(REFEREED RESEARCH)

THE EFFECT OF GLYOXAL CROSS-LINKER AND NaCl SALT ADDITION ON THE ROLLER ELECTROSPINNING OF POLY(VINYL ALCOHOL) NANOFIBERS

GLİOKSAL ÇAPRAZ BAĞLAYICI VE NaCl TUZ İLAVESİNİN SİLİNDİRLİ ELEKTRO LİF ÇEKİMİ İLE POLİVİNİL ALKOL NANO LİF ÜRETİMİ ÜZERİNE ETKİSİ

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ABSTRACT

In this study, the effects of the addition of glyoxal cross-linker and sodium chloride (NaCl) salt on the solution properties (conductivity, surface tension, viscosity), spinning performance and fiber properties (diameter and diameter uniformity) in roller electrospinning of poly(vinyl alcohol) (PVA) are discussed. According to the results, solution conductivity, viscosity and fiber diameter increase with the addition of glyoxal cross-linker and NaCl salt. On the other hand, the spinning performance of PVA increases with cross-linking treatment, but decreases as the NaCl salt concentration increases. In addition, there is no relation between NaCl concentration and fiber diameter uniformity. Generally, high fiber density, fine and uniform PVA nanofibers were obtained via the roller electrospinning method.

Key Words: Poly(vinyl alcohol), Cross-linking, NaCl, Roller electrospinning, Nanofiber.

ÖZET

Bu çalışmada; silindirli elektro lif çekimi ile polivinil alkol (PVA) nano lif üretiminde, glioksal çapraz bağlayıcı ve sodyum klorit (NaCl) tuz ilavesinin çözelti özellikleri (iletkenlik, yüzey gerilimi, viskozite), lif çekim performansı ve lif özellikleri (çap ve çap üniformitesi) üzerindeki etkileri tartışılmaktadır. Elde edilen sonuçlara göre; glioksal çapraz bağlayıcı ve NaCl tuz ilavesi ile çözelti iletkenliği, viskozite ve lif çapı artmaktadır. Diğer yandan, PVA lif çekim performansı çapraz bağlama işlemi ile artmakta, fakat NaCl tuz konsantrasyonu artışı ile azalmaktadır. Buna ilaveten; NaCl tuz konsantrasyonu ile lif çapı üniformitesi arasında herhangi bir ilişki bulunmamaktadır. Genel olarak, silindirli elektro lif çekim yöntemi ile yüksek lif yoğunluğu, ince ve homojen PVA nano lifler elde edilmiştir.

Anahtar Kelimeler: Polivinil alkol, Çapraz bağlama, NaCl, Silindirli elektro lif çekimi, Nano lif.

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1. INTRODUCTION

Poly(vinyl alcohol) (PVA) nanofibers and nanofibrous materials are very popular and important because of their potential applications in both research studies and industry (1-5). Electrospinning is the most common method of producing nanofibers and nanofibrous layers. Advances in electrospinning technology for mass production of nanofibers at an industrial scale have increased in recent years (6-10). Roller electrospinning is quite a new technique which provides mass production of nanofibers from a thin film of polymer solution without a needle or spinneret. This technique was invented and patented by Jirsak et al. (2005) at the Technical University of Liberec (7) and then commercialized under the name of Nanospider by Elmarco Company in Liberec. Up to now, roller electrospinning is the unique commercial procedure for producing nanofibrous web via needleless electrospinning technology. Therefore, roller electrospinning was used as a spinning technique in this study to enable the study to be useful at an industrial scale.

