Preparation and Characterization of Cellulose Nanofibril/Polyvinyl Alcohol Composite Nanofibers by Electrospinning¹

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ABSTRACT

This work undertook to prepare nanofibers of cellulose nanofibrils (CNF)/polyvinyl alcohol (PVA) composite by electrospinning, and characterize the electrospun composite nanofibers. Different contents of CNFs isolated from hardwood bleached kraft pulp (HW-BKP) by 2,2,6,6-tetramethylpiperidine-1-oxy radical (TEMPO)-mediated oxidation were suspended in aqueous polyvinyl alcohol (PVA) solution, and then electrospun into CNF/PVA composite nanofibers. The morphology and dimension of CNFs were characterized by transmission electron microscopy (TEM), which revealed that CNFs were fibrillated form with the diameter of about 7.07 ± 0.99 nm. Morphology of the electrospun nanofiber observed by field-emission scanning electron microscopy (FE-SEM) showed that uniform CNF/PVA composite nanofibers were manufactured at 1~3% CNF contents while many beads were observed at 5% CNF level. Both the viscosity of CNF/PVA solution and diameter of the electrospun nanofiber decreased with an increase in CNF content. The diameter and its distribution of the electrospun nanofibers helped explain the differences observed in their morphology. These results show that the electrospinning method was successful in preparing uniform CNF/PVA nanofibers, indicating a great potential for manufacturing consistent and reliable cellulose-based nanofibrils for scaffolds in future applications.

Keywords : Cellulose nanofibril, TEMPO, Polyvinyl alcohol, Electrospinning, Nanofiber, Diameter distribution

1. INTRODUCTION

Among the natural biomaterials, cellulose is the most abundant, renewable and biodegradable polymer in the world. Cellulose fibrils consist of different hierarchical microstructures. Parallel and long cellulose chains are stabilized

laterally by hydrogen bonds between hydroxyl groups, resulting in high structural strength and stiffness. The reported elastic modulus of native cellulose I crystal is 167.5 GPa (Tashiro & Kobayashi, 1991) and that of tunic in whiskers is 143 GPa (Sturcove *et al.*, 2005). Because of its excellent properties, nanocellulose has gen-

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erated a great deal of interest as nanometer size reinforcement agent for a range of biocomposites.

Advances in nanotechnology have attracted much attention with regard to the utilization of cellulose nanomaterials, such as cellulose nanowhiskers (CNWs), cellulose nanofibrils (CNFs), or crystalline cellulose particles for preparing high performance nanocomposites because highly crystalline cellulose-based nanofibers are environmentally compatible, and are endowed with several other unique and desirable features. Thus, cellulose-based nanomaterials are being increasingly employed for fabricating a wide variety of nanocomposites in combination with polymers, and the developments are benefitting from rapid advances in nanoscience and nanotechnologies (Azizi Samir *et al.*, 2005; Eichhorn *et al.*, 2010). Preparation and characterization related to CNFs-based nanocomposites have been extensively studied in anticipation of many desirable property contributions from CNFs, such as high strength, high stiffness, biodegradability and lightweight.

In the last two decades, the 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO), a water-soluble, commercially available and stable nitroxyl radical, has paved the way for a new field of conversion chemistry for efficient and selective conversion of alcoholic hydroxyl groups to aldehydes, ketones and carboxyl groups under mild conditions (de Nooy *et al.*, 1995; de Nooy *et al.*, 1996). Many related studies using TEMPO have been extensively carried out for CNFs from several wood pulps and cotton linters in the last few years (Fukuzumi *et al.*, 2009; Saito *et al.*, 2006; Saito *et al.*, 2007; Isogai *et al.*, 2011). CNFs prepared by TEMPO-mediated oxidation of native celluloses and successive

mechanical disintegration of the oxidized celluloses in water have also been extensively used for fabricating nanocomposites (Isogai *et al.*, 2011).

According to the TEMPO-mediated oxidation, the C6 primary hydroxyls of cellulose are oxidized to C6 carboxylate groups in water at pH 10~11. The oxidation process can be monitored from the pattern of aqueous NaOH consumption, which is continuously added to the reaction mixture to maintain the pH at 10~11 during the oxidation. Thus the CNFs obtained by the TEMPO-oxidation have a high crystallinity, mostly uniform widths (3~4 nm), and large aspect ratios (>50) compared with other nanocelluloses (Saito *et al.*, 2006; Saito *et al.*, 2007; Shinoda *et al.*, 2012). Moreover, these CNFs can be completely dispersed at the individual nanofibril level in water by electrostatic repulsion and/or osmotic effects due to anionically charged sodium carboxylate groups densely present on the surfaces (Saito & Isogai, 2004).

