the solution normally hardens at room temperature by virtue of solvent crystallization. NMMO was further removed by solvent exchange in the following coagulation program. In other works, melt blowing was used to spin polymer fibers from their solutions in volatile solvents (Medeiros, Glenn, Klamczynski, Orts, & Mattoso, 2009; Zhang, Kopperstad, West, Hedin, & Fong, 2009). Several synthetic polymers such as poly (methyl methacrylate), polystyrene, polyvinylpyrrolidone, and polyacrylonitrile were successfully spun, and their fibers diameters were in the range of hundreds of nanometers which was near to those produced by electrospinning. Here the solvents were removed by volatilization which was also similar to electrospinning. However, compared with electrospinning, high-voltage equipment is not required in the so-called solution blowing process, so it is

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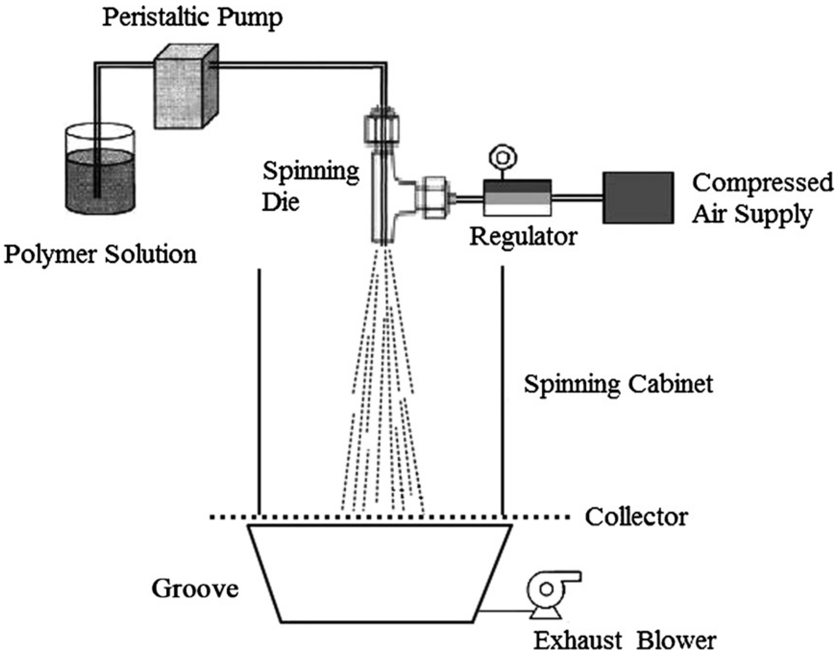

**Fig. 1.** Schematic of the solution blowing apparatus.

possible to use a die assembly with many nozzles without considering of electric field interference, which possesses several advantages such as convenient operation and mass productivity (Zhang et al., 2009).

In the present work, solution blowing was employed to produce submicron-scale cellulose fibers from its solution in LiCl/DMAc with two improvement measures: one was raising the air temperature in the spinning line to help evaporating the solvent and the other was coaxial solution blowing which was established to form a cellulose–polyethylene oxide (PEO) core–shell fiber. Cellulose fibers were then obtained after PEO shell was removed. Results of this study will help further understanding on the innovative process and expand it to other biopolymers.

## 2. Experimental

### 2.1. Materials

Wood cellulose pulp (degree of polymerization of 1120) was supplied by Chengdu Huaming Cellophune Co., Ltd. (Sichuan, PR China). Polyethylene Oxide (PEO, average Mn of 50,000) was purchased from Changchun Huagao Chemical Co., Ltd. (Jilin, PR China). LiCl, DMAc and N,N-dimethylformamide (DMF) were of analytical grade and purchased form Shanghai Jingchun Chemical Reagent Co., Ltd. (Shanghai, PR China).

### 2.2. Preparation of spinning solutions

Cellulose solution was prepared as follows: cellulose pulp chips was dipped in DMAc with a bath ratio of 1:10 and heated to 120 °C with stirring for 15 min. Then cellulose was filtered and dissolved in 8 wt.% LiCl/DMAc to form a homogeneous solution with polymer concentration ($c$) of 2 wt.%. PEO solution was prepared by directly dissolving PEO power in DMF with polymer concentration of 10 wt.%.

