Influence of Lignin on Rheological Behaviors and Electrospinning of Polysaccharide Solution

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ABSTRACT: The effect of lignin is a key issue in various cellulose processes. To study the effects of lignin state and content on cellulose electrospinning and fiber properties, two different types of cellulose solutions were prepared and electrospun under several different conditions. One was mixture of cellulose and lignin and the other one was hemp cellulose in which cellulose is naturally combined with lignin. In both the cases, the solutions were stably electrospun when the lignin concentration was lower than 5%. The lignin in the cellulose/lignin mixture resulted in film-like fiber and bimodal distribution of the fiber diameter, while the lignin in the hemp cellulose mainly increased the fiber diameter. It is originated from the different phase separation behaviors of the two solutions. The results can give the fundamental understandings for the roles and action of lignin in cellulose process. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40031.

INTRODUCTION

Cellulose is the most abundant bio-polymer produced in nature. It regained spotlight as a substitute of synthetic polymers, due to its eco-friendly characteristics[1–4] as well as its superior physical properties.[5,6] Cellulose can resolve significant drawbacks of synthetic polymers such as petroleum dependency, non-biodegradability after usage and huge amount of CO_2 release during manufacturing process. However, eco-hazard process is inevitable to obtain pure cellulose from ligno-cellulose. During the process, non-cellulose components such as lignin, hemicellulose, and pectin are decomposed, dissolved, and removed. Among the non-cellulose components, lignin is the major target to remove from ligno-cellulose biomass because the residual lignin gives negative influences on cellulose performance.[7] Due to its branched and 3-dimensional structure consisting of many phenolic carbons, lignin, strongly combined with cellulose, is not simple to remove all without cellulose degradation. It is, therefore, usual to utilize cellulose as combined with limited amount of lignin.[8–11] In that case, it is critical to understand the behavior and the influence of lignin on the microstructure development of cellulose during fiber forming process. However, a few studies were reported on the effect of lignin during various processes. Roger and coworkers[12] demonstrated the possibility of lignocellulosic biomass composite fibers production using ionic liquid. Kim and coworkers[13] studied the effects of

lignin and xylan on cellulose electrospinning. They obtained the kinked and curved fiber morphology by the electrospinning when the non-cellulosic components (lignin and xylan) were added to the spinning solution. Recently, the effect of residual lignin on the electrospinning and the properties was investigated using non-wooden plants.[14] In spite of all the efforts, the interaction between lignin and cellulose during spinning process is not clearly explained. The understanding of the interaction would improve the spinning process and in turns, result in better microstructure and properties of the fibers.

In this work, two different types of cellulose/lignin solutions were prepared; one is solution made of cellulose physically mixed with lignin and the other is the solution made of cellulose naturally combined with lignin. The two solutions were electrospun by changing the lignin content. The dependency of lignin type on the spinnability, the morphology, and the properties of the electrospun fiber were investigated. It will give the fundamental understanding for the action of lignin during fiber formation and the properties of the resulted fibers.

EXPERIMENTAL

Solution Preparation and Electrospinning

In the study, two types of cellulose were used; one is pure cellulose (Hyosung Co., Korea) obtained by pulping process and the other is hemp cellulose (Hempleekorea, Korea) as

Table I. Hemp Cellulose Treatment Conditions and Lignin Contents

Sample code	Conditions	Lignin contents (%)
HC1	Raw hemp cellulose	14.0
HC2	Hemp was treated NaOH and $NaClO_2$ aqueous solution at room temperature and boiling point for 1 h and 1 h, respectively.	5.2
HC3	Hemp was treated NaOH and $NaClO_2$ aqueous solution at room temperature and boiling point for 5 h and 1 h, respectively.	4.9
HC4	Hemp was treated NaOH and $NaClO_2$ aqueous solution at room temperature and boiling point for 5 h and 5 h, respectively.	4.2

