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Effect of co-solvent on the spinnability and properties of electrospun cellulose nanofiber

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ABSTRACT

The effects of the type and the concentration of the co-solvent on the spinnability during cellulose electrospinning and the properties of the fiber were studied using cellulose dissolved in ionic liquid and co-solvent (DMF or DMAc). The prepared solution was electrospun onto a wired collector and coagulated in ethanol. As the weight ratio of co-solvent against ionic liquid increased, the spinnability was improved with stable whipping and splaying motion. Regardless of the co-solvent type, the higher co-solvent concentration resulted in finer fiber diameter, better web uniformity, higher crystallinity and better thermal stability. Comparing to DMAc, DMF showed more significant influence on the fiber diameter and the crystallinity.

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1. Introduction

Cellulose is the most abundant bio-polymer existing on earth. It has been used in many industries such as textile, paper and food industries for long time. After invention of synthetic plastics, the importance of cellulose in industrial applications was decreased. However, cellulose regained spotlights due to its eco-friendly characteristics such as biodegradability, renewability and sustainability (Alemdar & Sain, 2008; Klemm, Heublein, Fink, & Bohn, 2005; Murakami, Kaneko, & Kadokawa, 2007). It is expected to overcome significant drawbacks of the synthetic plastics such as petroleum dependency, non-biodegradability and huge amount of CO_2 release.

Due to the strong inter- and intra-molecular interactions originated from hydrogen bonding, and rigid backbone structure, cellulose is not melted nor dissolved in conventional solvent systems. To find effective and eco-friendly solvent systems, huge amount of effort has been devoted for several decades. Currently, a few successful solvent systems are reported (Cuculo, Aminuddin, & Frey, 2001; Frey, 2008). Among these, ionic liquid has many advantages such as high thermal and chemical stabilities and simple recycle process (Gathergood, García, & Scammells, 2004; Jastorff et al., 2003; Liu et al., 2006; Wasserscheid et al., 2002). Recently, the distinguishable research results were published in preparation of cellulose nanofiber using ionic liquid (Freire et al., 2011; Miyauchi et al., 2010; Quan, Kang, & Chin, 2010; Xu et al., 2008). The nano-scale cellulose fibers can be used in various application areas such as tissue scaffold, wound dressing and filtration (Cuculo et al., 2001; Nge & Sugiyama, 2007; Nishio, 2006). Among nanofiber preparation processes, electrospinning attracted great amount of attention due to its simplicity and efficiency (Doshi & Reneker, 1995; Huang, Zhang, Kotaki, & Ramakrishna, 2003; Reneker & Chun, 1996; Subbiah, Bhat, Toch, Parameswaran, & Ramkumar, 2005). However, pure cellulose solution in ionic liquid is not easily electrospun due to its high viscosity and low volatility. To improve the spinnability, several methods such as addition of co-solvent (Freire et al., 2011; Miyauchi et al., 2010; Quan et al., 2010; Xu et al., 2008) or mixture with artificial polymers were reported (Changzhong, Linge, & Yong, 2007, 2011; Costas & Costas, 2008; Haitao et al., 2009; Khatri, Wei, Kim, & Kim, 2012; Zhang & Hsieh, 2008). However, those studies did not significantly improve the processibility nor provide the fundamental understanding for the roles of co-solvent or blended polymers on the electrospinning and the properties of the resulted fiber.

In this work, we prepared cellulose nanofiber using ionic liquid and co-solvent via electrospinning. The influences of the co-solvent type and concentration on the spinnability and the properties of the resulted fibers were observed and investigated. Based on the observations, the roles and actions of the co-solvents were explained in terms of the polarity and viscosity changes. The study can give a

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Table 1
Solution condition for electrospinning and sample code.

Sample code	Cellulose (g)	IL (g)	DMF (g)	DMAc (g)	Conc. (%)
ILF1	0.682	5	2.5	–	8.3
ILF2	0.682	5	3.75	–	7.2
ILF3	0.682	5	5	–	6.3
ILA1	0.682	5	–	2.5	8.3
ILA2	0.682	5	–	3.75	7.2
ILA3	0.682	5	–	5	6.3

fundamental understanding of the cellulose electrospinning and is also expected to improve the properties and the performance of the cellulose nanofiber produced by electrospinning.