Electrospinning is a very simple, reproducible, continuous and scalable one-step technology for the preparation of nanofibers with a controllable morphology from solutions of both natural and synthetic polymers (Bhardwaj & Kundu, 2010). In this process, an electrical potential is applied between a droplet of a polymer solution, or melt, held at the end of a capillary tube and a grounded target. When the applied electric field overcomes the surface tension of the droplet, a charged jet of polymer solution is ejected and is controlled by the electric field (Chronakis, 2005). Several factors can affect the electrospinning process: a) solution properties such as viscosity, conductivity and surface tension, b) controlled variables like hydrostatic pressure in the capillary, electric po-

tential at the tip, and the collection screen, and c) ambient parameters including temperature, humidity, and air velocity in the electrospinning chamber (Doshi & Reneker, 1995). Electrospun polymer nanofibers are increasingly finding a number of applications, such as filtration systems and in medical prosthesis, mainly in grafts and vessels. Other targeted applications include tissue templates, electromagnetic shielding, composite delimitation, and liquid crystal devices. It is worth noting that most of these applications are still within the laboratory settings and have yet to be commercialized (Haung *et al.*, 2003). Electrospun fibers produced from PVA have been widely studied over the last two decades (Zhang *et al.*, 2005; Koski *et al.*, 2004; Son *et al.*, 2005; Rosic *et al.*, 2013). Electrospinning has also been used for preparing cellulose-based nanofibers (Khil *et al.*, 2005; Suwantong *et al.*, 2007; Ahn *et al.*, 2012). In recent years, inclusion of CNWs isolated from native cellulose by sulfuric acid hydrolysis significantly improved the elastic modulus of the electrospun nanofibers of CNW/PVA composites, due to the strong interactions of the hydrogen bonding network (Peresin *et al.*, 2010), and uniform and high quality nanofibers of CNW/PVA blends were successfully prepared by electrospinning method (Cho *et al.*, 2012).

However, very little work has been done to prepare cellulose-based nanofibers using CNFs isolated by TEMPO oxidation method that provides a good way of separating CNFs by combining with mechanical defibrillation. In this work, we prepared nanofibers of CNF/PVA blends by the electrospinning method, and characterized their morphology, diameter and diameter distribution by scanning electron microscopy.

2. Experimental

2.1. Materials

A sample of hardwood bleached kraft pulp (HW-BKP) was obtained from Moorim Paper Co. Ltd., Korea and stored in a humidity chamber at 25°C before use. TEMPO, sodium bromide (NaBr), sodium hypochlorite (NaOCl) solution and other chemicals were purchased from Sigma-Aldrich and PVA (Mw 66,000) from Duksan Pure Chemical Co., Ltd., Korea, and all chemicals were used as received. PVA solution (10 wt%) with degrees of hydrolysis between 98 and 99% was first prepared at 80°C with stirring for 6 hours.

2.2. Isolation of CNFs

CNFs were isolated from cellulose pulp according to a modified procedure of the TEMPO-oxidation method (Saito *et al.*, 2006). In brief, 2 g of kraft pulp sample was suspended in water (150 mL) containing TEMPO (0.025 g) and sodium bromide (0.25 g). The TEMPO-mediated oxidation of the cellulose slurry was initiated by adding 5 mmol of 13% NaClO per gram of cellulose and carried out at room temperature under gentle agitation. The pH was maintained at 10.5 by adding 0.5 M NaOH. When no more decrease in pH was observed, the reaction was finished and pH was adjusted to 7 by adding 0.5 M HCl. The TEMPO-oxidized product was thoroughly washed with water by filtration and physically fibrillated by ultra-sonication with a sonicator (Sonosmasher, Jeio Tech, Korea) for 20 min. The suspension was then centrifuged at about 3,000 g in two to three times for 30 minutes each. The super-

natant was decanted and collected as the CNF suspension. The yield of CNFs was calculated as a percentage of the initial weight of CNF suspension after drying in a drying oven at 105°C. The final concentration of the CNFs was determined as 0.1% by weight/volume.

2.3. Preparation of CNF/PVA Solutions and Viscosity Measurement

The CNF suspension was first concentrated to 0.2% (w/v) by rotary evaporation (Rotovapor R110, BÜCHI, Switzerland) and then mixed with a 10 wt% PVA solution that had been obtained by vigorous mechanical stirring at 80°C for 4 hours, followed by continuous stirring until the solution reached room temperature. CNFs of different contents (0, 1, 3, and 5 wt%) were added into the PVA solution, and the final mixtures were sonicated for 10 min (Sonosmasher, Jeio Tech, Korea) at 50% power output to get homogeneous suspensions. The viscosity of final mixtures at different CNF concentrations was measured by rheometry (MARS III, Hakke, Germany) with a cone and plate geometry at a shear rate of 10 s^{-1} and 25°C. The radius and angle of the cone was 60 mm and 1°, respectively.