ligno-cellulose source. The pure cellulose was mixed with lignin for spinning solution. The lignin content in the cellulose/lignin mixture was changed from 0 to 40% in the solution. The lignin content in hemp cellulose was controlled by removing the lignin by alkali treatments using 17.5% NaOH and 0.7% $NaClO_2$ aqueous solutions under the condition as shown in Table I. To investigate the influence of lignin on the spinnability and the micro- and macro-morphologies, the two types of cellulose (prepared cellulose/ lignin mixture and hemp cellulose) were individually dissolved in 1-ethyl-3-methylimiazolium acetate ([EMIM][OAc], BASF). The total concentration of cellulose and lignin in each solution was kept constant as 8.3 wt %. To improve the spinnability and the fiber microstructure, dimethylforamide (DMF, Daejung Chemicals & Metals Co., Korea) was added to each solution as reported in the previous work.[15] The weight ratio of DMF against ionic liquid was kept as 50% for the all cellulose/lignin solutions. The preparing conditions for the cellulose/lignin spinning solution were summarized in Table II. The treated hemp cellulose were dissolved in ionic liquid and DMF (ionic liquid : DMF = 1 : 1.75) with 14 wt % at 70°C.

The prepared solutions were electrospun using a conventional syringe type apparatus onto a rotating wired cylinder type collector. The applied voltage and the tip to collector distance were

kept constant through the whole experiments as 30 kV and 12 cm, respectively. The as-spun fiber was immersed in ethanol at 4°C for 1 day and sequentially washed several times using deionized water until remained solvents were completely removed.

Characterizations

The rheological properties of the cellulose solutions were obtained using a parallel disk type rheometer (Dynamic stress rheometer, RS-1, Haake). The chemical compositions of the electrospun fibers and the raw material were measured using Fourier transform infrared spectroscopy (FT-IR, FT-IR300E, JASCO). The spinnability of each solution during the electrospinning was observed and evaluated by naked eyes based on the formations of the drop and the jet. The morphologies of the electrospun fibers were studied using scanning electron microscopy (FE-SEM, JSM-6380, JEOL). The fiber diameters were measured from the SEM images using image analysis software (EyeViewAnalyzer, Digiplus Inc.). The microstructures of the electrospun fiber were investigated by Wide-angle X-ray diffraction (WAXD) analysis using X-ray diffraction (XRD, Ultima IV, Rigaku).

RESULTS AND DISCUSSION

Chemical Composition of Electrospun Fibers

Figure 1 shows the chemical composition of the materials (pure cellulose, cellulose/lignin mixture powder, and hemp cellulose) and the fibers electrospun from the mixture of cellulose and lignin mixture (refer as cellulose/lignin), and the hemp cellulose solutions. Obviously, the characteristic peaks corresponding to lignin at 1240, 1430 and 1510 cm^{-1} were observed for both the cases. For the fibers from the hemp cellulose, the characteristic peak of ester (1738–1709 cm^{-1}, C=O stretching in unconjugated ester bond) and ether bonding (1086 cm^{-1}, C—O deformation in ether) remarkably appeared. It shows that cellulose and lignin are chemically bonded to each other by ester and ether bonding in the hemp cellulose.[16–19] The size of the peak at 1720 cm^{-1} became negligibly small as the amount of the residual lignin was decreased, whereas the peak at 1086 cm^{-1} was still noticeable even when most of lignin was removed. It means that the bonding between cellulose and lignin was not completely broken during the alkali treatment and they were chemically bonded to each other in the solution. In the case of cellulose/lignin mixed solution, the peaks corresponding to cellulose–lignin bonding did not

Table II. Solution Condition of Cellulose/Lignin for Electrospinning, Sample Code, and Spinnability

Sample code	Cellulose (g)	Lignin (g)	IL (g)	DMF (g)	Conc. (%)	Spinnability
Cell	0.682	–	5.000	2.500	8.300	++[a]
C/L1	0.648	0.034	5.000	2.500	8.300	++
C/L2	0.614	0.068	5.000	2.500	8.300	+[b]
C/L3	0.579	0.102	5.000	2.500	8.300	+
C/L4	0.546	0.136	5.000	2.500	8.300	+
C/L5	0.477	0.205	5.000	2.500	8.300	–[c]
C/L6	0.409	0.273	5.000	2.500	8.300	–