2. Experimental

2.1. Materials

Cellulose for the study was kindly obtained as powder form from Hyosung (Korea) and 1-ethyl-3-methylimidazolium acetate ([C_2min][OAc]), ionic liquid as a cellulose solvent was purchased from BASF (USA). Two types of co-solvents, DMF (dimethylformamide) and DMAc (dimethylacetamide) were purchased from Daejung Chemicals & Metals Co. (Korea). Ethanol, coagulant solvent for the electrospun fiber was also obtained from Daejung Chemicals & Metals Co. All the chemicals were used without further purification.

2.2. Solution preparation and electrospinning

For electrospinning, cellulose was dissolved in [C_2min][OAc]. To study the effects of the type and the concentration of the co-solvent on the spinnability and the micro- and macro-morphologies, different amounts of DMF or DMAc were added to the cellulose/ionic liquid solution. The preparing conditions for the spinning solution were summarized in Table 1.

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 (TCD) were kept constant through the whole experiments as 30 kV and 15 cm, respectively. The as-spun fiber was immersed in ethanol at 4 °C for 2 h to remove the residual ionic liquid and the co-solvent. The coagulated fiber was dried in an oven at 50 °C for a day.

2.3. Characterizations

The residual solvents in the as-spun and the coagulated fibers were detected using FT-IR (FT-IR 300E, JASCO). The spinnability of each solution during the electrospinning was observed and evaluated by naked eyes based on the drop at the tip and the jet formation. The morphologies of the electrospun fiber were observed by scanning electron microscopy (FE–SEM, JSM-6380, JEOL). The fiber diameters were measured from the SEM images using image analysis software (EyeViewAnalyzer, Digiplus Inc.). Wide-angle X-ray diffraction (WAXD) analysis was carried out using X-ray diffraction (XRD, Ultima IV, Rigaku, Japan). The thermal properties of the resulted fiber were evaluated using thermogravimetric analysis (TGA, Q500, TA Instruments, USA) in the nitrogen gas atmosphere with the temperature range from room temperature to 700 °C.

3. Results and discussion

3.1. Spinnability of cellulose solutions

Table 2
Spinnability of cellulose/ionic liquid solution.

Sample code	Spinnability
ILF1	+
ILF2	++
ILF3	+++
ILA1	+
ILA2	++
ILA3	+++

+: Electrospinning with much mist.
++: Electrospinning with semi-stable jet formation.
+++: Stably electrospun.

Table 2 shows the spinnability of the cellulose solutions prepared in the different conditions. The cellulose solution dissolved only in ionic liquid did not form a stable Taylor cone and was not electrospun into fibrous structure. Regardless of the co-solvent types, the addition of the co-solvent improved the spinnability of the solution. The concentrations of the both co-solvents showed significant effects on the spinnability. As the co-solvent concentration increased, the spinnability was improved. When the weight ratio of the co-solvent against ionic liquid was 0.5 (the weight was 2.5 g), the solutions were sprayed into mist type droplets or formed solution drops from the nozzle. However, the solutions became quasi-stable in electrospinning with the increases of the co-solvent contents. When the weight ratio was increased up to 1 (the weight was 5 g), the solutions produced the most stable jet and then showed the best spinnability among the solutions prepared in the study. The improvement was resulted from the changed charge induced partial polarity of the co-solvent and the viscosity reduction by the dispersion of the co-solvent. The co-solvent with partial polarity helps effective elongation because the strong electrical force affected to the solution. Due to strong electrical attraction onto the collector, the solution underwent stable whipping and splaying motion in electrospinning process. At the same time, the solution viscosity was decreased by the co-solvent. It can be attributed to the co-solvent dispersion in the cellulose solution. As the co-solvent was mixed with the cellulose/ionic liquid solution, the co-solvent was dispersed in the solution and increased the mobility of the cellulose chain as a similar way of plasticizers. When cellulose was dissolved only in ionic liquid, the anion of the ionic liquid combines with the proton in the cellulose's hydroxyl groups while the imidazolium cation combines with the hydroxyl group's oxygen. It makes the molecular chain apart from the neighboring chains and weakens the inter- and intra-molecular hydrogen bonds, in turns. The co-solvent penetrates into the gaps made by the ionic liquid between the chains and reduced the chain-to-chain interaction. It resulted in the better chain movements. Due to active chain mobility by weak interaction between the cellulose chains, the cellulose solution could be easily elongated and fibrillated through stable whipping and splaying.

