Preparation and Characterization of Electrospun Composite Nanofibers from Poly(vinyl alcohol) /Lignocellulose Nanofibrils with Different Chemical **Compositions**

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Lignocellulose nanofibrils (LCNFs) were prepared using Liriodendron tulipifera L. wood flour. Electrospun nanofibers were fabricated by mixing the LCNFs with poly(vinyl alcohol) (PVOH). The lignin and hemicellulose contents of the wood flour were controlled with an alkaline-peroxide treatment at a pH of 11.5 using various hydrogen peroxide concentrations. The morphological characteristics, mean diameter, and filtration time of the LCNFs subjected to wet disk milling (WDM) and high-pressure homogenization were determined. Furthermore, the spinning suspension viscosity was measured with various LCNF concentrations and PVOH/LCNF addition ratios. After the alkalineperoxide treatment, the lignin and hemicellulose contents decreased with an increasing hydrogen peroxide concentration and reaction time. As the lignin content decreased, the nanofibril diameter decreased and the filtration time increased. The diameter decreased further after the homogenization treatment following WDM. The viscosity of the mixed solution increased with an increasing PVOH and LCNF mixed solution concentration and LCNF addition ratio, and decreasing lignin content. Scanning electron micrographs revealed that the diameter of the electrospun nanofibers increased as the mixed solution concentration and LCNFs addition increased, the lignin content decreased, and with the homogenization treatment.

Keywords: Lignocellulose nanofibril; Alkaline-peroxide treatment; Wet disk milling; High-pressure homogenization; Electrospinning

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INTRODUCTION

Electrospinning is a method employed for fabricating micro- and nanometer-scale fibers, and it has been highlighted as a more efficient process than conventional spinning methods (Liao et al. 2018; Guo et al. 2019; Huang et al. 2019). Many variables are considered in electrospinning, such as the solution concentration, viscosity, surface tension, electric field intensity, spinning speed, spinning time, and collector distance. The shape of the fibers obtained by electrospinning differs with the manner in which each of these variables are controlled (Sun et al. 2014). Electrospun nanofibers have a large specific surface area and fiber-to-fiber voids, unlike those prepared by other spinning methods, and hence they can be developed into porous fibers (Wang and Hsiao 2016;

Wang *et al.* 2019). Because of this feature, electrospun nanofibers have widespread applications in filters, sensors, catalysts, and tissue engineering. Thus, research into the use of various polymers to prepare electrospun fibers is actively being performed (Yun *et al.* 2007; Liu *et al.* 2009; Fang *et al.* 2011; Hu *et al.* 2014; Alvarado *et al.* 2018).

Poly(vinyl alcohol) (PVOH) has been highlighted as one of the most commonly used polymers for electrospinning. PVOH is a hydrophilic polymer produced by the hydrolysis of poly(vinyl acetate) and is used in a wide range of applications, such as tissue support, drug release, and filters because of its semi-crystallinity, environmental friendliness, and biodegradability (Wu *et al.* 2005; Bolto *et al.* 2009; Islam *et al.* 2015). Because PVOH has a high solubility and surface activity, it can be easily mixed with other natural polymers, thereby improving the mechanical properties of the latter (Folkes and Hope 1993). Nanocellulose, by virtue of its biodegradability, renewability, and excellent mechanical properties, has been attracting attention as a PVOH reinforcing material. PVOH, which is a water-soluble polymer, is hydrogen-bonded to the hydroxyl group of nanocellulose to obtain a composite material with an excellent thermal stability and compatibility. Therefore, many studies have been conducted to prepare composite nanofibers by electrospinning a mixed suspension of PVOH and nanocellulose (Lu *et al.* 2008; Medeiros *et al.* 2008; Peresin *et al.* 2010; Sutka *et al.* 2013; Park *et al.* 2014).

In this study, *Liriodendron tulipifera* L. wood flour was subjected to alkalineperoxide (AP) treatment to prepare lignocellulose nanofibrils (LCNFs) with controlled amounts of lignin and hemicellulose, and defibrillated to a nanosize scale by a wet disk milling (WDM) treatment. Furthermore, high-pressure homogenization of the WDMtreated LCNFs was conducted to prepare LCNFs with uniform dimensions. Then, the PVOH/LCNF suspension was prepared by mixing LCNF with PVOH at various concentrations and ratios; thus, electrospun composite nanofibers were prepared. The effects of the chemical composition of the LCNFs, additional homogenizer treatment, and viscosity of the PVOH/LCNF suspension on the properties of the electrospun composite nanofibers were investigated.