### 2.3. Solution blowing procedure

The schematic of the solution blowing apparatus is illustrated in Fig. 1. In the present work, an annular spinning nozzle which was coaxial surrounded by a gas cavity was used as a single nozzle spinning die. The schematic is briefly described as follows: the polymer solution is supplied to the nozzle by controlling the peristaltic pump, and the compressed air is delivered to the air gas cavity with controlling the pressure regulator. As soon as the polymer solution stream is pressed out of the nozzle tip, it is subsequently blown into fibers by the streams of gas flow to the mesh-like collector. Along the spinning line set a cylindrical metallic spinning cabinet around which equipped a heating unit to heat air within the spinning cabinet. The evaporated solvent is removed with air by the exhaust blower through a groove under the collector.

In blowing the cellulose solution, a 24-gauge needle was used which inner diameter was 0.33 mm and the outer diameter was 0.55 mm, respectively. For coaxial solution blowing, a 24-gauge needle was used for cellulose solution and an 18-gauge one was used for PEO solution which inner diameter was 0.86 mm and the outer diameter was 1.26 mm, respectively. The inner diameter of the annular gas cavity is 1.82 mm. The distance between the nozzle tip to the collector screen is 45 cm. The process variables included solution feeding rate ($r$), gas pressure supplied to the gas cavity ($p$), and air temperature of the spinning cabinet ($t$).

### 2.4. Characterization

Morphologies of the blown fibers were observed using a Quanta 200 (FEI) SEM or a Hitachi S-4800 FE-SEM at an accelerating voltage of 5 kV or 10 kV after sputtering with gold. Microstructure observations were carried out with a JEM-2100F FETEM (JEOL) microscope operating at 200 kV. The samples were prepared by directly putting a thin layer core–shell fiber on carbon-coated copper grids. The transformation of the crystalline structure of the samples was confirmed with X-ray diffraction (XRD) method using a using a Bruker AXS D8 Discover machine. The diffraction angle $2\theta$ was recorded from 10° to 45°. The thermal properties were investigated by thermogravimetric analysis (TGA) using a Perkin Elmer DSC7 under the nitrogen atmosphere at a heating rate of 10 °C/min.

## 3. Results and discussion

### 3.1. Solution blowing of cellulose nanofiber

In solution blowing, after the solution streams are pressed out of the nozzle, they are stretched to the extreme by the high-velocity gas flow to the collector accompanied by solvent evaporation and fiber formation. The process is similar to electrospinning but with different fiber formation driving forces. For solution blowing, high-velocity gas flow deforms the solution streams, evaporates the solvent, and solidifies them into fibers; while electric force performs in electrospinning.

Compared with synthetic polymers such as PAN, cellulose solution is more difficult to blown to fibers. As for blowing a PAN solution, nanofibers can be produced at a wide polymer concentration range of 5–20 wt.% and with high solution feeding rate of 0.3–0.8 mL min$^{-1}$. However, it is difficult to produce fibers even at a low solution feeding rate of 0.08 mL min$^{-1}$ for cellulose fibers. Regardless of gas pressure and collection distance, a film-like cellulose sample was obtained. One reason comes from the composite structure of LiCl/DMAc solvent, and another is the high viscosity of the solution. The concentration of cellulose in solutions depends on both the cellulose molecular weight and the solvent composition (Kim et al., 2006). In the present work, a cellulose with DP of 1120 was selected and its solution of 2 wt.% even got a high shear rate viscosity of 967 mPa s. With a lower concentration, it requires the removal of more solvent to solidify the fibers. Raising air temperature along the spinning line is helpful for accelerating the evaporation of solvent. However, it is infeasible to blow hot air as performed in the melt blowing process because it will solidify the solution streams and block it at the nozzle tip. The approach used in this work is using a cylindraceous spinning cabinet between the spinning die and the collector (Fig. 1), and the spinning cabinet was equipped with a heating unit that could heat air inside the cabinet through thermal radiation. Also, the evaporated solvent was collected inside the closed environment and taken away by an exhaust blower, which was propitious to recycle the solvent than in an open environment. Considering the temperature of the air inside the cabinet was not uniform, and there was a temperature gradient along the radius and the spinning line, it was difficult to give the exact temperature of each point. The temperature of the end of spinning line, i.e., the junction of the center axis of the spinning cabinet and the collector ($t_c$), was used to make an approximate comparison of the temperature changes.