3.2. Morphology of electrospun cellulose fiber

Fig. 1 shows the SEM images of the electrospun web. It was composed of curved and knotted fibers with large difference in the diameters, while the fibers electrospun from synthetic polymer were straight with uniform diameters. Without regarding to the co-solvent type, the fiberweb morphology was changed into more fibrillated and more uniform structure as the weight ratio of the co-solvent increased. This result was coincident to the spinnability observed during the electrospinning. As explained above, the co-solvent decreased the viscosity of the spinning solution, which helped the whipping motion. By the stable whipping behavior, the cellulose solution was uniformly elongated and fibrillated. It resulted in smaller diameter and improvement of the uniformity. In order to quantitatively compare the effect of the co-solvent on the fiber diameter, the average and the standard deviation of the

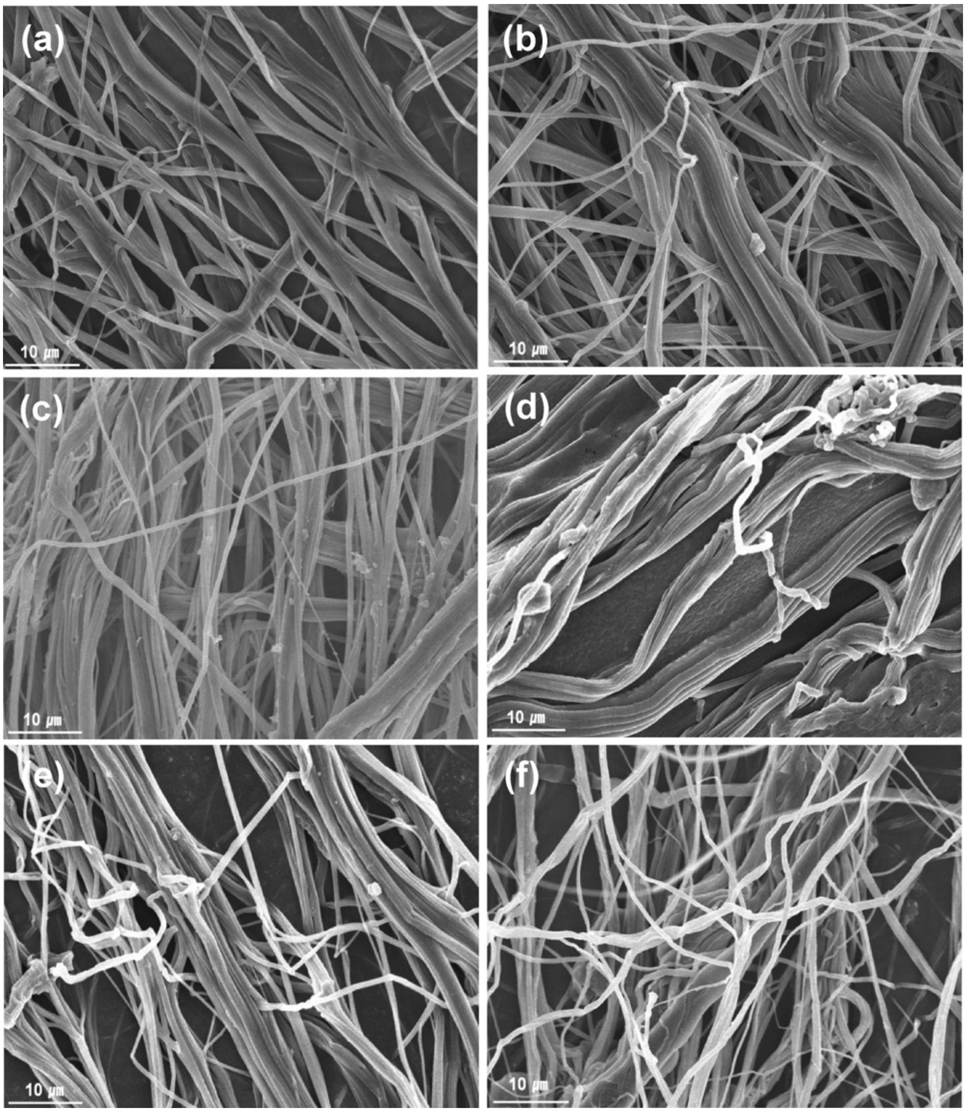

Fig. 1. SEM images of electrospun cellulose fiber; (a) ILF1, (b) ILF2, (c) ILF3, (d) ILA1, (e) ILA2 and (f) ILA3.