2.4. Electrospinning of CNF/PVA Composite Blends

The electrospinning of CNF/PVA suspensions was performed with the electrospinning apparatus (NNC-ESP200, NanoNC, Seoul, Korea). The CNF/PVA solutions were loaded into a plastic syringe using a 22 gauge stainless steel needle at the tip. The needle was electrified by a high voltage DC supply at an applied voltage of 16 kV. The tip to collector distance was 19

cm. After electrospinning, the collected CNF/PVA composite nanofibers were stored in a desiccator at room temperature.

2.5. Characterization of CNFs

2.5.1. Morphology and Dimension of CNFs

CNFs were examined and their dimensions measured with a transmission electron microscope (TEM) (H-7600, Hitachi, Japan), operating at an acceleration voltage of 100 kV. The sample was diluted to a concentration of 0.01% w/v. To examine the morphology of the CNFs, three droplets of the suspension were placed on Cu-grids coated with a thin carbon film and then allowed to dry at 30°C for 10 min. To enhance the contrast in the TEM, the grids were floated on drops of 3% solution of uranyl acetate for 3 min and then dried at 70°C for 10 min. The particle dimensions were obtained by measuring 30 individual CNFs on TEM micrographs.

2.5.2. Morphology and Dimension of Electrospun CNF/PVA Composite Nanofibers

The morphology of the CNF/PVA composite nanofibers was investigated using a field emission scanning electron microscope (FE-SEM, S-4300, Hitachi, Japan), operating at an accelerating voltage of 15 kV. A small piece of nanofiber mat was placed on carbon applied to stub and coated with Pt/Au. The average diameter of the composite nanofibers was obtained by measuring 50 individual fibers on FE-SEM micrographs using an image analysis software (Ver. 8.5, IMT i-solution Inc., Canada).

Fig. 1. TEM images of CNFs isolated by TEMPO- Oxidation from HW-BKP. (a) $\times 60,000$, (b) $\times 100,000$.

3. RESULTS AND DISCUSSION

3.1. CNFs' Morphology and Dimension and Viscosity of CNF/PVA Solution

High magnification TEM images of the CNFs prepared by the TEMPO-oxidation method at different magnification levels are depicted in Fig. 1. While the majority of CNFs were fibrillated, some were not fully fibrillated into nano-scale structure (arrows in Fig. 1). As determined by TEM, the average diameter of fibrillated CNFs was about 7.07 ± 0.99 nm, a value that matches other measurements (Shinoda *et al.* 2012). It was considered that the fibrillated CNFs would provide an efficient reinforcement with electrospun nanofibers of CNF/PVA blends, while unfibrillated or macrofibrils cause inconsistencies. Prior to preparing nanofibers by electrospinning,

the viscosity of CNF/PVA solutions was determined as a function of CNF content. As expected, the viscosity of the suspension decreased with an increase in the CNF content (Fig. 2) because the amount of water in the CNF suspension increased with an increase in the CNF content in the CNF/PVA solution. It is expected that the viscosity of CNF/PVA solution will have an influence on the quality of electrospun nanofibers.

3.2. Morphology and Dimension of Electrospun CNF/PVA Nanofibers

Fig. 3 shows the morphology of the electrospun CNF/PVA composite nanofibers observed by FE-SEM. Figs. 4 and 5 represent average diameter and diameter distribution, respectively, of CNF/PVA composite nanofibers as a func-

Fig. 2. The viscosity of CNF/PVA solution blends as a function of CNF content.

tion of CNF content. FE-SEM images from (a) to (h) in Fig. 3 display the morphology of the CNF/PVA composite nanofibers at different CNF contents (0~5 wt%) after electrospinning. The average diameter of the nanofibers of CNF/PVA blends decreased as the CNF content increased (Fig. 4). In general, the fiber diameter increased with an increase in the viscosity (Gupta *et al.*, 2005; Mit-uppatham, Mithitanakul, & Supaphol, 2004), showing a good correlation between the diameter of electrospun fiber and solution viscosity. Other studies have also reported that a higher viscosity resulted in a larger fiber diameter in eletrospinning (Hamad, 2002; Baumgarten, 1991; Doshi & Reneker, 1995). Therefore, the decrease of fiber diameter with an increase in the CNF content is attributed to the viscosity of dope suspension.