[a] Electrospinning with a few droplet.
[b] Electrospinning with many mist and droplet.
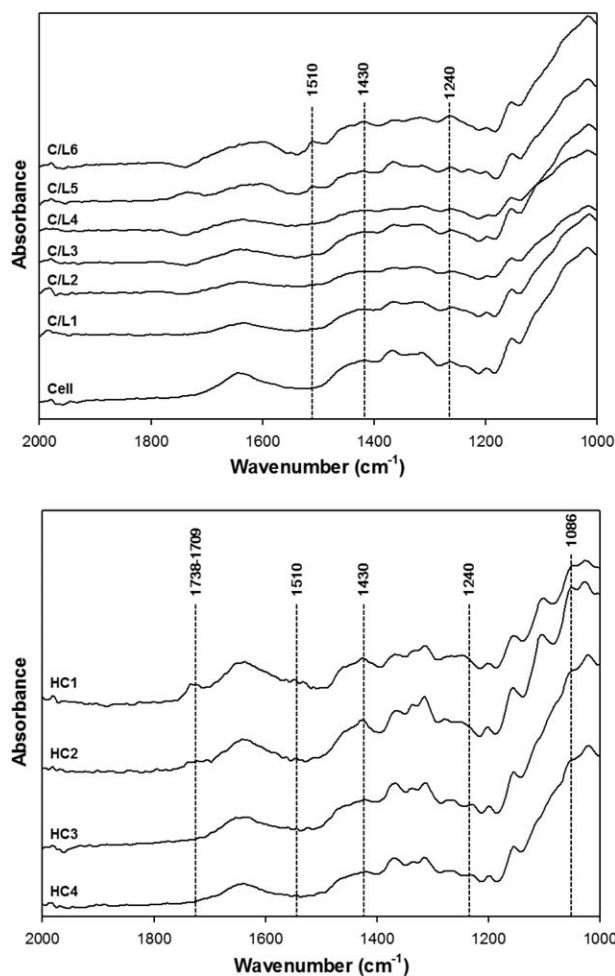[c] Rarely electrospinning.

Figure 1. FTIR spectra of electrospun cellulose/lignin and hemp cellulose fiber.

Rheological Behaviors of Solutions

To investigate the effects of the lignin content and state on the rheological properties, the shear viscosities of each cellulose solution were measured as a function of shear rate under steady state using parallel disks. As displayed in Figure 2, all the solutions showed typical shear thinning behaviors as similar to conventional polymer solutions. The shear thinning behaviors was, however, dependent on the cellulose solution types. For the hemp cellulose solution, the shear thinning started at lower shear rate as the lignin content increased. Contrarily, the shear thinning began at higher shear rate when the cellulose/lignin solution contained more lignin.

The zero shear viscosity was calculated based on the viscosity measurement (Figure 2) and displayed in Figure 3. The lignin content also significantly influenced on the zero shear viscosities for the both solutions in the different ways. The difference seems originated from the different combining state of lignin with cellulose as explained in FT-IR results. For the cellulose/lignin solution, the initial addition of lignin significantly decreased the viscosity. The further addition decreased the viscosity linearly. However, the viscosity of the hemp cellulose solution increased as the lignin content in the solution was increased. As explained above, the opposite polarities of cellulose and lignin resulted in phase separation between the two
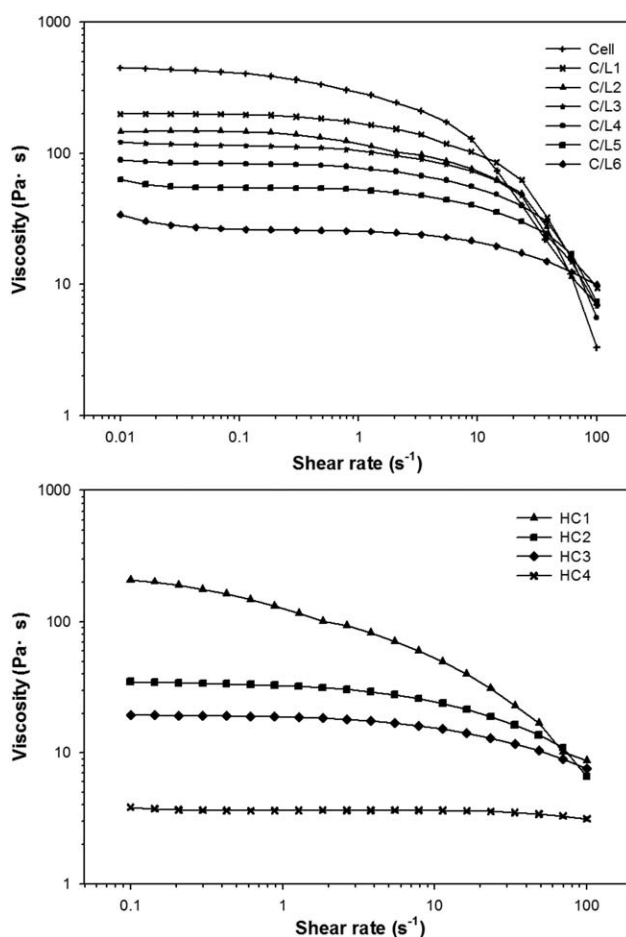
appear. Apparently, the bonding between cellulose and lignin was not generated by simple mixing.

