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Short communication

Electrospinning of lignocellulosic biomass using ionic liquid

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ABSTRACT

Nanoscale fiber was successfully electrospun from lignocellulosic biomass (hemp) dissolved by IL (1-ethyl-3-methylimiazolium acetate [C_2min][OAc]). The biomass was treated by alkalis, NaOH and $NaClO_2$ for different time to reduce the lignin content. For better spinnability, excess DMF was added to the spinning dope. When the residual lignin content was higher than 6%, the solution was sprayed into mist type droplets or formed large drops at the end of the nozzle without forming stable jet. The further reduction of the lignin resulted in more stable jet and better spinnability as well as smaller and uniform fiber diameter.

1. Introduction

Mass-consumption of petroleum-based materials leaves the devastated environment and global warming, which are the lethal threats for human races. In order to eliminate the threats, sustainability and green chemistry are directing the development of the next generation of materials, products, and processes. Biodegradable plastics and composites generated from renewable biomass feedstock are regarded as promising materials to replace synthetic polymers and to reduce global dependence on fossil fuel. Cellulose is considered as the strongest potential candidate for the substitution of petroleum-based polymers due to its eco-friendly properties such as bio-degradability, bio-compatibility, and renewability. Its superior properties such as high thermal stability and desirable mechanical strength have also drawn many attractions from researchers. The applications of cellulose have taken great amount attentions in various areas such as textile engineering, food science and biomedical engineering. Especially, textile industries have long history in use of cellulose for fibers and apparels. However, the potential of cellulosic materials has not been fully exploited because cellulose cannot be dissolved in conventional solvents due to strong inter- and intra-molecular hydrogen bonding.

Rayon process, the first successful process to regenerate the cellulose, has critical drawbacks such as significant reduction of molecular weight and release of toxic chemicals during the manufacturing process. As a result of endeavoring effort to find less-toxic and more stable solvent system for cellulose, NMMO (M-methylmorpholine-N-oxide) system was developed recently. The process offers many benefits such as simple dissolving process, better dimensional stability and higher mechanical properties in the resulted fibers. Still, this system has drawbacks such as significant reduction of molecular weight of cellulose, undesirable fibrillation of the fiber and high energy consumption during the process. Recently, ionic liquid, which can be used in various areas such as fuel cell, electrolyte and lubricant as a clean solvent and catalysts, was reported that it can dissolve cellulose successfully (Swatloski, Spear, Holbrey, & Rogers, 2002). Comparing with NMMO, ionic liquid can dissolve cellulose easily with lower energy consumption.

The electrospinning has been recognized as a simple and versatile method for producing ultrathin fiber with an extremely high surface area on a sub-cellular scale (Huang, Zhang, Kotaki, & Ramakrishna, 2003). In medical field, fibrous mats made by electrospinning are expected to be candidates for tissue engineering scaffolds, in wound dressing and as protective clothing (Sill & von Recum, 2008). Recently, electrospinning methods have used non-volatile ILs as solvents to fabricate ultrathin fibers of unmodified cellulose (Xu et al., 2008). The dry-jet wet electrospinning process with ILs is stable system at atmosphere, no need of gas recovery, and a fire-safety system. Sub micro-scale cellulose fibers could be

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Table 1
Hemp treatment conditions.

Sample code	Treatment conditions
R	Untreated hemp fiber
H1	17.5% NaOH at RT for 1 h
H5	17.5% NaOH at RT for 5 h
H1L1	17.5% NaOH at RT for 1 h and 0.7% $NaClO_2$ at b.p. for 1 h
H5L1	17.5% NaOH at RT for 5 h and 0.7% $NaClO_2$ at b.p. for 1 h
H1L5	17.5% NaOH at RT for 1 h and 0.7% $NaClO_2$ at b.p. for 5 h
H5L5	17.5% NaOH at RT for 1 h and .07% $NaClO_2$ at b.p. for 5 h

obtained by electrospinning using 1-butyl-3-methylimidazolium chloride ([C_4mim][Cl]), one of the typical ionic liquids (Quan, Kang, & Chin, 2010). Although several results in the electrospinning of cellulose using ILs have been reported, raw lignocellulosic biomass has not been successfully electrospun. It is an interesting issue whether raw lignocellulosic fiber can be formed or not, because it will have many potential applications in the textile and biomedical fields.