EXPERIMENTAL

Materials

Liriodendron tulipifera L. was provided by the Experimental Forest Kangwon National University (Chuncheon, South Korea), ground to 50-mesh size wood flour, and used as the study material. Hydrogen peroxide (H₂O₂, 35%), sodium hydroxide (NaOH, 50%), sulfuric acid (H₂SO₄, 95%), sodium chlorite (NaClO₂), acetic acid (C₂H₄O₂), and tert-butyl alcohol were purchased from Daejung Chemicals & Metals Co., Ltd. (Siheung, South Korea). Poly(vinyl alcohol) ([CH₂CH(OH)]_n) ($n \approx 2000$) was purchased from Tokyo Chemical Industry (Tokyo, Japan).

AP treatment and WDM defibrillation

The lignin and hemicellulose contents were adjusted by treating the wood flour with AP, as described in Seo *et al.* (2019) by applying the Gould's method (Gould 1984). For the alkali pretreatment, 5% wood flour and 0.4% NaOH suspensions were prepared and reacted in a water bath at 60 °C for 1 h. For the AP treatment, the alkali-pretreated wood flour was added to 0.2% and 12% H_2O_2 solutions, and the suspensions with a solids content of 2% were stirred in a water bath at 80 °C for 1 h and 5 h, respectively, with a

pH of 11.5. The untreated and AP-treated wood flour were repeatedly defibrillated with 15 passes of WDM to prepare the LCNFs. Based on the lignin content, the LCNFs were named LCNF-32, LCNF-30, and LCNF-13, and their chemical compositions and reaction conditions are shown in Table 1.

| Sample | H ₂ O ₂ Concentration (%) | Reaction Time (h) | Composition (%) | | | |
|---------|---|----------------------|-----------------|---------------|---------------|--|
| | | | Cellulose | Hemicellulose | Klason Lignin | |
| LCNF-32 | - | - | 45.4 | 26.3 | 32.1 | |
| LCNF-30 | 0.2 | 1 | 53.9 | 22.7 | 30.4 | |
| LCNF-13 | 12.0 | 5 | 79.1 | 6.0 | 13.0 | |

| Table 1 | Chemical | Compositions | of the AP | -treated | Products |
|---------|----------|--------------|-----------|----------|----------|
| | Chemical | Compositions | | -incalcu | 1 100000 |

Note that the NaOH concentration was 0.4%, pH was 11.5, and reaction temperature was 80 $^{\circ}\text{C}$

High-pressure homogenization

The LCNF suspension prepared by the WDM treatment was diluted to 0.3% and subjected to high-pressure homogenization (HPH) (M-110 EH-30, Microfluidics, Newton, MA, USA) three times at a pressure of 1300 bar. The obtained LCNFs were named WDM-LCNF and HPH-LCNF to differentiate the LCNFs according to the treatment method.

Methods

LCNF morphological analysis

To prepare scanning electron microscopy (SEM) samples for morphological analysis of the LCNFs, a 0.001 wt% LCNF concentration was prepared and treated using an ultrasonicator (VCX130PB, Sonics and Materials Inc., Newtown, MA, USA) for 60 s. Then, the suspension was filtered through a PTFE membrane filter (ADVANTEC®, Toyo Roshi Kaisha Ltd., Tokyo, Japan), and the filtration time was measured. The residue obtained on the filter was immersed in tert-butyl alcohol for 20 min three times and then dried at -55 °C in a freeze dryer for 2 h. The LCNF samples were coated with iridium using a sputter coater (EM ACE600, Leica Microsystems, Seoul, South Korea) and observed with field emission scanning electron microscopy (FE-SEM) (S-4800, Hitachi, Tokyo, Japan). The LCNF diameters were measured at least 100 times using image analysis software (Version 1.45, Windows, ImageJ, U. S. National Institutes of Health, Bethesda, MD, USA).

