

Properties of Composite Nanofiber Produced by Single and Coaxial Nozzle Method used for Electrospinning Technique

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Abstract—In this study, single nozzle method used for electrospinning technique which composite polymer solution with cellulose nanowiskers (CNW) was treated by ultrasonic sonicator have been compared with coaxial (double) nozzle method, in terms of mechanical, thermal and morphological properties of composite nanofiber. The effect of water content in composite polymer solution on properties of nanofiber has also been examined. It has been seen that single nozzle method which polymer solution does not contain water has better results than that of coaxial method, in terms of mechanical, thermal and morphological properties of nanofiber. However, it is necessary to make an optimization study on setting condition of ultrasonic treatment to get better dispersion of CNW in composite nanofiber and to get better mechanical and thermal properties

Keywords—cellulose nanowiskers, coaxial nozzle, composite nanofiber, electrospinning

I. INTRODUCTION

STUDIES related with nanofibers and nanofiber web have attracted significant interest in the last few decades because of their excellent properties such as high surface area to volume ratio, nano pores on the surface, etc. Nanofibers can have very wide range of application areas such as medical, filtration, energy storage, fiber reinforced composite materials.

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One of technique used for nanofiber production is electro spinning, which is based on the whipping of polymer solution under an applied electric field between two electrodes. It is possible to manufacture fiber with diameters ranging from several microns down to 50 nm or less. During electrospinning, solvent in the jet solution evaporates and nanofiber web is collected on grounded collector (Fig. 1) [1].

Composite electrospun micro and nanofibers have wide range of application area such as drug delivery system, electromagnetic shielding system; fiber reinforced composite materials, etc. There are many studies related with composite nanofibers filled by nanosized fillers as silver nano particles, carbon nanotubes, nano clay, etc. Among such material, cellulose nano whiskers (CNW) have great properties such as high aspect ratio, high modulus (143 GPa), high strength (estimated as 14.3-28.6 GPa) renewability, biodegradability [2], [3]. However, limited study is available on the literature related with composite nanofiber filled by CNW [2], [4]-[6]. From these studies, it has been seen that use of CNW as a filler results to an increase of Young's modulus and tensile strength of composite nanofiber web [4] and decrease of nanofiber's diameter [2]. Thus, in this study, it is also aimed to make a contribution to a limited study made on composite nanofiber filled by CNW.

There are also several methods to produce composite nanofiber such as single nozzle and coaxial method (double nozzle) (Fig. 1). Generally, the process at coaxial technique is some harder than single nozzle method [7]-[9]. At single nozzle method, matrix polymer and filler is previously mixed and then fed through the single nozzle (Fig. 1), while at coaxial method, polymer matrix and filler are fed through two separate nozzles which are axially centered to each other (Fig. 1). At single nozzle method, filler have tendency to be placed to whole places of nanofiber, while at coaxial technique, filler are forced to be placed in the axial direction (center) of nanofiber (Fig. 1).

However, in the literature, it is not too much of study related with comparison of these two methods. Thus, in this study, coaxial method and single nozzle method which polymer solution was prepared by ultrasonic homogenizator have been compared to each other, in terms of nanofiber morphology, thermal and mechanical properties of composite nanofiber. During production of composite polymer solution by ultrasonic homogenizator, two different composite polymer solution have been prepared, i.e., composite polymer solution

with water and composite polymer solution without water. Thus, the effect of water content on the nanofiber morphology and also thermal and mechanical properties of composite nanofiber have been also examined.

II. MATERIALS AND METHODS

A. Materials

As a polymer matrix, Polystyrene-block-poly (ethylene-ran-butylene)-block-polystyrene-graft-maleic anhydride from Sigma Aldrich (it was called as Mah Elastomer) was used. Cellulose nano whiskers (CNW) produced from microcrystalline cellulose (Avicel type GP1030 from FMC Biopolymer) by acid hydrolysis method was used as nanofiller.