When $t_c$ was lower, seldom fiber was found and when $t_c$ elevated, a spot of fibers was collected. The fibers obtained at $t_c$ of 35, 45, 50 and 55 °C are shown in Fig. 2(a–d). When $t_c$ was 35 °C, big droplets and bulk with fibers were observed (Fig. 2(a)). When $t_c$ was over 45 °C, relative smooth fibers were obtained. The diameter distributions of the fibers in Fig. 2(a–d) are 355–1900 nm, 260–780 nm, 340–950 nm, and 450–1500 nm, and their average diameters are 878, 456, 634, and 827 nm, respectively. This indicates that raising the temperature along the spinning line appropriately helps in fiber forming and refinement, but too high temperature will prevent the formation of a larger number of finer fibers. The reason is attributed to the high volatility of solvent at higher temperature, which makes the solution lose mobility prematurely and prevents refinement of the solution streams. Thus, there should be a balance between stretching and solvent evaporation in order to spin a larger number of finer fibers.

Interestingly, electrospun cellulose nanofibers usually follow a coagulation process to avoid partial solvation by the residual solvent (Kim et al., 2006; Quan et al., 2010), whereas solution blown fibers can keep their shape all along without any special treat-

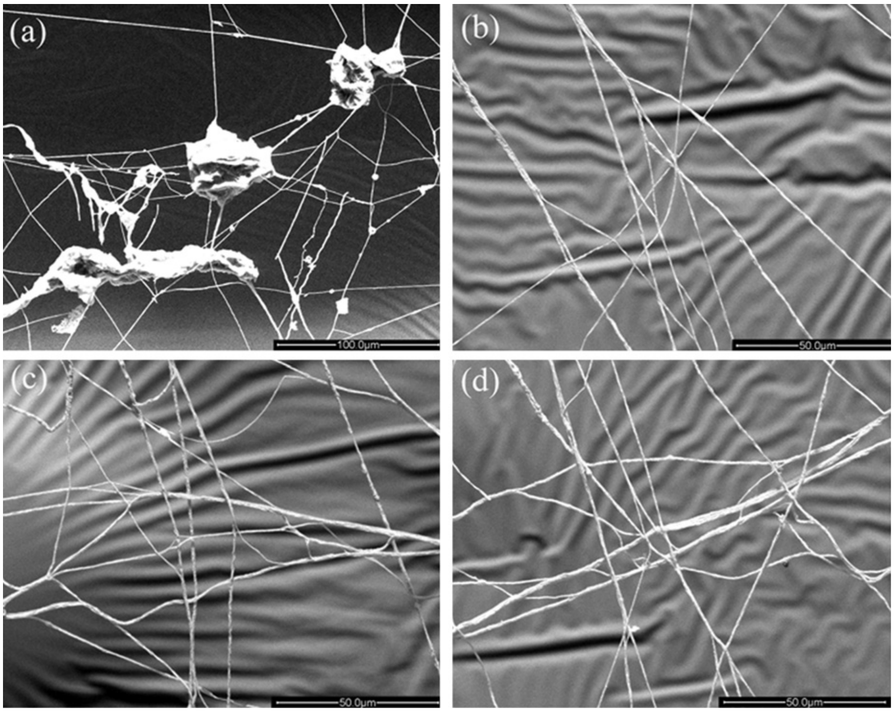

**Fig. 2.** SEM photographs of the solution blown cellulose fibers from 2 wt.% cellulose solution in LiCl/DMAc with the following parameters: solution feeding rate ($r$) was fixed 0.08 mL min$^{-1}$, gas pressure ($p$) was 0.25 Mpa, temperature of center axis of spinning cabinet ($t_c$) were: (a) 35 °C, (b) 45 °C, (c) 50 °C and (d) 55 °C, respectively. The background of the SEM photographs was conductive adhesive tap to fix the fibers.

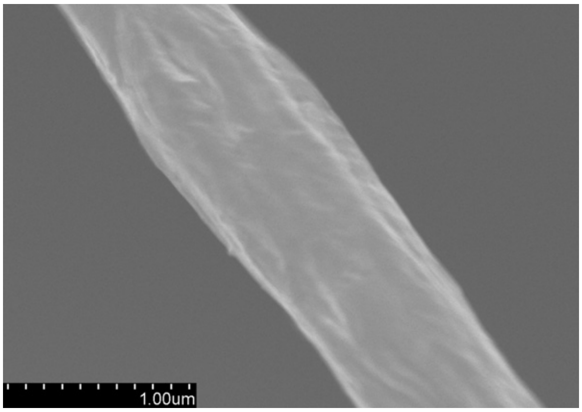

**Fig. 3.** SEM photograph of cellulose fiber after removing LiCl.

ment. The mesh-like collector and the continuous airflow seemed to aid more effective removal of DMAc. After removing LiCl content by dipping in water and washing several times, the fibers diameters did not change obviously. A representative SEM was shown in Fig. 3.