Preparation of the Composite Nanofibers

Preparation of the PVOH/LCNF mixed suspension and viscosity measurement

To prepare an aqueous PVOH solution, 10 g of PVOH were added to 90 g of distilled water and stirred at 80 °C until it completely dissolved. Then, the PVOH/LCNF mixed suspensions of various concentrations were prepared by mixing the PVOH solution and the LCNFs water suspension at various ratios. The PVOH/LCNF ratios were set to be 99/1, 97/3, and 95/5. The concentration of the mixed suspensions ranged from 2% to 8%. The PVOH and LCNFs were mixed and stirred at 60 °C for 1 h and cooled at room temperature. The viscosity of the mixed suspension was measured using a viscometer

(DV-II+, Brookfield Engineering, Inc., Middleborough, MA, USA) equipped with a SC4-18 spindle at shear rates ranging from 0.4 s^{-1} to 132 s^{-1} at 25 °C. *Electrospinning*

The PVOH/LCNF mixed suspension was placed in a 15-mL syringe and mounted on an electrospinning pump (ESR200RD, NanoNC, Seoul, South Korea), which was operated at a voltage of 15 kV and spinning rate of 10 μ L/min. A 21G metal nozzle with an inner diameter of 0.5 mm was used. The collector was covered with aluminum foil, and the tip-to-collector distance was fixed at 15 cm. For morphological characterization of the electrospun nanofibers formed on the aluminum foil, the electrospun nanofibers were cut and stuck onto the SEM grid. Then, the SEM samples were coated with iridium using the sputter coater and observed with FE-SEM. The fiber diameters were measured using the image analysis software.

RESULTS AND DISCUSSION

Figure 1 shows the SEM images of the LCNFs prepared by the WDM and HPH treatments. The WDM treatment time was 6.02 h/kg, 5.42 h/kg, and 7.3 h/kg for LCNF-32, LCNF-30, and LCNF-13, respectively, and the HPH treatment was then performed three times. In the case of LCNF-32, which was not subjected to the AP treatment, agglomerated fibers were observed. This would be mainly due to the high lignin and hemicellulose contents. The LCNF-30 and LCNF-13 showed more uniform fibers, compared to LCNF-32. The diameters of the separated fibers are summarized in Table 2. The diameters decreased to 37.5 nm, 34.4 nm, and 24.4 nm after the WDM treatment and to 31.1 nm, 27.2 nm, and 21.3 nm after the HPH treatment for LCNF-32, LCNF-30, and LCNF-13.

| Sample | Diameter (nm) | | |
|-------------|---------------|--|--|
| WDM-LCNF-32 | 37.5 ± 21.7 | | |
| WDM-LCNF-30 | 34.4 ± 20.9 | | |
| WDM-LCNF-13 | 24.4 ± 4.4 | | |
| HPH-LCNF-32 | 31.1 ± 8.4 | | |
| HPH-LCNF-30 | 27.2 ± 6.3 | | |
| HPH-LCNF-13 | 21.3 ± 5.2 | | |

Table 2. Average Diameters of the WDM-LCNF and HPH-LCNF with Different

 Chemical Compositions

Figure 2 shows the filtration times of the six types of LCNFs subjected to the WDM and HPH treatments with various lignin contents. After the HPH treatment, the filtration time for LCNF-32 was largely unchanged, but that for LCNF-30 and LCNF-13 increased, which may have been because of the increase in the surface area from the decreased LCNF diameter.

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Fig. 1. SEM images of the WDM-LCNFs and HPH-LCNFs with different chemical compositions: (a) WDM-LCNF-32 (WDM time = 6.02 h/kg); (b) HPH-LCNF-32; (c) WDM-LCNF-30 (WDM time = 5.24 h/kg); (d) HPH-LCNF-30; (e) WDM-LCNF-13 (WDM time = 7.35 h/kg); and (f) HPH-LCNF-13

Figure 3 shows the effects of the PVOH/WDM-LCNF suspension concentration (2%, 4%, 8%) and ratio (99/1, 97/3, 95/5) on the rheological properties. The PVOH/LCNF suspension viscosity increased with an increase in the LCNF content and decrease in the lignin content. As the suspension concentration increased, the viscosity increased remarkably. When the concentration was higher, the difference in the viscosity was more noticeable because of the addition of LCNFs. Sutka *et al.* (2013) also reported that the PVOH/CNF suspension viscosity increased with an increasing CNF content because of the stronger hydrogen bonding between the PVOH and CNFs, which was confirmed by Fourier transform infrared analysis.