Cyclohexane, Dimethylformamid (DMF) and Tetrahydrofuran (THF) from Merck were used as solvent in the ratio of 70:20:10 (70 % Cyclohexane, 20% DMF, and 10% THF) to prepare 10 % Mah Elastomer solution (the weight ratio of Mah Elastomer to solvents is 10%). The weight ratio of CNW to Mah Elastomer polymer matrix is 20:80 (25 %, i.e., 20 % CNW and 80 % Mah Elastomer).

B. Preparation of CNW

As described in the literature [3], [10], CNW was produced by acid hydrolysis of microcrystalline cellulose (MCC, Avicel type GP1030 from FMC Biopolymer). MCC was treated with sulfuric acid (95-98 % ,Merck) at 45 °C for 130 min. Then, deionized water was added and the solution was kept for between 17 and 24 hours. Repeated centrifuge was applied in order to remove the excess sulfuric acid (9 cycles and each cycle is 8000 rpm for 40 minutes-Nüve NF 800 R). The supernatant was removed from the sediment and it was replaced by deionized water. The centrifugation continued until the supernatant became turbid. NaOH was added into the solution at the last two cycles to decrease acidity of the solution until the final suspension had a pH value of 9 [11].

C. Preparation of Samples

Polymer matrix (Mah Elastomer) was solved in Cyclohexane, DMF and THF as described in Material Section. It is possible to use just only Cyclohexane, however, DMF and THF were also used to improve the electrospinnability [1], [3].

Two different production methods were used to produce nanofiber, one is single nozzle method and other is coaxial method. At single nozzle method, two different composite nanofibers were produced, one is composite nanofiber produced by composite polymer solution with water, and other is composite nanofiber produced by composite polymer solution without water. Thus; four different nanofibers have been produced and compared to each other. One is reference nanofiber which does not contain any nanofiller (CNW). The other of three nanofibers is composite nanofiber which contains CNW. Test samples and their corresponding codes are summarized in Table I.

For single nozzle method, ultrasonic homogenizator (Bandelin) was used to mix and disperse CNW with polymer matrix (Mah Elastomer) at low amplitude for 15 minutes. The

weight ratio of CNW to Mah Elastomer is 25 %. Two different composite polymer solutions were used to prepare single nozzle composite nanofiber. One is composite polymer solution without water. Other is composite polymer solution with water. To prepare composite polymer solution with water, CNW was dispersed in water by ultrasonic homogenizator, then this CNW solution (the weight ratio of CNW to water is 20 %) was added into solved Mah Elastomer polymer matrix. CNW with water and polymer matrix solution were sonificated by ultrasonic homogenizator.

Electrospinning set up parameters are 20 kV (Matsusada , high power supply), 1 ml/h feeding rate (Sino mdt, sn-50c6/c6, syringe pump) and 15 cm distance between Aluminum collector and needle nozzle which gauge is 0.80 x3 8mm.

For coaxial (double nozzle) method, while polymer matrix solution (10 % Mah elastomer solved in Cyclohexane, DMF, THF in the ratio of 70:20:10, respectively) was fed through outer nozzle by 0.8 ml/h feeding rate, CNW solution (the weight ratio of CNW to water is 20 %) was fed through inner nozzle by 0.1 ml/h feeding rate (Fig. 1). The applied voltage and distance are 15 kV and 15 cm, respectively. The outer and inner diameter of inner nozzle is 0.8 mm and 3.3. mm, respectively. The inner diameter of outer nozzle is 4 mm.