In this work, we studied the electrospinning of raw lignocellulosic biomass using ILs. Nanoscale fiber was successfully electrospun from the raw hemp solution in a mixture of [C_2mim][OAc] and DMF. In order to investigate the effect of lignin content in hemp on the spinnability, the hemp was treated with various alkaline conditions to partially remove lignin. To our knowledge, this is the first result of making lignocellulosic biomass-based fiber by electrospinning using ILs.

2. Materials and methods

2.1. Solution preparation and electrospinning

To study the feasibility of lignocellulosic biomass for fiber formability, hemp was treated by alkaline, dissolved and electrospun. To partially remove lignin, the hemp was treated by two alkalis, 17.5% NaOH and 0.7% $NaClO_2$ aqueous solutions under the conditions (Table 1).

The treated and untreated hemps were dissolved in 1-ethyl-3-methylimidazolium acetate ([C_2mim][OAc], BASF, USA) with a concentration of 14 wt%. For better spinnability, excess N,N-dimethylformamide (DMF, purity 99.0%, DaeJung Chemicals & Metals, Korea) was added to the solution.

The solution was electrospun using a syringe type apparatus onto a rotating wired cylinder type collector. The applied voltage and the tip to collector distance (TCD) were kept constant through the whole experiment as 35 kV and 15 cm, respectively. The residual IL in the fiber was removed using ethanol at 4 °C for 2 h and the fiber was washed by deionized water. The coagulated fiber was obtained after drying at 50 °C for a day.

2.2. Characterizations

The compositional analysis of hemp was conducted before and after the alkaline treatments by the standard NREL procedure No. 002. Briefly, the sample was treated with 72% (v/v) sulfuric acid at 30 °C for 3 h, followed by dilute acid (4%) at 121 °C for 1 h. The glucose contents were determined by HPLC (Young-Lin Model YL9100, Korea) equipped with a RI detector and a Shodex sugar SP0810 column operated at 85 °C. The acid-insoluble lignin after acid hydrolysis was measured as the mass of insoluble residue remaining (Lee, Doherty, Linhardt, & Dordick, 2009).

The morphologies of electrospun fibers were observed 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.).

Table 2
Effect of pretreatment method on composition of hemp.

Sample code	Cellulose content (%)	Acid-soluble lignin content (%)	Acid-insoluble lignin content (%)	Total lignin content (%)
R	74.5	0.7	6.4	7.1
H1	92.3	0.5	6.1	6.6
H5	79.8	0.4	5.7	6.1
H1L1	92.3	0.5	4.7	5.2
H5L1	89.1	0.5	4.4	4.9
H1L5	78.8	0.4	4.6	5.0
H5L5	76.1	0.4	3.8	4.2

3. Results and discussion

3.1. Compositional analysis of alkali-treated hemp

Table 2 shows the compositional analysis results of the alkaline treated hemp. The total lignin contents were decreased as the total treatment time was increased, regardless to the alkaline types. The total relative weight of acid-insoluble lignin was decreased dramatically from 6.4% to 3.8% by the treatment. The combined treatments of NaOH and $NaClO_2$ reduced the lignin content more effectively. The cellulose content was also influenced by the treatment. When the fiber was treated only by NaOH for 1 h, the cellulose content increased up to 92%. However, further treatment decreased the cellulose contents. It indicates that the alkaline decompose the acid-insoluble lignin as well as cellulose.

3.2. Spinnability of alkali-treated hemp

For better spinnability, excess DMF (1.75 time of the ionic liquid used by weight) was added to the solution. The addition of DMF decreased the surface tension of the spinning solution. It also increased the conductivity and decreased viscosity of the electrospinning dopes distinctly without any cellulose precipitate forming. It seems that the spinning dopes containing DMF benefit the fiber formation.