Fig. 2. Filtration time of the WDM-LCNF and HPH-LCNF samples with different chemical compositions



Fig. 3. Rheological properties of the PVOH/WDM-LCNF-32 and PVOH/WDM-LCNF-13 suspensions with different concentrations: (a) 2%, (b) 4%, and (c) 8%

Figure 4 shows the effect of the defibrillation degree of the LCNFs on the PVOH/LCNF suspension rheological properties with different lignin contents. The viscosity of the PVOH/HPH-LCNF suspension was higher than that of the PVOH/WDM-LCNF. This may have been because of the increased hydrogen bonding between the PVOH and HPH-LCNFs with a higher specific surface area for the cellulose than for the WDM-LCNF. Zheng *et al.* (2014) reported that cellulose nanofibrils (CNFs) with a large aspect ratio increased the suspension viscosity with PVOH by forming a three-dimensional network structure to enhance hydrogen bonding. Zhou *et al.* (2016) demonstrated that when cellulose nanocrystals (CNCs) and CNFs were mixed with PVOH, the CNFs with a higher aspect ratio than that of the CNCs had a greater number of hydrogen bonding sites with the hydroxyl group in the PVOH. Consequently, the suspension viscosity increased.



Fig. 4. Rheological properties of the PVOH/WDM-LCNF and PVOH/HPH-LCNF suspensions with different chemical compositions with a 97/3 PVOH/LCNF ratio and 2% suspension concentration

Figures 5 and 6 show the SEM images of the electrospun nanofibers from the 2%, 4%, and 8% PVOH/WDM-LCNF-32 suspensions, and the 2% and 4% PVOH/WDM-LCNF-13 suspensions, respectively. With an increasing LCNF content in the PVOH solution and PVOH/LCNF suspension concentration, the diameter of the electrospun nanofibers increased in all of the samples.

The electrospun nanofibers made from the 2% PVOH/WDM-LCNF-32 suspension showed a uniform size and their diameters increased from 163 nm to 222 nm as the LCNF ratio in the PVOH solution increased from 1 to 5. As the suspension concentration increased, some agglomerated fibers and beads, as well as uniform fibers were observed. In the electrospun nanofibers from the 8% PVOH/WDM-LCNF-32 suspension, the fiber diameter was 371 nm to 398 nm, and some agglomerated fibers and beads were found, irrespective of the LCNF addition ratio.

In the case of PVOH/WDM-LCNF-13, only the 2% and 4% suspensions were used because electrospinning was difficult at an 8% concentration. Greater amounts of agglomerated fibers and beads were observed with an increasing LCNF content in the PVOH. Furthermore, the amount of independent electrospun nanofibers decreased in PVOH/WDM-LCNF-13 when compared with that in PVOH/WDM-LCNF-32 with the same concentration. As the lignin content in the LCNFs decreased, the hydrophilicity of the LCNFs increased, which resulted in an increased affinity with the PVOH. This in turn resulted in an increase in the electrospun nanofiber diameter and spinning suspension viscosity.

The average diameters of the electrospun nanofibers made from PVOH/WDM-LCNF-32 and PVOH/WDM-LCNF-13 are summarized in Table 3. As the LCNF content in the PVOH and suspension concentration increased, the electrospun nanofiber diameter increased. Peresin *et al.* (2010) reported that the diameters of the electrospun nanofibers from a PVOH and CNC suspension were 280 nm to 300 nm. Park *et al.* (2014) reported that electrospun nanofibers from TEMPO-oxidized CNF and PVOH had an average diameter of 60 nm to 160 nm. As the CNF content was increased from 1% to 5%, the diameter distribution broadened and more beads were observed. Kumbar *et al.* (2008) reported that the fiber diameter increased as the spinning polymer solution concentration and viscosity increased. It was concluded that the electrospun nanofiber diameter could be controlled by changing the spinning polymer solution concentration.