fiber diameter were measured from the SEM images (Fig. 2). The average and the standard deviation of the fiber diameter in the both cases decreased as the weight ratio of the co-solvent increased. The improved spinnability by the co-solvent resulted in the finer and the more regular fibers. According to the co-solvent types, there are significant differences in the average and the standard deviation in the fiber diameter. The average and the standard deviation of the fiber diameter in the fiberweb prepared from the solution with DMF were significantly small comparing to the one with DMAc. The dependence on the co-solvent type could be explained in terms of the difference of charge induced partial polarity between the two co-solvents. Comparing to DMAc, DMF has higher partial polarity by the electrical charge for spinning. The solution with DMF would have better chance to be effectively elongated during whipping process. The improved whipping produced finer and more uniform fibers.

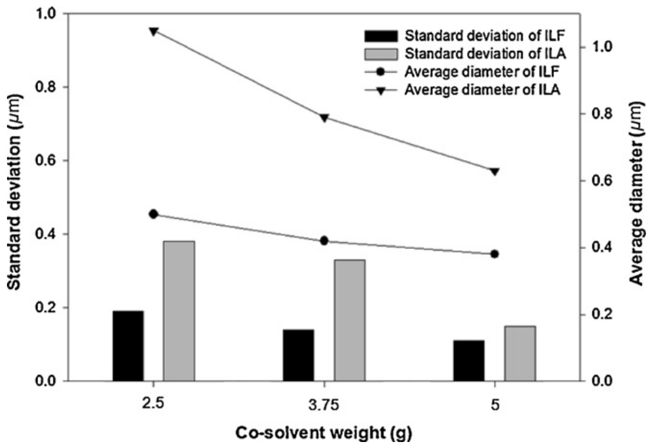

Fig. 2. Average diameter and Standard deviation of electrospun cellulose fiber.

3.3. Chemical composition of electrospun cellulose fiber

In order to detect to the residual contents of the co-solvents, FT-IR was employed to the as-spun and the coagulated fibers (Fig. 3). For the as-spun fiber, the characteristic peak of ionic liquid appeared at 1562 cm^{-1}, while the characteristic peaks for DMF and DMAc appeared in 1360–1180 and 1675–1655 cm^{-1}, respectively. However, the peaks for the ionic liquid and the co-solvents were not detected in the coagulated fibers. It indicates that the solvents were not fully evaporated during electrospinning and the as-spun