The spinnability of each solution was summarized in Table 3. When the residual lignin content was higher than 6%, the solution was sprayed into mist type droplets or formed into large drops at the end of the nozzle without forming stable jet. However, the solution was quasi-stably electrospun when the lignin content was lower than 6%. The further reduction of the lignin ($\leq$5.0%) resulted in more stable jet and better spinnability. When the lignin content was lower than 4.5%, the solution produced the most stable jet and then showed the best spinnability among the solutions prepared in the study. The better spinnability resulted in finer and more uniform fiber on the collector as shown in Fig. 1. When the lignin content was higher than 5.0%, the web was composed of the fibers with large different diameters. Not only large difference in fiber diameter, but also other irregularities such as fiber bent, knots and films were also found from the webs. Due to the residual lignin, the cellulose was neither easily fibrillated by the splaying nor efficiently elongated by whipping motions to produce fine and uniform fibers.

Table 3
Spinnability of hemp/ionic liquid solution.

Sample code	Spinnability
R	Drop formation at the nozzle end
H1	Electrosprayed
H5	Electrosprayed
H1L1	Elctrospun with many droplets
H5L1	Electrospun with unstable jet formation
H1L5	Electrospun with unstable jet formation
H5L5	Stably electrospun

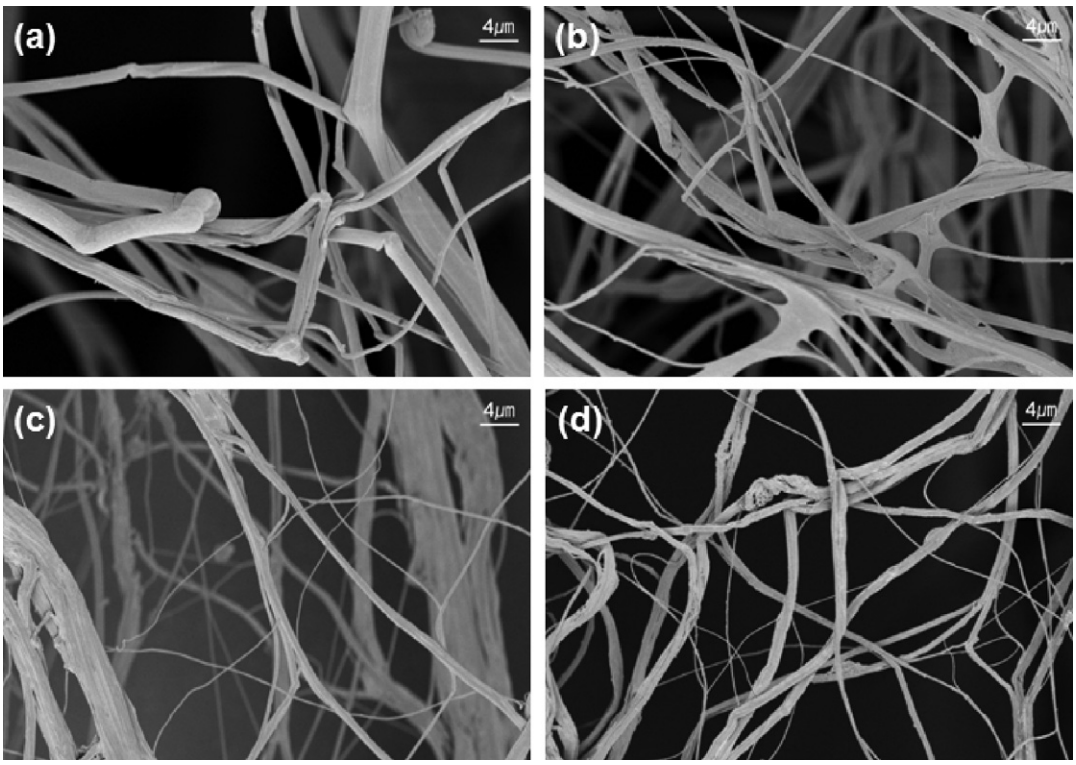

Fig. 1. FE-SEM images of electrospun hemp fibers: (a) H1L1, (b) H5L1, (c) H1L5 and (d) H5L5.