Fig. 5. Morphology of the PVOH/WDM-LCNF-32 electrospun nanofibers with different ratios and concentrations: (a) 99/1 and 2%; (b) 97/3 and 2%; (c) 95/5 and 2%; (d) 99/1 and 4%; (e) 97/3 and 4%; (f) 95/5 and 4%; (g) 99/1 and 8%; (h) 97/3 and 8%; and (i) 95/5 and 8%



Fig. 6. Morphology of the PVOH/WDM-LCNF-13 electrospun nanofibers with different ratios and concentrations: (a) 99/1 and 2%; (b) 97/3 and 2%; (c) 95/5 and 2%; (d) 99/1 and 4%; (e) 97/3 and 4%; and (f) 95/5 and 4%

| Table | 3. Average Diamet | er of the PVO | H/WDM-LCNF Ele | ectrospun Nanofibers |
|--------|---------------------|----------------|----------------|----------------------|
| with D | ifferent Ratios and | Concentrations | S | |

| | Concentration (%) | PVOH/LCNF Ratio | Diameter (nm) |
|----------------------|----------------------|--------------------|---------------|
| PVOH | 8.0 | 100/0 | 345 ± 25 |
| | 2.0 | 99/1 | 163 ± 109 |
| | | 97/3 | 172 ± 94 |
| | | 95/5 | 222 ± 103 |
| | 4.0 | 99/1 | 224 ± 122 |
| PVOH/WDM-LCNF- 32 | | 97/3 | 231 ± 131 |
| - | | 95/5 | 255 ± 165 |
| | | 99/1 | 371 ± 37 |
| | 8.0 | 97/3 | 374 ± 35 |
| | | 95/5 | 398 ± 45 |
| | 2.0 | 99/1 | 197 ± 95 |
| | | 97/3 | 202 ± 84 |
| PVOH/WDM-LCNF- | | 95/5 | 244 ± 94 |
| 13 | 4.0 | 99/1 | 248 ± 48 |
| | | 97/3 | 275 ± 54 |
| | | 95/5 | 289 ± 69 |

Figure 7 shows the SEM images of the electrospun composite nanofibers from the PVOH/WDM-LCNF and PVOH/HPH-LCNF samples. The average diameters are summarized in Table 4. In all of the samples, uniform fibers were observed. The diameter of the PVOH/WDM-LCNF electrospun nanofibers increased from 172 nm to 202 nm as the lignin content decreased, which was smaller than that of the PVOH/HPH-LCNF electrospun nanofibers (190 nm to 220 nm). This may have been because of the higher viscosity of the PVOH/HPH-LCNF suspension, in which a greater number of fine fibers were formed by the HPH treatment than by the WDM treatment.



Fig. 7. SEM images of the electrospun nanofibers from PVOH/WDM-LCNF and PVOH/HPH-LCNF suspensions with different chemical compositions (97/3 PVOH/LCNF and 2% suspension concentration): (a) PVOH/WDM-LCNF-32; (b) PVOH/HPH-LCNF-32; (c) PVOH/WDM-LCNF-30; (d) PVOH/HPH-LCNF-30; (e) PVOH/WDM-LCNF-13; and (f) PVOH/HPH-LCNF-13

Table 4. Average Diameters of the Electrospun PVOH/WDM-LCNF andPVOH/HPH-LCNF Nanofibers with Different Chemical Compositions

| Sample | Diameter (nm) |
|------------------|---------------|
| PVOH/WDM-LCNF-32 | 172 ± 94 |
| PVOH/WDM-LCNF-30 | 184 ± 52 |
| PVOH/WDM-LCNF-13 | 202 ± 84 |
| PVOH/HPH-LCNF-32 | 190 ± 69 |
| PVOH/HPH-LCNF-30 | 203 ± 55 |
| PVOH/HPH-LCNF-13 | 222 ± 64 |

CONCLUSIONS

- 1. The high-pressure homogenization (HPH) treatment was performed after wet disk milling (WDM) defibrillation to obtain lignocellulose nanofibers (LCNFs) with a more uniform size distribution. The diameter of the WDM-treated LCNFs decreased after the HPH treatment. The filtration time of the LCNF water suspension increased with a decreasing lignin content and was longer for the HPH-LCNFs than for the WDM-LCNFs with the same lignin content because of the larger surface area.
- 2. The viscosity of the suspension of LCNF in poly-(vinyl alcohol) (PVOH/LCNF) increased with a decreasing lignin content in the LCNF and increasing suspension concentration and LCNF content in the PVOH.
- 3. The high viscosity of the PVOH/LCNF suspension adversely affected its ability to electrospin. With a decreasing lignin content in the LCNFs and increasing suspension concentration and LCNF content in the PVOH, the diameter of the electrospun fibers increased.
- 4. The electrospun fibers made of the PVOH and HPH treated LCNFs had more uniform morphological characteristics and lower diameters than those made of the PVOH and only WDM treated LCNFs.

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