It is well known that PVA is the most common and useful polymer in the electrospinning process because of its non-toxicity and water solubility (11). There are only a few studies about roller electrospinning of PVA nanofibers (12-

14). PVA fibers can be cross-linked to improve their mechanical properties and anti-water solubility. The cross-linked PVA nanofibers can be used as filter paper to filtrate the solution with microscaled particles (15). In the literature, there are some studies about cross-linking of PVA nanofibers. Ding et al. cross-linked PVA by glyoxal and used phosphoric acid as a catalyst activator. They determined that cross-linked PVA fibers have better anti-water solubility than non cross-linked PVA fibers (16). Qin and Wang used maleic acid as the cross-linking agent and vitriolic acid as a catalyst activator for the PVA nanofiber production. From the result, it was found that the filtration efficiency increased when using cross-linked PVA nanofiber layers (17). Lee et al. prepared and characterized PVA nanofibers cross-linked using blocked isocyanate prepolymer (BIP). They reported that the water resistance and mechanical properties of PVA nanofibers were significantly improved by the cross-linking treatment (18). Tang et al. produced water insoluble PVA nanofibers using cross-linking agent, glutaraldehyde (GA), with hydrochloric acid (HCl) as a catalyst. They found that the rheological properties of PVA solution changed significantly during cross-linking treatment and this affected the electrospinnability and fiber morphology (19). All these studies were achieved by needle electrospinning, but there is only one study about roller electrospinning of cross-linked PVA nanofiber fabrication. Dao and Jirsak researched the effect of cross-linking agent on the rheological properties of PVA solution and also spinnability for roller electrospinning. Sequarez 755 and phosphoric acid were used as the cross-linking additives. They used non-spinnable PVA with a low molecular weight and made it spinnable by adding cross-linking agent. They found that the rheological properties of PVA solution change significantly and spinning performance increases in time with cross-linking treatment (11).

The aim of this study is the fabrication of cross-linked PVA nanofibers via roller electrospinning and also the determination of the effects of cross-linker addition and NaCl salt concentration on the solution properties (conductivity, surface tension, viscosity), spinnability and fiber morphology (fiber diameter, diameter uniformity, etc.).

2. MATERIAL AND METHOD

2.1 Materials

In this study, atactic PVA (Sloviol Company) polymer, which has 80.000 g/mol molecular weight and is 88 % hydrolysed, was used as a polymer and distilled water was used as a solvent. In addition, phosphoric acid (PENTA) was used as a catalyst activator to reduce strength losses during cross-linking. Glyoxal (Aldrich Company), regarded as a good cross-linking agent, was used to have an important bearing on the permeation. All the solutions were prepared at 12 wt % PVA concentration. Six different PVA samples were prepared, as shown in Table 1.

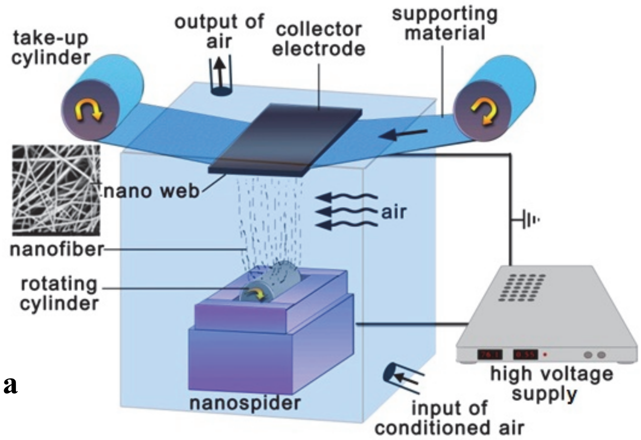
Table 1. Properties of PVA samples.

Polymer	Cross-linking	NaCl % wt
PVA-0	Non cross-linked	0
PVA-1	Cross-linked	0
PVA-2	Cross-linked	0.1
PVA-3	Cross-linked	0.5
PVA-4	Cross-linked	1
PVA-5	Cross-linked	2
PVA-6	Cross-linked	3

2.2. Methods

Firstly, all solutions were prepared under the same conditions (room temperature, stirring time, etc.). Then, solution properties such as conductivity, surface tension and viscosity were determined. Conductivity and surface tension properties were determined by a conductivity meter (Radelkis, OK-102/1) and Wilhelmy method (Krüss) using a platinum plate and a highly precise electronic balance respectively. In Wilhelmy method, a thin plate is used to measure equilibrium surface or interfacial tension at air-liquid or liquid-liquid interfaces (20). PVA solution viscosity was measured using a Rheometer HAAKE Roto Visco 1 at 25 °C.