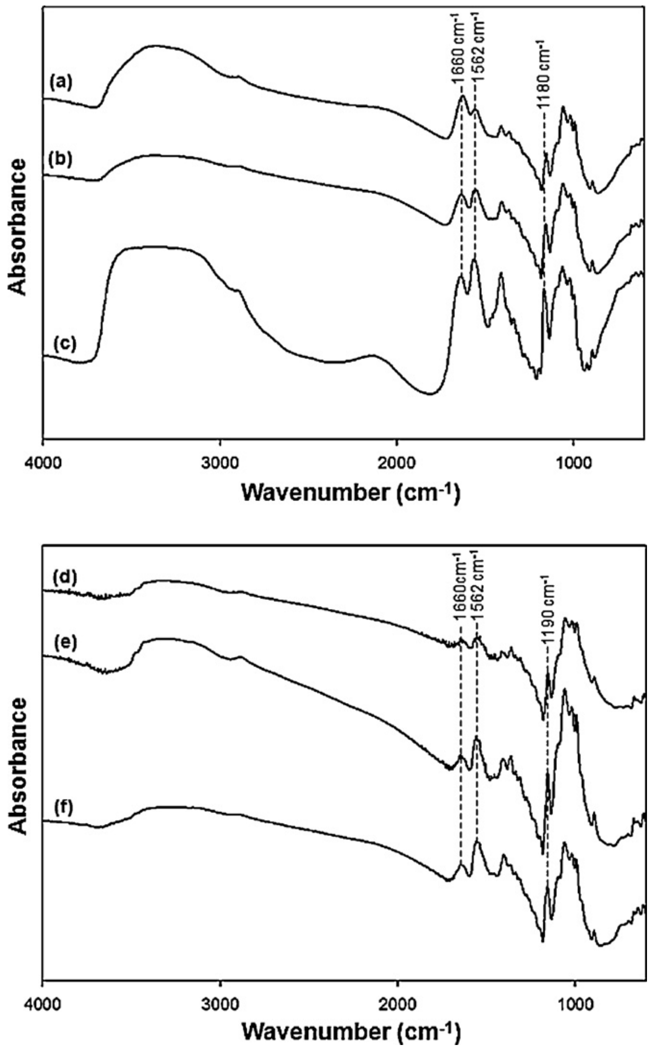

Fig. 3. FT-IR spectra of as-spun cellulose fiber; (a) ILF1, (b) ILF2, (c) ILF3, (d) ILA1, (e) ILA2 and (f) ILA3.

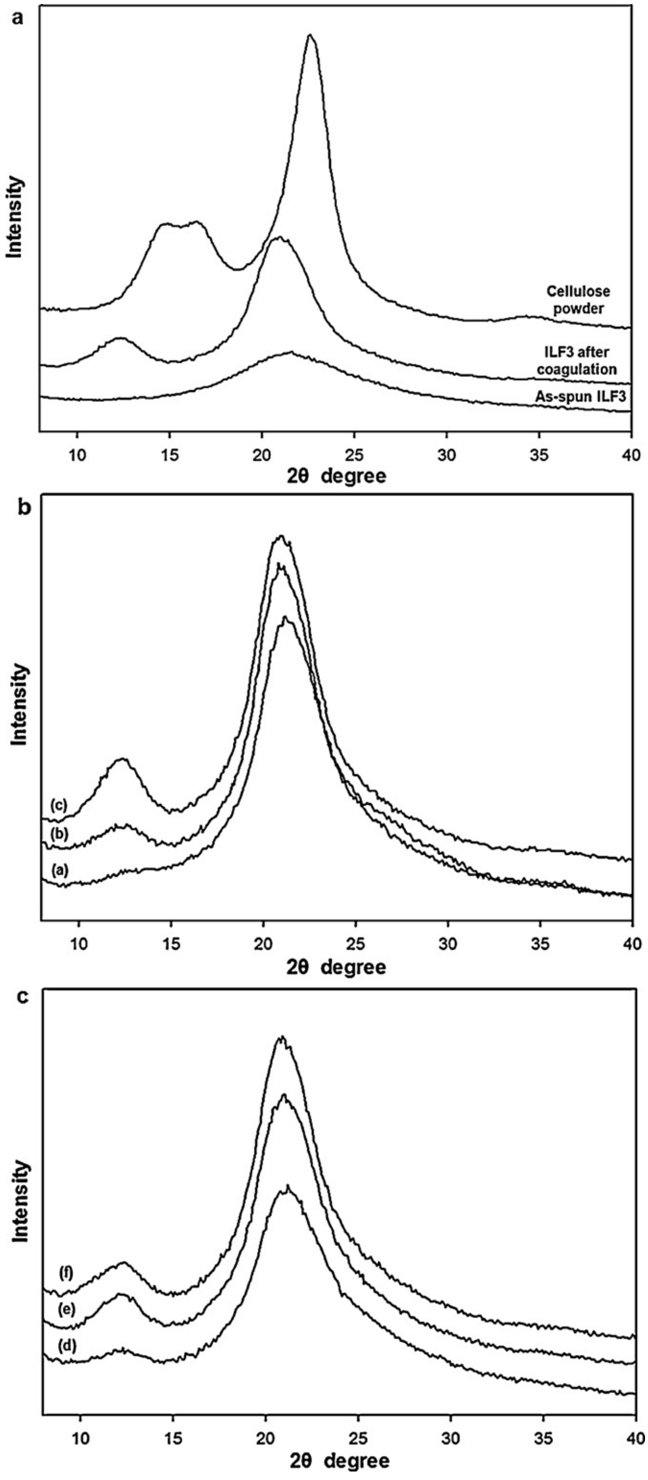

Fig. 4. XRD curves of cellulose powder, as-spun cellulose fiber and coagulated cellulose fiber; (a) ILF1, (b) ILF2, (c) ILF3, (d) ILA1, (e) ILA2 and (f) ILA3.

fiber was not fully solidified. The fiber was solidified and crystallized, while the remnant of the ionic liquid and the co-solvent in the fiber was removed by the coagulant.