Considering the amount of lignin initially mixed with cellulose, the lignin characteristic peaks were small for the fibers from the cellulose/lignin solution. The peak disappeared when the lignin concentration was lower than 30% because the lignin was removed during washing process after electrospinning. When lignin was mixed and dissolved with cellulose, the phases of lignin and cellulose were separated due to the opposite polarities of cellulose and lignin. Cellulose is hydrophilic due to its hydroxyl groups while lignin is hydrophobic due to its phenyl groups. Due to the relative amount of two components, cellulose consisted of continuous phase whereas lignin consisted of discontinuous phase. The decrease of lignin content reduced the size of lignin phase and in turn the lignin could be removed during the washing process.

For the electrospun hemp cellulose fiber, the lignin characteristic peak got smaller as the remaining lignin was reduced. However, the peak did not completely disappear regardless of the lignin content. It demonstrated that the lignin in hemp cellulose was not completely removed due to its chemical bonding with the cellulose.

Figure 2. Viscosity of cellulose/lignin and hemp cellulose solutions as function of shear rate.
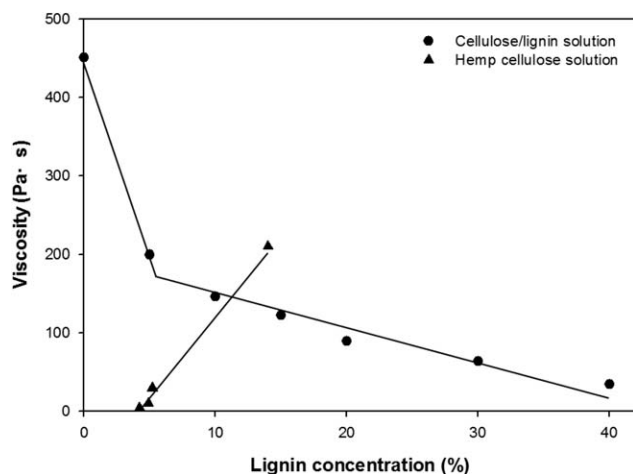
Figure 3. Zero shear viscosity of cellulose/lignin and hemp cellulose solutions.

components in the cellulose/lignin solution. In the solution, the phase-separated lignin hindered the chain entanglement between cellulose and reduced the solution viscosity. The lignin in the hemp cellulose, however, could not form discontinuous phase because lignin was combined to cellulose with ester or ether bond. It resulted in the decrease of the mobility of the

cellulose chain. The decreased mobility of the cellulose increased the viscosity.