After the solution properties were determined, PVA solutions were electrospun via roller electrospinning to obtain PVA nanofibrous layers (Figure 1).



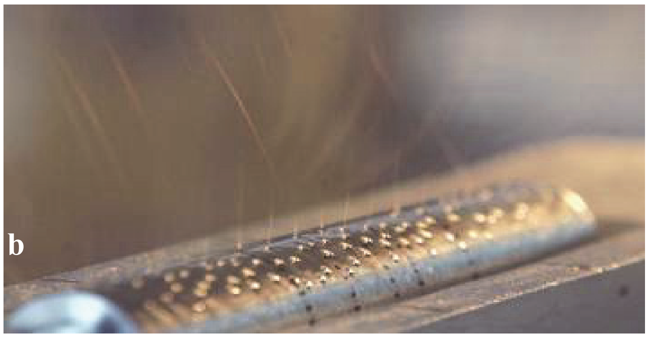


Figure 1. a) Schematic diagram of roller electrospinning method (21); b) Taylor cones and solution jets on the roller (22).

In roller electrospinning, a slowly rotating roller and high voltage supplier are the main factors to spin nanofibers directly from the polymer solution. The rotating roller is partially immersed in a bath of liquid polymer solution. There is a collector electrode at a specific distance from the rotating roller (spinning space) and the high voltage supplier has a connection with this collector and solution. Therefore, it is possible to create an electrostatic area between the roller and collector electrode. During the spinning process, a thin layer of polymer solution is taken to the roller surface as the roller rotates. After the high voltage is switched on, high electric potential inserted in the solution leads to the formation of Taylor cones and jets. A great number of Taylor cones and solution jets are generated on the roller surface, which gives a high spinning performance and makes the process industrially significant (Figure 1.b). The creation of Taylor cones on the surface of the roller was described by Lukas et al. in 2008 (23).

For all spinning experiments, optimum process parameters of the roller electrospinning were applied, as shown in Table 2.

Table 2. Process parameters of the roller electrospinning.

Roller Length (cm)	Roller Diameter (cm)	Roller Speed (rpm)	Take-up Cylinder Speed (m/min)	Distance between the Electrodes (cm)	Voltage (kV)
14	2	3.2	0.12	11	50

Also during the spinning process, conditioned air is blown into the spinning device from a suitable air-conditioner which is able to keep the relative humidity between 18 and 60 % and the temperature between 18 and 30 °C. In this study, the optimum values of relative humidity and temperature to spin PVA nanofibers by roller electrospinning are 38.5% and 21°C, respectively, which were determined from the preliminary experiments (12, 13). Then, PVA nanofibers were collected on polypropylene (PP) spunbond non-woven antistatic material. As is known from the literature, PP spunbond non-woven material is the most common and useful supporting material for roller electrospinning (14, 24).

After the PVA nanofibrous layers were collected on the supporting material (PP non-woven), the spinning performance (SP) value was calculated for each PVA sample. As known from the literature, spinning performance or polymer throughput is the most important parameter of the roller electrospinning method (21, 25). Spinning performance is the amount of nanofiber material in grams per minute produced using a 1 m-long roller (*grams/ minute/metre*). The equation of spinning performance is given below (21):

$$SP = \frac{V \times W \times M}{l} \quad [g/\min/m] \qquad (1)$$

SP = spinning performance (g/min/m)

V = take-up cylinder speed (m/min)

W = width of nanofiber web on collected non-woven material (m)

M = area weight of nanofiber web (g/m^2)

l = length of spinning roller (m)

Pictures of the microstructure of the nanofiber membrane were taken by scanning electron microscopy (SEM) under 15.000x magnification. From the SEM pictures, average fiber diameter (nm) and diameter uniformity were determined with the aid of LUCIA software. Average fiber diameter was calculated using 100 different diameter values for each sample. The fiber diameter uniformity coefficient was calculated using the number and weight average calculations method. The number average has been used as an arithmetic mean in mathematical science, and the method which was used to calculate the uniformity coefficient has the same principle as the molar mass distribution in macromolecular chemistry (26). Both of these values were calculated using equations 2 and 3 given below:

d_i = fiber diameter

n_i = fiber number

$$A_n = \frac{\sum n_i d_i}{\sum n_i} \text{ (number average)} \qquad (2)$$

$$A_w = \frac{\sum n_i d_i^{\,2}}{\sum n_i d_i} \text{ (weight average)} \qquad (3)$$