### *3.2. Coaxial solution blowing of cellulose–PEO core–shell fibers*

Coaxial electrospinning is an effective way of fabricating nanofibers from polymer solutions with limited electrospinnability. In this technique, two different solutions are simultaneously spin through a spinneret composed of two coaxial capillaries to produce core–shell structured nanofibers. Several biopolymers such as chitosan, cellulose nanofibers were successfully prepared with the aid of synthetic polymers as the core or shell materials. In the present coaxial solution blowing, 10 wt.% PEO solution and 2 wt.% cellulose were supplied into the outer and inner nozzles, respectively. PEO solution was expected to improve the spinnability of cellulose solution by encapsulating it as core and forming a core–shell fiber. The core–shell fiber-forming mechanism was considered similar to coaxial electrospinning. Here, DMF was used to dissolve PEO to obtain good volatility and low interfacial tension between the core and shell solutions. Feeding rate of the cellulose solution was fixed as 0.08 mL min$^{-1}$, while that of the PEO solution was varied from 0.1 to 0.3 mL min$^{-1}$. In the experiments, solution streams were clearly observed and fiber webs were obtained. Representative SEM photographs are shown in Fig. 4. Diameter distributions of the fibers in Fig. 4(a, b and d) are 200–1770 nm, 190–1400 nm, and 250–980 nm, and their average diameters are 867, 628, and 582 nm, respectively. Moreover, big bulks were observed when $r$ was 0.3 mL min$^{-1}$. This indicates an increasing trend of fiber fineness when PEO feeding rate increases. When a higher-magnification SEM photograph was taken for the fibers with 0.2 mL min$^{-1}$ PEO feeding rate, a “joint-like” structure was observed (Fig. 4(c)). From the photograph, a core–shell structure was clearly observed due to the PEO shell being partly destroyed because of its lower thermal stability.

The fibers were further observed by transmission electron microscopy. Seldom fibers with core–shell structure was observed when the PEO solution feeding rate was set as 0.1 mL min$^{-1}$. When the PEO solution feeding rate was enhanced, the core–shell structure formed, as indicated in Fig. 5. The dark and bright regions represent the core and shell of the nanofibers, respectively. The core–shell nanofibers are mostly concentricity with clear interface. The selected figures show the diameters of the shell and core are approximately 396 nm and 587 nm respectively for 0.2 mL min$^{-1}$ feeding rate sample, and the data are 154 nm and 509 nm respectively for 0.3 mL min$^{-1}$ feeding rate one. Increasing PEO solution feeding rate leaded to a thicker shell because of more PEO content were conglutinated on the surface of cellulose.

After removing the PEO shell by dipping in water for 48 h and washing several times, cellulose fibers were obtained. The fibers, with diameters between 160 and 960 nm, maintained good shape, as indicated in Fig. 6. The result confirmed the feasibility of blowing cellulose fiber with the aid of high spinnability of PEO solution.