Spinnability of Solutions

The spinnability of the cellulose/lignin solution was observed during electrospinning and summarized in Table II. As shown in the table, the lignin concentration showed a significant influence on the spinnability of the cellulose/lignin solution. As expected, the lignin concentration gave negative influence on the spinnability. The solution with no lignin was stably electrospun into fibers. When the lignin concentration was 5 wt % against the total solution, the spinnability became slightly worse. During the electrospinning, a few mists and droplets were observed. The further increase of lignin concentration in the solution resulted in worse spinnability. When the lignin concentration increased over 40%, the solution could not be electrospun, but mostly dropped with mist. The lignin in the solution caused unstable whipping motion and jet formation at the tip. Although the addition of lignin decreased the solution viscosity, the spinnability was worsened rather than improved. The dependence of spinnability on the lignin concentration can be explained in terms of chain entanglement and the miscibility between the two components as mentioned above. The phase separated lignin disturbed the chain-to-chain entanglement of cellulose and in turn caused the spinline breakage during whipping motion of the jet. The spinnability of the hemp cellulose
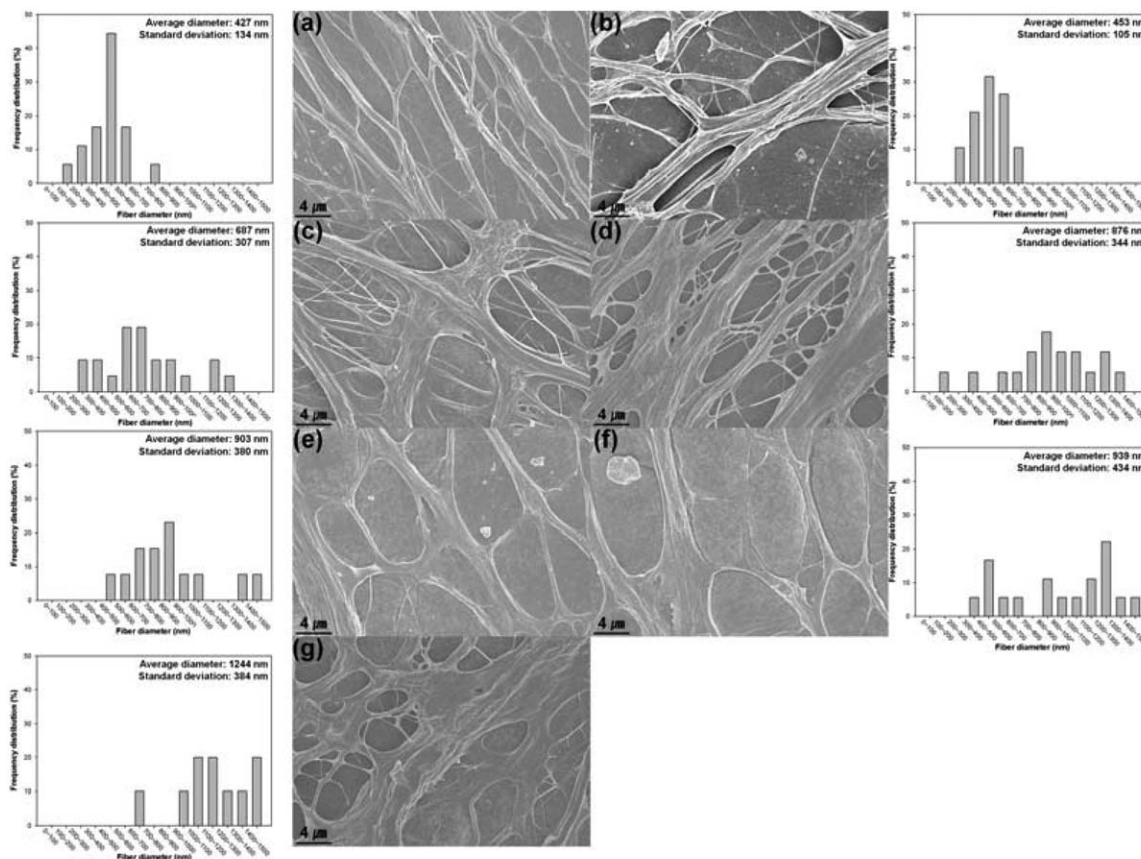