The fiber diameter uniformity coefficient (FDUC) was determined using equation 4; the optimum value should be very close to 1 for uniform fibers (21).

$$\text{FDUC} = \frac{A_w}{A_n} \qquad (4)$$

3. RESULTS AND DISCUSSION

3.1. Determination of polymer solution properties

The conductivity and surface tension results of the PVA solutions are given in Figure 2. Solution surface tension does not change significantly with the cross-linking treatment and addition of various concentrations of NaCl. On the contrary, solution conductivity increases strongly with the addition of cross-linking agent and NaCl salt. It is possible to explain that the addition of NaCl does not affect the structure of PVA solution, but only slightly increases the friction coefficient between molecules (13). As is also well known from the literature, solution conductivity increases with the addition of salt (27), because ions act as charge carriers in a static electric field (21).

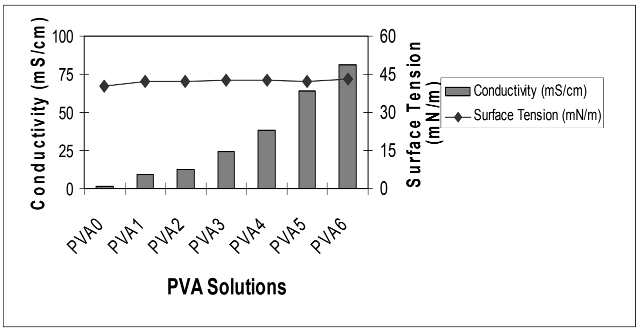


Figure 2. Conductivity and surface tension results of PVA solutions.

The effect of cross-linking treatment and NaCl salt concentration on the conductivity is statistically significant, while surface tension is not (ANOVA test).

Figure 3 presents the PVA solution viscosity results versus shear rate. According to the figure, viscosity increases with cross-linking treatment and NaCl concentration increment.

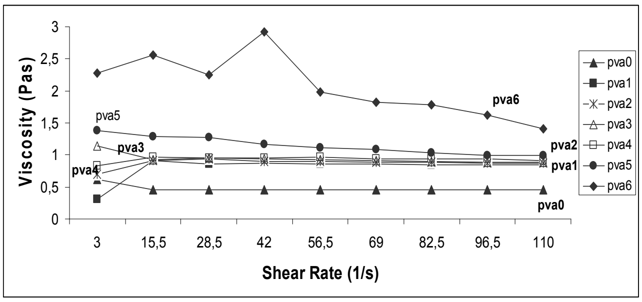


Figure 3. Viscosity versus shear rate of PVA solutions.

The cross-linking agent will make covalent bonds between polymer chains inside the polymer solution (11). The number of chain entanglements in the solution increases with the addition of cross-linker and therefore solution viscosity increases (28).

3.2. Spinning and analysis of fiber properties

Here, we present the spinning performance and fiber properties such as diameter and diameter uniformity coefficient results. Figure 4 shows the spinning performance results of the PVA samples.

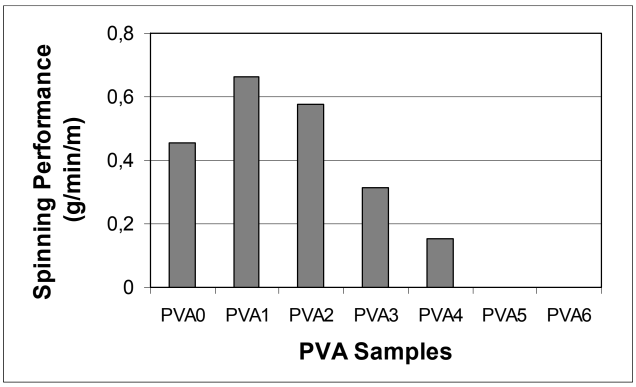


Figure 4. Spinning performance results of PVA samples.