Electrospun nanofibers prepared from the pure PVA solution showed very smooth and uniform nanofibers without any beads (Fig. 3,

a, b). The average diameter of the control nanofibers was about 144.7 nm (Fig. 4). More than 84% of the nanofibers had diameters, ranging from 120 nm to 180 nm (Fig. 5, a).

When 1% CNFs was added into the PVA solution, the nanofibers of the CNF/PVA blend also showed fairly uniform and high quality nanofibers without any beads (Fig. 3, c and d). The average diameter of the electrospun nanofibers was about 102 nm (Fig. 4). No beads were observed for the electrospun nanofibers of 1% CNF/PVA blend, and 84% nanofibers had a diameter range of 80~120 nm (Fig. 5, b).

As the CNF content increased to 3% and 5%, there were elliptical beads formed in the electrospun nanofibers. Measurements of the nanofiber diameter were done for normal nanofibers with no elliptical beads. The number of elliptical beads were relatively small at 3% CNF content. However, the majority of the nanofibers were uniform, and the frequency of

Fig. 3. The FE-SEM images of electrospun nanofibers of CNW/PVA composites at different CNF loadings. (a) ~ (b) 0% CNF, (c) ~ (d) 1% CNF, (e) ~ (f) 3% CNF, and (g) ~ (h) 5% CNF.

Fig. 4. Average nanofiber diameters with standard deviation of CNFs/PVA composites as a function of CNF content.

beads was relatively low (Fig. 3, e and f). The average diameter of nanofibers was 85 nm, a value lower than that for 1% CNF content. About 88% of the electrospun nanofibers were in the range of 60~80 nm (Fig. 5, c).

At the highest CNF content of 5%, the electrospun nanofibers contained many elliptical beads with a large variation in the nanofiber diameter (Fig. 3, g and h), and with twisted and irregular forms. There was also a relatively large deviation in the average diameter (92 nm) of the nanofibers (Fig. 4), which could be attributed to the presence of frequent beads. The diameter of nanofibers widely ranged from 40 nm to 160 nm which could explain the large deviation. About 60% nanofibers of 5% CNF/PVA blend were greater than 80 nm in diameter (Fig. 5, d).

In electrospinning, an electric field is used to create a charged jet of polymer solution. As

this jet travels in air, the solvent evaporates leaving behind a charged fiber. So, the electrospinning process is affected by many parameters (Doshi & Reneker, 1995). The observed beads in the electrospun nanofibers at 3% and 5% CNF content could be related to the applied conductivity and surface tension of the CNF/PVA suspensions. As the charged jet travels in air, its diameter decreases due to the simultaneous effect of stretching of the jet and evaporation of the solvent. Thus, it was difficult to form a stable jet as the CNF content increased. So, a decrease in the viscosity and PVA content in the CNF/PVA suspension could result in a reduced surface tension of the jet, and consequent production of nanofibers with small diameter as well as elliptical beads. Thus, a decrease in the viscosity of 3% and 5% CNF solutions could be mainly responsible for the formation of beaded fibers prepared by electro-

Fig. 5. Diameter distributions of the electrospun CNF/ PVA composites nanofiber as a function of CNF content. (a) 0% CNF, (b) 1% CNF, (c) 3% CNF, and (d) 5% CNF.

spinning, which was compatible with the reported result (Fong, Chun, & Reneker, 1999). In addition, unfibrillated CNFs (Fig. 1) might also influence the formation of unstable jet which could contribute to the formation of beads at high CNF contents, (3% and 5% levels).

4. CONCLUSION

This study reports the preparation of cellulose-based polymer nanofibers by electrospinning, using CNFs isolated from native cellulose by TEMPO oxidation and aqueous PVA solution. Morphology and dimension of CNFs

were characterized by TEM, while the morphology of the nanofibers was observed by FE-SEM. In addition, the viscosity of CNF/PVA blend suspension was determined to explain variations in the diameter and its distribution of nanofibers. The following conclusions are drawn from the results obtained:

1) The CNFs as observed with TEM were mainly fibrillated structures in an aggregated form, with an average diameter of about 7.07 ± 0.99 nm. Unfibrillated fiber bundles were also observed in CNFs, which impacted electrospun nanofiber diameter and the formation of beads at high CNF contents.

2) Electrospinning was successfully employed to prepare uniform nanofibers from CNF/PVA blends. The viscosity of CNF/PVA suspension and the diameter of nanofibers decreased as the CNF content increased. Nanofiber diameter distribution also followed a similar trend.

3) These results indicate that electrospinning of CNF/PVA solutions can produce uniform nanofibers suitable for a variety of novel and high value applications.

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