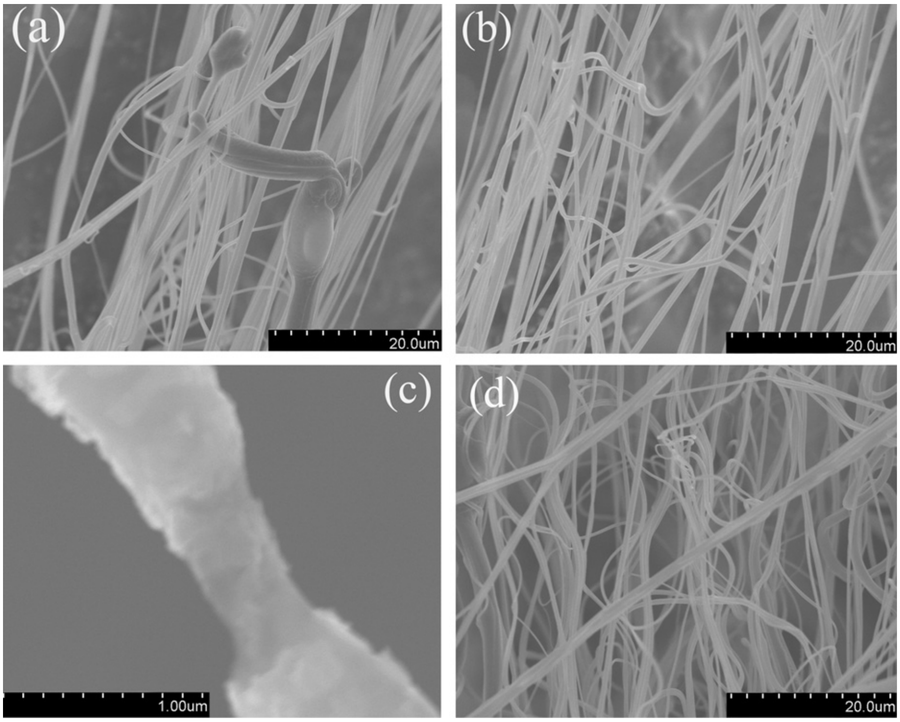

**Fig. 4.** SEM photographs of the coaxial solution blown fibers with different PEO solution feeding rate: (a) 0.3 mL min$^{-1}$, (b) and (c) 0.2 mL min$^{-1}$, and (d) 0.1 mL min$^{-1}$.

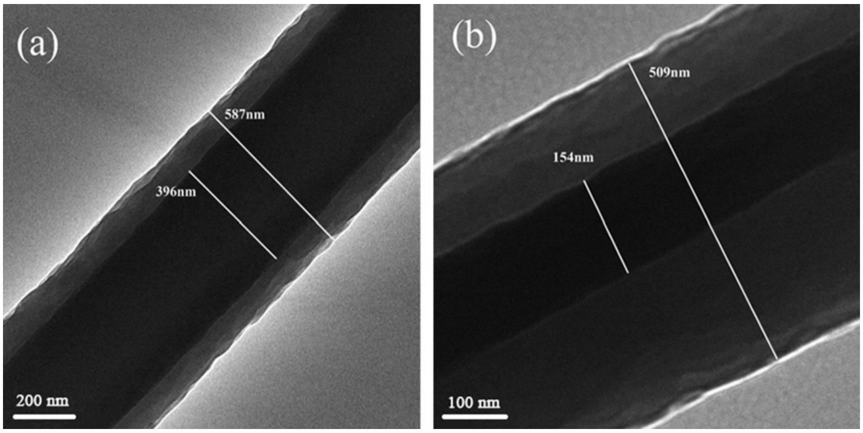

**Fig. 5.** TEM photographs of the coaxial solution blown fibers with PEO solution feeding rate of: (a) 0.2 mL min$^{-1}$, and (b) 0.3 mL min$^{-1}$.

### 3.3. Structure of submicron-scale cellulose fibers

It is well known that cellulose forms a variety of crystalline allomophs (Biganska, Navard, & Bedu e, 2002). The native cellulose generally presents polymorph of Cellulose-I with the highest degree of intermolecular and intramolecular hydrogen bonding, and the crystalline polymorph of Cellulose-II forms when cellulose is solubilized and regenerated (Chen, Burger, & Fang, 2006). In this study, the polymorphs of native cellulose pulp and the two kinds of cellulose fibers were examined. As shown in Fig. 7, X-ray diffraction patterns revealed that the native cellulose presented the polymorph of Cellulose-I with characteristic peaks at $2\theta = 14.6^\circ$, $16.6^\circ$ and $22.7^\circ$, while the cellulose fiber from the neat cellulose solution (cellulose fiber I) and one obtained from coaxial spinning (cellulose fiber II) were mostly amorphous with amorphous peak at $2\theta = 20.4^\circ$. The result was similar to almost electrospun cellulose nanofibers which were attributed to the shorter timescale of spinning than that for cellulose crystallization (Kim et al., 2006; Ohkawa et al., 2009; Qi et al., 2010).