Figure 4. SEM images and distribution of fiber diameter from cellulose/lignin solution; (a) Cell, (b) C/L1, (c) C/L2, (d) C/L3, (e) C/L4, (f) C/L5, and (g) C/L6.
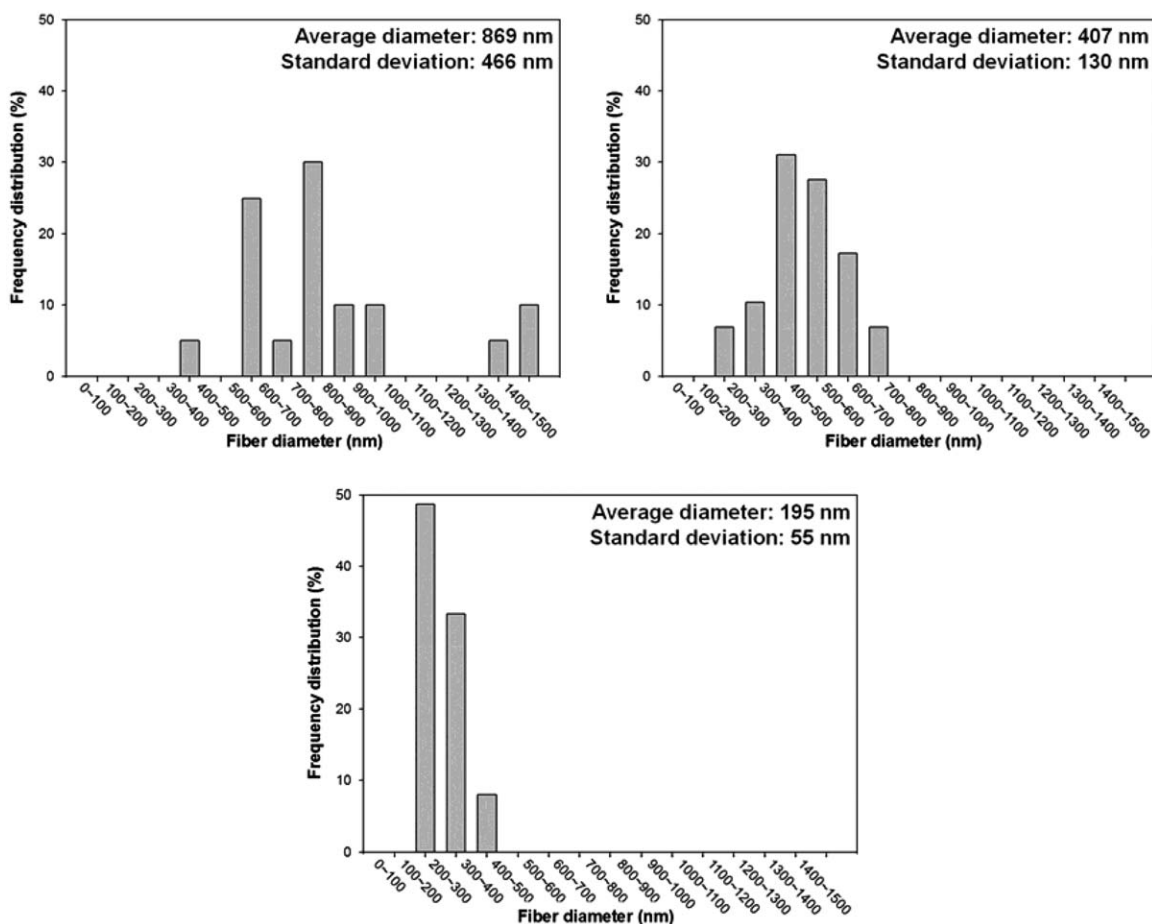
Figure 5. Distribution of fiber diameter from hemp cellulose solution; (a) HC2, (b) HC3, (c) HC4.

solution also became worse with the increase of lignin remained in the solution.[14] The large volume of the lignin combined to cellulose gave less chance for the cellulose to get close each other. This different actions of lignin in each solution resulted in the different fiber forming behavior which will be discussed later.

Morphology of Electrospun Fibers

Figure 4 shows the SEM images and the diameter distribution of the electrospun fiber from the cellulose/lignin solutions. As illustrated in the figure, the morphology of the fiber including the average and the distribution of the fiber diameters was strongly influenced by the lignin content in the spinning solution. The fibers obtained from the pure cellulose solution (lignin 0%) were fairly fibrillated and showed small average fiber diameter with narrow distribution. As the lignin concentration increased, the average fiber diameter significantly increased and the fiber diameter distribution became broader. The increase of lignin resulted in film-like flat fibers. The flat fibers were more frequently observed as the lignin concentration increased in the solution. Due to the flat fibers, the average fiber diameter increased and the diameter distribution became broader. When the lignin concentration increased up to 15%, the fiber diameter distribution began to change from single to the bimodal distribution. When the lignin concentration was 30%, the bimodal distribution became more distinguishable and the frequency of