3.3. Size and distribution of electrospun hemp fiber

The solution with lower lignin content resulted in finer and uniform fiberwebs. The average fiber diameter was coincident to the spinnability results. As shown in Fig. 2, the average and the standard deviation of the fiber diameter simultaneously decreased as the lignin content was decreased. Especially, when the total alkaline treatment time was longer than 6 h, both the average and the standard deviation of diameter was decreased dramatically. When the lignin content was low, the solution had low viscosity which made the jet easily extended then produced smaller and uniform fibers. It indicates that the dispersion of the residual lignin in the solution depends on the lignin content. In the solution from the lignocelluloses with low lignin content, the lignin has more chance to be dispersed uniformly comparing to the solution with high lignin content. Unevenly dispersed lignin prevented uniform whipping and splaying motions for fibrillation of the spinlines. This resulted in large distribution of the electrospun fiber diameter. Adverse effect of lignin on the fiber formation can be partly understood by the characteristics of cellulose–lignin film prepared by using ILs. Cellulose–lignin composite film prepared by casting of cellulose and lignin solution in ILs showed heterogeneous surface and became brittle with increasing lignin content, while pure cellulose film showed smooth surface and higher tensile strength (Simmons et al., in press).

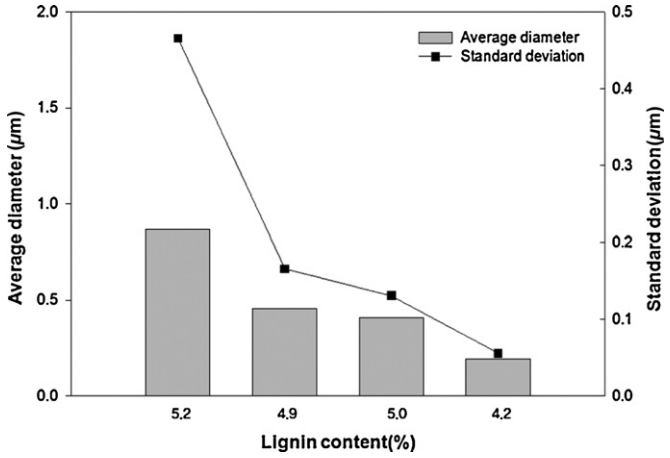

Fig. 2. Average and standard deviation of electrospun fiber.

4. Conclusions

In this work, micrometer-sized fiber was successfully electrospun from the raw lignocellulosic biomass using ILs. The spinnability and the web morphology were strongly depended on the lignin contents. When the residual lignin content was higher than 6%, the solution was sprayed into droplets or formed large drops at the end of the nozzle, instead of producing fibers. As the lignin content decreased, the spinnability was improved and resulted in smaller fiber diameter and more uniform diameter distribution.

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References

Huang, Z. M., Zhang, Y. Z., Kotaki, M., & Ramakrishna, S. (2003). A review on polymer nanofibers by electrospinning and their applications in nanocomposites. *Composites Science and Technology*, *63*, 2223–2253.

Lee, S. H., Doherty, T. V., Linhardt, R. J., & Dordick, J. S. (2009). Ionic liquid-mediated selective extraction of lignin from wood leading to enhanced enzymatic cellulose hydrolysis. *Biotechnology and Bioengineering*, *102*, 1368–1376.

Quan, S.-L., Kang, S.-G., & Chin, I.-J. (2010). Characterization of cellulose fibers electrospun using ionic liquid. *Cellulose*, *17*, 223–230.
Sill, T. J., & von Recum, H. A. (2008). Electrospinning: Applications in drug delivery and tissue engineering. *Biomaterials*, *29*, 1989–2006.
Simmons, T. J., Lee, S. H., Miao, J., Miyauchi, M., Park, T. -J., Bale, S. S., Pangule, R., Bult, J., Martin, J. G., Dordick, J. S., & Linhardt, R. J. Preparation of synthetic wood composites using ionic liquids. *Wood Science and Technology*, in press.
Swatloski, R. P., Spear, S. K., Holbrey, J. D., & Rogers, R. D. (2002). Dissolution of cellulose with ionic liquids. *Journal of American Chemistry Society*, *124*, 4974–4975.
Xu, S., Zhang, J., He, A., Li, J., Zhang, H., & Han, C. C. (2008). Electrospinning of native cellulose from nonvolatile solvent system. *Polymer*, *2008*, 2911–2917.