3.4. Microstructure of electrospun cellulose fiber

Fig. 4(a) shows the XRD patterns of the cellulose powder, as-spun cellulose fibers and the coagulated cellulose fibers. The cellulose powder exhibited a typical diffraction pattern for cellulose I having characteristic peaks at 15.0°, 16.8° and 22.5°. When the cellulose was electrospun using the ionic liquid, the as-spun fiber shows broad XRD pattern of non-crystalline structure. As the cellulose solution was electrospun, the as-spun fiber was deposited on the wired drum collector and then partially solidified. Although large part of the co-solvent was evaporated, the cellulose solvent, ionic liquid still remained in the as-spun fiber. The remained solvent disturbed the glucose polymer crystallized. However, when the electrospun cellulose fiber was coagulated in ethanol, the characteristic peaks for cellulose II (at 12.0°, 20.5° and 21.5°) appeared with huge reduction of the crystallinity comparing with the cellulose powder. As previous studies mentioned (Kim, Kim, Kang, Marquez, & Joo, 2006; Quan et al., 2010; Xu et al., 2008), hydrogen bonding in cellulose was mostly separated when dissolving in the ionic liquid. The severe interaction of ionic liquid and the fast coagulation of cellulose from the ionic liquid did not allow enough time to form hydrogen bonding, which decreased the crystallinity of the resulted fiber.

Fig. 4(b) and (c) shows the XRD curves of the electrospun cellulose after the coagulation. To estimate the degree of crystallinity, the peak area and the peak height at 20.5° were measured using the XRD curves and summarized in Table 3. With the increase of the co-solvent concentration, the crystallinity of the coagulated fiber was increased regardless of the co-solvent types. The ionic liquid

Table 3
The degree of crystallinity of electrospun cellulose.

Sample code	The degree of crystallinity	
	By peak height	By peak area
ILF1	0.67	0.59
ILF2	0.71	0.66
ILF3	0.71	0.75
ILA1	0.61	0.63
ILA2	0.68	0.69
ILA3	0.70	0.72

and the co-solvent remained in the as-spun cellulose fiber were simultaneously extracted from the cellulose fiber into ethanol during the coagulation process. The two solvents were competitively extracted by the coagulant. The competition could slow down the extraction rate of each solvent. In turns, it provided the glucose polymer chain more time to be re-crystallized as the weight ratio of the co-solvent increased. The fiber prepared from higher co-solvent concentration had the higher degree of crystallinity. In addition, the degree of crystallinity was dependant on the co-solvent type. The crystallinity of the electrospun fiber with DMF was higher comparing to the one with DMAc. This result is caused by the diffusion rate of the co-solvent type. Comparing to DMAc, DMF has higher partial polarity. This high partial polar solvent could be extracted faster than the other. It gave more time for ionic liquid to stay with cellulose. As the same reason mention above, it resulted in higher crystallinity in the fiber with DMF.

3.5. *Thermal stability of electrospun cellulose fiber*

The thermal property of the electrospun cellulose fiber was characterized using TGA (Fig. 5). The ranges of decomposition temperatures for regenerated cellulose fibers in the study were lower than conventional cellulose (320–400 °C). The decomposition temperature drop was observed in electrospun cellulose fiber (Freire et al., 2011; Miyauchi et al., 2010; Quan et al., 2010; Xu et al., 2008). It was resulted from the effect of the cellulose crystalline on the thermal stabilities (Beatriz et al., 2011; Quan et al., 2010). The co-solvent concentration in cellulose solutions showed influence on the decomposition peaks. When the weight ratio of the co-solvent was low, the regenerated fibers started decomposing at 350 °C. The further addition of the co-solvent slightly improved the thermal stability of the coagulated fiber. When the weight ratio of the co-solvents was 1, the decomposition peak appeared in the high temperature near the pure cellulose. These results can be attributed to the micro-structure of the regenerated cellulose fiber. As mentioned, the coagulated cellulose fiber had more hydrogen bonding and higher crystallinity when the larger amount of the co-solvent was added to the solution. It increased the decomposition enthalpy and sequentially resulted in the higher decomposition temperature. Also, there was significant difference in the ranges of decomposition temperatures according to the co-solvent type although the main decomposition temperatures were remained similar. At the same weight ratio of the co-solvent, the initial decomposition temperatures of the cellulose fibers with DMAc were lower than ones with DMF. This can be related to homogeneous crystalline state in cellulose fiber (Filho et al., 2007). The cellulose solution with DMF stably formed the fine and uniform fiber by whipping and splaying motions, which could give better chance to make homogeneous crystalline. It resulted that the cellulose fiber from the solution with DMF had the higher initial decomposition temperature.