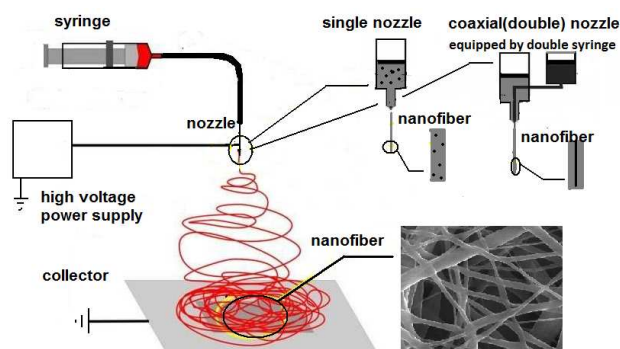


Fig. 1 Schematic illustration of single and coaxial electrospinning method

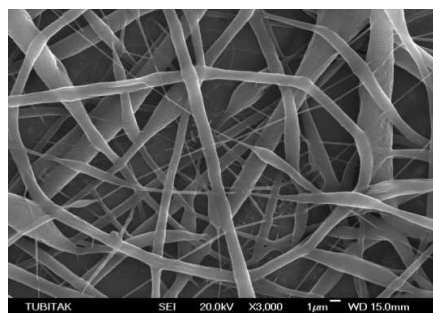
TABLE I
TEST SAMPLES AND THEIR CORRESPONDING CODES

Sample code*	Method	Nozzle number	CNW content (wt% in polymer matrix)	Availability of water in polymer solution
N	Single nozzle	1	0	-
Single-NW	Single nozzle	1	25	available
Single-N	Single nozzle	1	25	-
Coaxial-N	Coaxial (double nozzle)	2	25	-

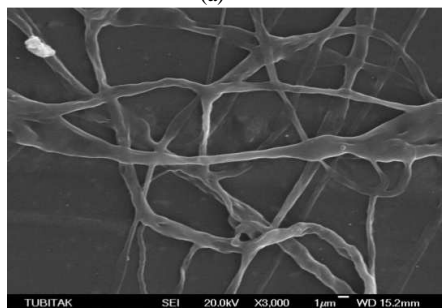
* N: nanofiber without CNW, Single-NW: composite nanofiber with CNW which is produced by polymer solution with water and single nozzle, Single-N: composite nanofiber with CNW which is produced by polymer solution without water and single nozzle, Coaxial-N: composite nanofiber with CNW which is produced by double (coaxial) nozzle.

D. Characterization of Nanofiber

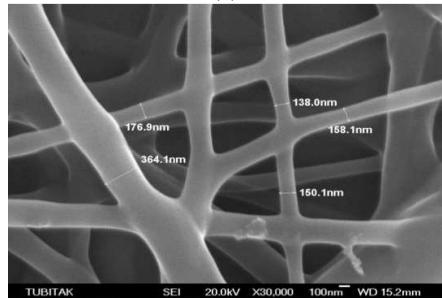
Scanning Electron Microscopy (JEOL Model JSM-6335-F FEG-SEM) was used to observe the morphology/size of neat and composite nanofiber (accelerating voltage 20 kV) (Fig. 2). The sample was sputtered with an approximately 5nm layer of gold/palladium (Au/Pd-80-20%). The diameter of nanofiber is average of 50 measurements (Table II).



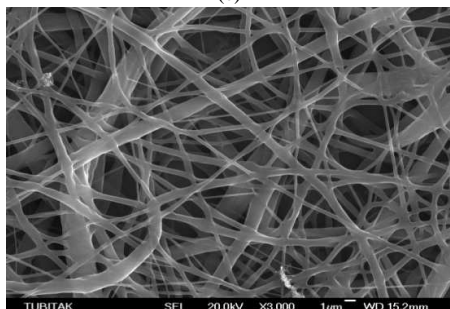
(a)



(b)



(c)



(d)

Fig. 2 SEM (a): nanofiber without CNW, (b): nanofiber with CNW which is produced by polymer solution with water and single nozzle, (c): composite nanofiber with CNW which is produced by polymer solution without water and single nozzle, (d): composite nanofiber with CNW which is produced by double (coaxial) nozzle

TABLE II
THE DIAMETER OF ELECTROSPUN FIBER

*	N	Single-N	Single-NW	Coaxial-N
Electrospun fibers Diameter (nanometers)	971	355	1073	512

* N: electrospun fibers without CNW, Single-NW: composite electrospun fiber with CNW which is produced by polymer solution with water and single nozzle, Single-N: composite nanofiber with CNW which is produced by polymer solution without water and single nozzle, Coaxial-N: composite nanofiber with CNW which is produced by double (coaxial) nozzle.

E. Fourier Transform Infrared Spectroscopy (FTIR)

Thermo Scientific Nicolet IS10 was used for the FTIR analysis (Fig. 3).