The thermal stability of the cellulose nanofibers and native cellulose pulp was investigated. The TGA test was carried out in a nitrogen atmosphere with a 10 °C/min heating rate and the results were shown in Fig. 8. The native cellulose pulp began to lose weight at about 277 °C, and the temperature was 243 °C and 268 °C for cellulose fiber I and fiber II, respectively. Apparently, the thermal stability of the blown fibers is lower than that of native cellulose. Similar results were also reported in electrospun cellulose fibers elsewhere (Frenot, Henriksson, & Walkenstrom, 2007). When

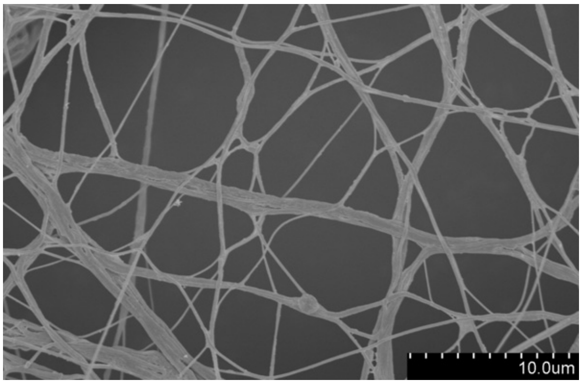

**Fig. 6.** Selected SEM photograph of the coaxial solution blown fibers after removing PEO shell.

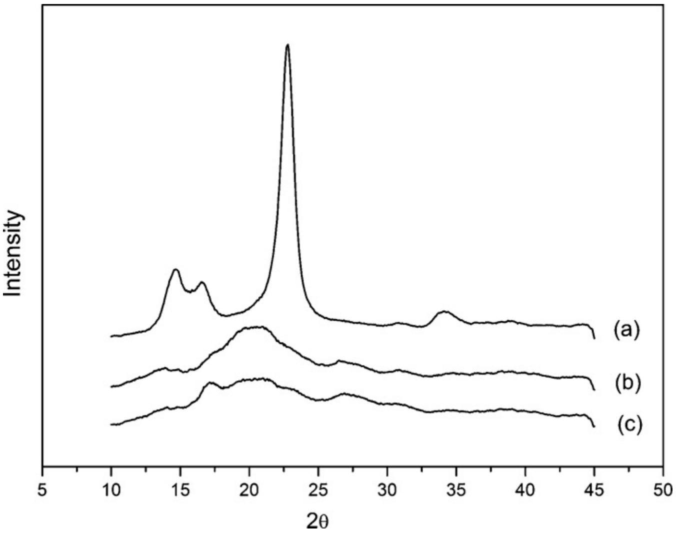

**Fig. 7.** XRD patterns of native cellulose pulp and solution blown cellulose fibers: (a) native cellulose pulp, (b) cellulose fiber I, and (c) cellulose fiber II.

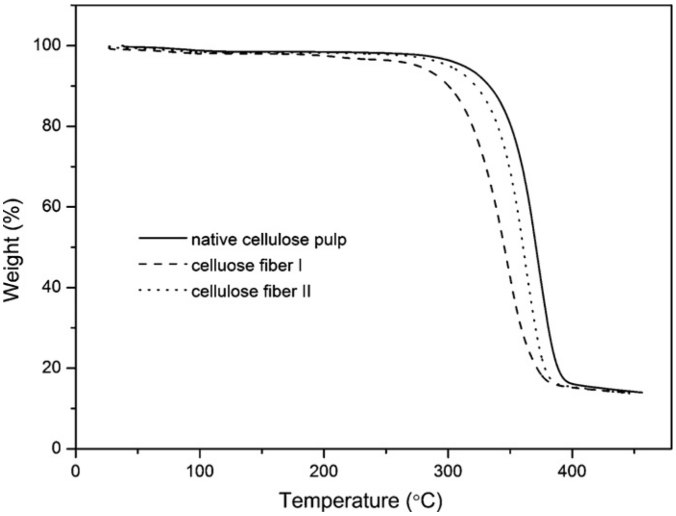

**Fig. 8.** TGA data of native cellulose pulp and solution blown cellulose fibers.

comparing the two kinds of blown cellulose fibers, cellulose fiber I show lower thermal stability which is attributed to the higher temperature along the spinning line.

## 4. Conclusions

In summary, for the first time, we succeeded in preparing cellulose fibers in submicron scale using the solution blowing technique. To accelerate the evaporation of solvent, a heating spinning cabinet was equipped to heat the air along the spinning line and the method helped to form fibers. Coaxial solution blowing was also attempted using PEO solution as shell liquid. The core–shell structure of cellulose–PEO fibers was confirmed by TEM and SEM. Submicron-sized cellulose fibers were obtained by removing the PEO shell. Solution blowing of cellulose offers an easy formation process for fibers in submicron-sized scale. The method is also expected to be applicable to other biopolymers.

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