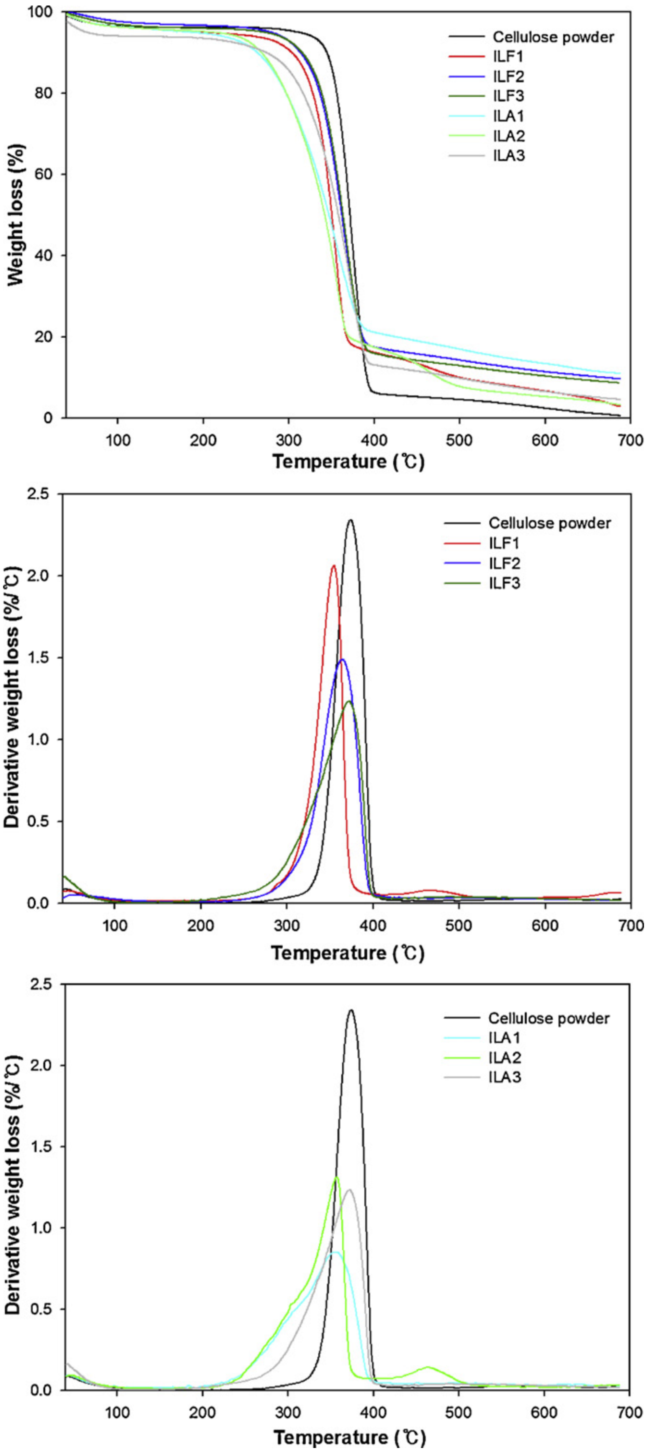

Fig. 5. TG-DTG curves of electrospun cellulose fiber.

4. Conclusion

The cellulose fiber was successfully electrospun using ionic liquid and co-solvent. The type and the concentration of the co-solvent showed significant effects on the spinnability and the diameter and the properties of the fiber. The addition of the co-solvent improved the spinnability and produced finer and more uniform fibers due to reduced viscosity and the partial polarity of the co-solvent. In the similar way, the degree of crystallinity in the resulted fiber was increased as the weight ratio of the co-solvent in the spinning solution increased. Also the fiber with higher crystallinity showed higher thermal decomposition temperature.

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