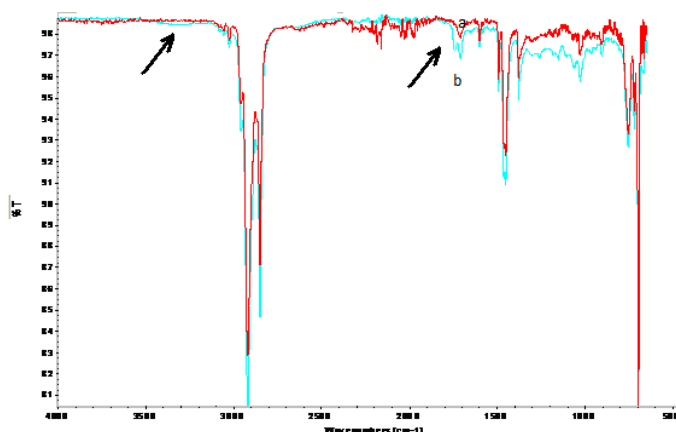


Fig. 3 FTIR - a: Nanofiber without CNW, b: composite nanofiber with CNW produced by coaxial method

F. Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis (TA Q Series TGA Q50) was used to examine thermal behavior of samples. The samples were heated from 30 °C up to 800 °C with a heating rate of 20 °C/min and 10 ml/min nitrogen flow rate (Table III, Fig.4)

TABLE III
THE DIAMETER OF ELECTROSPUN FIBER

*	N	Single-NW	Single-N	Coaxial-N
Temperatures with 5% weight loss (° centigrade)	384	356	376	340

* N: nanofiber without CNW, Single-NW: composite nanofiber with CNW which is produced by polymer solution with water and single nozzle, Single-N: composite nanofiber with CNW which is produced by polymer solution without water and single nozzle, Coaxial-N: composite nanofiber with CNW which is produced by double (coaxial) nozzle

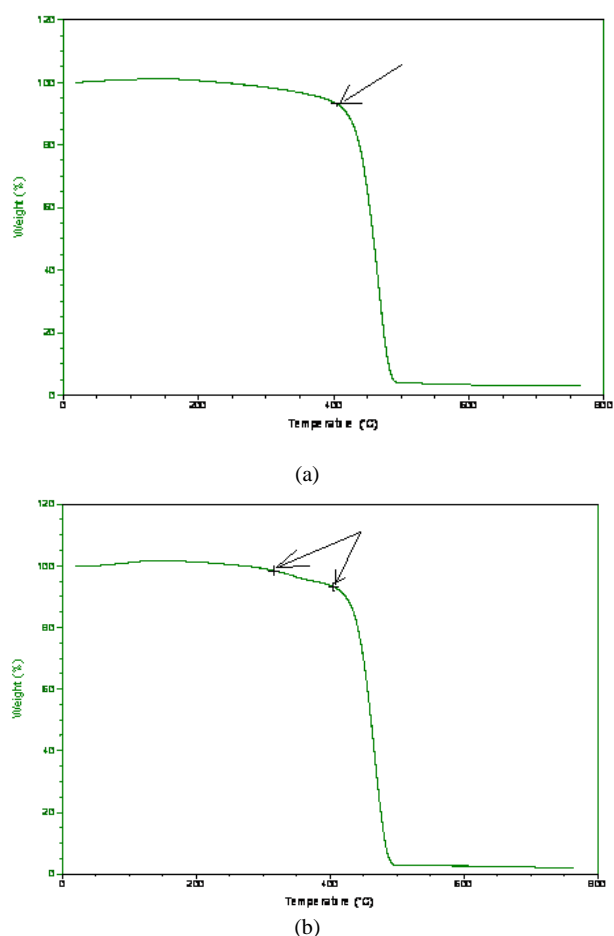


Fig. 4 TGA graphics, a- nanofiber without CNW, b- composite nanofiber with CNW which is produced by single nozzle and polymer solution without water

G. Tensile Testing

Instron 3345 Tensile tester with a 100 N load cell was used for breaking strength and breaking elongation test. The length and width of the specimens, gage distance and cross head speed were 35 mm, 5 mm, 15 mm and 10 mm/min. respectively. At least 10 specimens were tested for each sample (Table IV)

TABLE IV
BREAKING STRENGTH AND ELONGATION

Sample*	Breaking Strength, MPa	Breaking Elongation, %
N	2.8	582
Single-NW	1.4	312
Single-N	2.0	398
Coaxial-N	1.7	548

* N: nanofiber without CNW, Single-NW: composite nanofiber with CNW which is produced by polymer solution with water and single nozzle, Single-N: composite nanofiber with CNW which is produced by polymer solution without water and single nozzle, Coaxial-N: composite nanofiber with CNW which is produced by double (coaxial) nozzle.