The spinning performance of PVA solutions increases with cross-linking treatment. However, it decreases with the addition of NaCl salt and this result is compatible with previous studies (29). Rheological studies revealed the solutions' lack of elastic character when NaCl is present. The PVA polymeric network is highly elastic if the solution does not include salt. In the presence of salt, intermolecular interactions are weak, which leads to viscous behaviour (29).

It can be seen from Figure 5 that fiber diameter increases with the addition of cross-linker and NaCl salt.

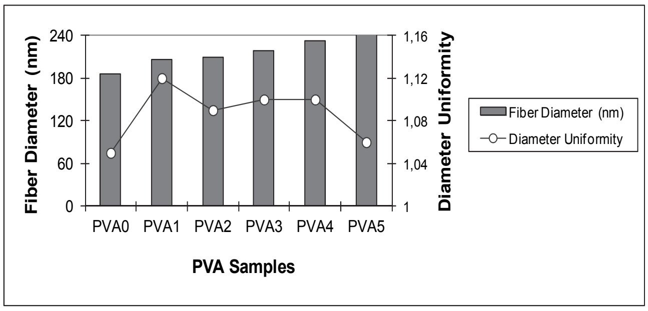


Figure 5. Fiber diameter and diameter uniformity coefficient results.

Dao and Jirsak also found that fiber diameter increases with NaCl (27). The fiber diameter increment with NaCl addition is not statistically significant (ANOVA test).

When the fiber diameter uniformity coefficient (FDUC) results are analysed, it can be seen that uniformity decreases with cross-linking treatment. But there is no relation between the concentration of the NaCl salt and the fiber diameter uniformity coefficient.

SEM images of PVA nanofibers and fiber diameter histograms are given in Figure 6.

Generally, fine and uniform nanofibers were obtained from this study. The finest and most uniform fibers were obtained from PVA0 sample. All the results of the solution, spinnability and fiber properties are given in Table 3.

The spinning performance of the PVA5 sample includes 2 % NaCl, which is very low, and the PVA6 sample includes 3 % NaCl, which is non-spinnable. The highest spinning performance was obtained from the PVA1 (cross-linked and without NaCl) sample.

Table 3. All results of PVA solutions and fiber properties.

PVA Solutions	Properties					
	Conductivity (mS/cm)	Surface Tension (mN/m)	Viscosity (Pas) (110 1/s)	Spinning Performance (g/min/m)	Fiber Diameter (nm)	Fiber Diameter Uniformity Coefficient
PVA0	1.5	40.32	0.454	0.4552	186	1.05
PVA1	9.5	42.06	0.844	0.6644	206	1.12
PVA2	12.35	42.02	0.867	0.5746	209	1.09
PVA3	24.35	42.56	0.883	0.31419	218	1.1
PVA4	38	42.55	0.917	0.15378	232	1.1
PVA5	64	42.36	0.991	very low	251	1.06
PVA6	81.5	43.06	1.401	non-spin	no fiber	no fiber