the larger mode became dominant. All the phenomena could be explained in terms of the phase separation and the influence of the lignin on the chain entanglement, as explained above. As well known, lignin is not able to form fiber due to its branched non-linear structure. As a result, the lignin rich phase formed film-like fiber instead fibrillated fiber, when the lignin rich
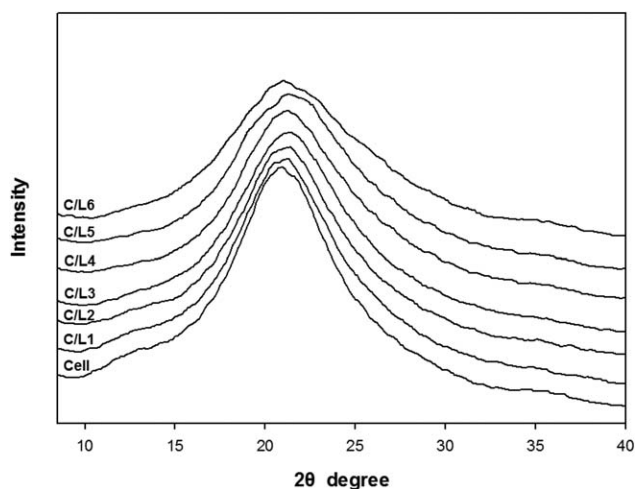

Figure 6. XRD curves of electrospun cellulose/lignin fiber.

phase was spun. On the other hand, cellulose formed fibrillated fiber successfully during the electrospinning.

Using the SEM images in the previous work,[14] the diameter distribution of the hemp cellulose fiber was obtained and compared with the fiber of cellulose/lignin as shown in Figure 5. As reported, the fiber became more fibrillated and more uniform when the solution contained less lignin. Unlike to the fiber from cellulose/lignin solution, the film-like flat fiber was not observed. Instead of the flat fiber, the large drops and the agglomeration of the electrospun fibers were observed. The average and the standard deviation of the fiber diameter increased simultaneously as the lignin content increased. As similar to the cellulose/lignin case, the distribution became broader with the increase of lignin content in the solution. Most of the fibers electrospun from the hemp cellulose solution had single modal diameter distributions due to no phase separation between cellulose and lignin. The lignin combined to cellulose was elongated and fibrillated together with cellulose during electrospinning. However, bimodal fiber diameter distribution was found in the fibers spun from the hemp cellulose treated in short time. It can be attributed to non-cellulosic components which were not completely removed because of insufficient treatment time. The residual non-cellulose components were associated with cellulose and resulted in large fibers.

Microstructure of Electrospun Fibers

The X-ray diffractions of the fibers electrospun from the cellulose/lignin solution are shown in Figure 6. The crystalline structure has been changed from cellulose I to cellulose II after regeneration. The crystallinity was also influenced by the lignin concentration in the spinning solution. As the lignin concentration increased in the solution, the peaks at 12°, 20.5°, and 21.5° became smaller and broader. When the lignin concentration was 40 wt %, the peaks disappeared and showed a single broad peak. It indicates that cellulose could not form crystalline structure because the lignin disturbed the crystallization of the cellulose chains. Compared to the fiber from the hemp cellulose solution presented in a previous study,[14] the fibers from the cellulose/lignin solution showed poor crystallinity. When the fibers contained the same lignin content (i.e., 5 wt %), the fiber from the hemp cellulose showed a distinct characteristic peak at 12° whereas the fiber from cellulose/lignin solution did not. As Blackwell et al.[20] explained, the presence of lignin in the solution prevents structure conversion into crystalline due to the different polarities of the two components. It can be similarly applied to the results in this study. The lignin phase resulted in unstable whipping motion as described above. It gave less change for chains to be elongated and crystallized.

CONCLUSIONS

The cellulose fibers were successfully electrospun from two different types of cellulose solutions. The type and the content of lignin showed significant effects on the viscosities, the spinnability, and the morphologies of the resulted fibers. The viscosity of the cellulose/lignin decreased with lignin concentration, while the viscosity of the hemp cellulose showed the opposite behaviors. For both the cases, the spinnability became worse with the increase of lignin. The lignin in the cellulose/lignin resulted in film-like flat fiber and bimodal distribution of the fiber diameter, while the lignin in the hemp cellulose mainly increased the fiber diameter. It is due to the different phase separation behaviors of the two solutions. For the cellulose/lignin solution, the lignin could form its own phase while the lignin in the hemp cellulose was chemically combined with cellulose.

AUTHOR CONTRIBUTIONS

Mr. Ahn performed electrospinning and analyzed rheological properties; Mr. Kang measured FTIR spectra of electrospun fiber; Mr. Park classified types of cellulose structure and measured crystallinity index; Ms. Ku measured fiber diameter and standard deviation from SEM images of electrospun fiber; Dr. Lee analyzed lignin structure and state of lignin into cellulose solution; Dr. Kim supervised overall research and carried out documentation.

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