III. RESULTS AND DISCUSSION

As seen from Fig. 2 and Table II, morphology of Single-NW composite nanofiber which polymer solution contains water is not homogenous, compared to composite nanofiber without water (Single-N), coaxial composite nanofiber (Coaxial-N) and nanofiber without CNW (N). There are some cavities and protrusions on the surface of the composite nanofiber with water (Single-NW). These may be resulted from agglomeration of CNW during water evaporation [12], [13] and interaction of different solvents (water, cyclohexane, DMF, THF) which have a different evaporation behavior and incompatibility between water and polymer matrix [3]. Thus, the diameter of composite nanofiber with water (Single-NW) is higher than the others, due to high degree of agglomeration. The diameter of composite nanofiber without water (Single-N) and coaxial composite nanofiber (Coaxial-N) are less than nanofiber without CNW (N), because of an increase of conductivity of polymer solution due to presence of CNW [2], [5]. However, the diameter of composite nanofiber produced by single nozzle method (Single-N) is less than that of coaxial composite nanofiber produced by double nozzle. Thus, it may be said that single nozzle system could produce less agglomerated and thinner nanofiber than that of coaxial (double) nozzle system.

As seen from FTIR graphic (Fig. 3), the characteristic band of stretching of -OH in the zone of 3200-3550 cm^{-1} [2] is available, resulted from presence of CNW. An increase of the peak intensity in the zone of 1700-1850 cm^{-1} is possibly resulted from the interaction between CNW and polymer matrix (Mah Elastomer).

As seen from Table III and Fig. 4, presence of CNW results to a decrease of temperature which 5% weight loss is available. This decrease is more evident in coaxial nanofiber and composite nanofiber with water. There is two bending point on the curve (Fig. 4 (b)), first bending point is related with beginning decomposition of CNW, while second bending point is related with beginning of decomposition of polymer matrix (Fig. 4)

As seen from Table IV, all composite nanofibers containing CNW have lower breaking strength and breaking elongation than nanofiber without CNW. This indicates that all composite nanofibers with CNW have agglomeration and not proper wetting, since literatures pointed out that well dispersed CNW results better mechanical properties such as higher breaking strength [2], [4]. However, in terms of breaking strength, the worst one is composite nano with water, then coaxial composite nanofiber, and then composite nanofiber without water. Presence of water can lead to more agglomeration and worst wetting of CNW. Water is available in both composite nanofiber, i.e., Single-NW and Coaxial-N. At Single-NW, polymer solution contains water. At Coaxial-N, water is used to carry the CNW through the inner nozzle. Although all composite nanofiber with CNW has lower breaking elongation than nanofiber without CNW, the higher breaking elongation among nanofiber with CNW is coaxial nanofiber. This may be explained by the placement of CNW in the nanofiber. It could not be possible to make a TEM analysis because of difficulties

sample preparation, however, it can be said that inner nozzle in coaxial system forced the CNW to place in the axial direction of nanofiber (center of nanofiber), while placement of CNW in composite nanofiber produced by single nozzle method may be in all direction of nanofiber, resulting more restriction of mobility of polymer matrix (Fig.1).

IV. CONCLUSION

In this paper, nanofiber, which is composed of elastomeric polymer composite with cellulose nanowhisker was successfully electrospun by single nozzle and coaxial nozzle method. It has been seen that single nozzle method which polymer solution does not contain water has better results than that of coaxial method, in terms of mechanical, thermal and morphological properties of nanofiber. For further studies, it is necessary to make an optimization study on setting condition of ultrasonic treatment to get better dispersion of CNW resulting better mechanical and thermal properties.

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