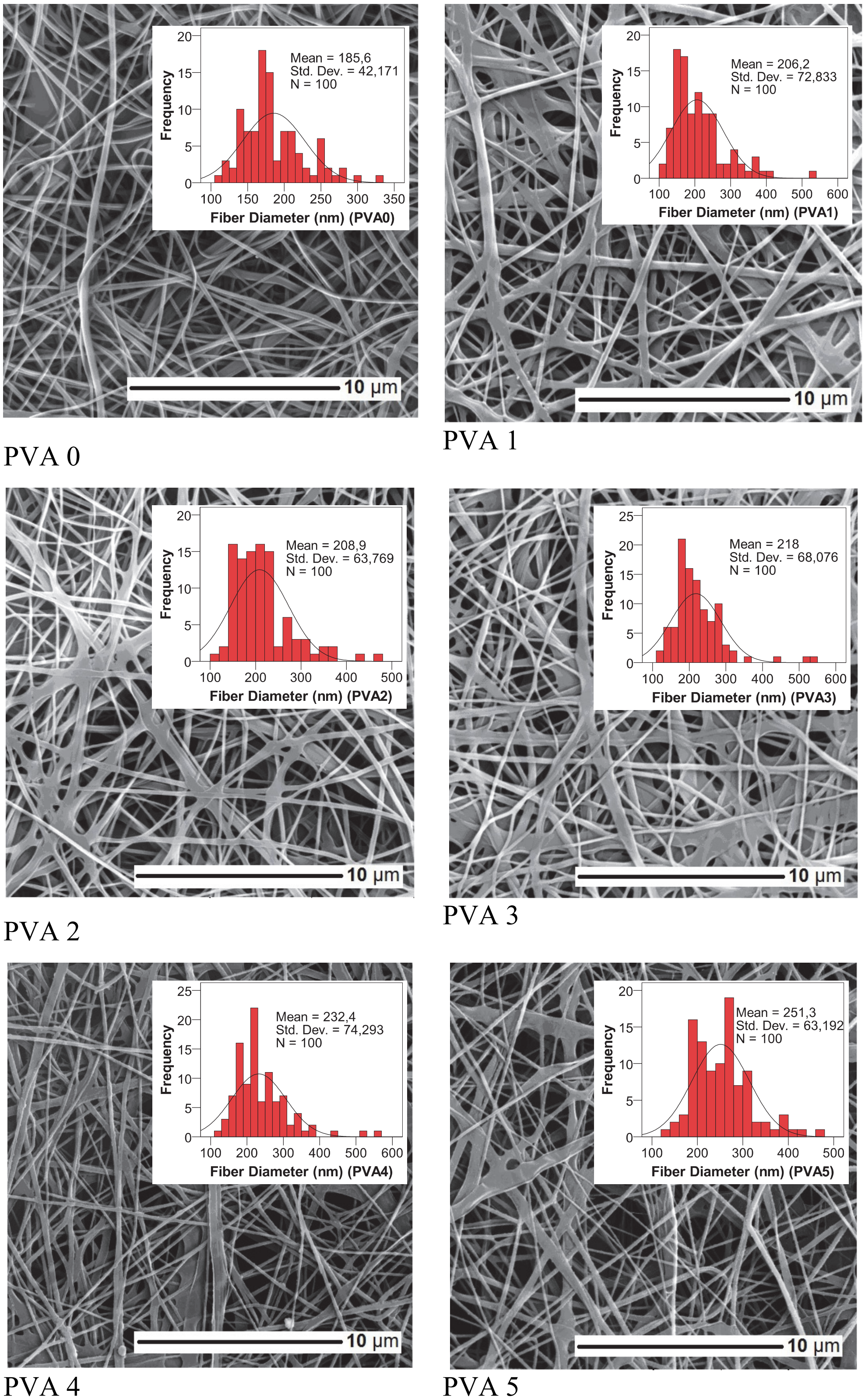


Figure 6. SEM images of PVA nanofiber samples and fiber diameter histograms (15.000x).

4. CONCLUSION

In this paper, the effects of cross-linking treatment and NaCl salt concentration on the roller electrospinning of PVA nanofibers were investigated. Firstly, solution properties (conductivity, surface tension and viscosity), spinnability and fiber properties (diameter and diameter uniformity coefficient) were determined. It was observed from the results that cross-linking treatment and the addition of NaCl salt have major effects on the spinnability of PVA nanofibers via the roller electrospinning technique. Solution conductivity, viscosity and fiber diameter increase with cross-linking treatment and also NaCl salt concentration while surface tension does not change significantly. Spinning performance increases with cross-linking treatment, but decreases with NaCl salt addition. Notably, PVA solution that includes more than 1 % NaCl salt has very low spinnability and also it is non-spinnable at 3 % NaCl. In addition, cross-linking agent and the addition of NaCl salt did not affect the fiber properties significantly. Generally, high fiber density, fine and uniform nanofibers were obtained from this study.

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