(REFEREED RESEARCH)

PRODUCTION OF ELASTOMERIC POLYMER FIBER WEB BY ELECTROSPINNING PROCESS

ELEKTROSPINNING PROSESİ İLE ELASTOMERIK POLİMER LİF AĞININ ÜRETİMİ

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ABSTRACT

There are many of parameters that affect the morphology and diameter of electrospun fiber, such as concentration, viscosity, conductivity, molecular weight, moisture and temperature of environment, applied potential, solution feed rate, collector material and collection type, etc. In this study, elastomeric polymer which can be important for some area such as wound dressing, filtration, etc. has been used for electrospinning process. Three different elastomeric polymer, different solvent type and different production parameters (applied voltage, distance, and feed rate) have been tried for experimental studies. Electrospinibility and morphology/diameter of the electrospun fiber based on the appearance obtained from SEM have been analyzed. It has been seen that Cyclohexane could have better performance in terms of electrospinibility than that's of Toluene. Clogging of needle was decreased, when DMF was replaced with THF. However, diameter of electrospun fiber increased because of high viscosity resulted from use of DMF and high boiling point of DMF. The diameter of electrospun fiber are mostly affected from the change of applied voltage, then distance and feed rate. According to t-test (0.05 level, two tailed), the effect of applied voltage on the diameter of electrospun fiber is statistically significant, the effect of distance and feed rate is not statistically significant

Key Words: Electrospinning, Nano fiber web, Elastomeric polymer, SEM, Morphology-diameter.

ÖZET

Elektrospining işleminde, elde edilen lifin morfoloji ve çapını etkileyen pekçok faktör vardır. Çözelti konsantrasyonu, vizkozitesi, iletkenliği, polimer molekül ağırlığı, ortam sıcaklığı ve nemi, uygulanan voltaj, solüsyon besleme hızı, toplayıcı malzemesi ve toplama tipi, vb. bunlardan birkaçı olarak sayılabilir. Bu çalışmada, yara örtüsü, filtrasyon, vb. alanlarda önemli kullanım alanları bulabilecek olan elastomerik polimer tipleri, elektrospinning işleminde kullanılmıştır. Deneysel çalışma esnasında, üç farklı elastomerik polimer, farklı solvent tipleri ve farklı elektrospinning çalışma koşulları (voltaj, besleme hızı, mesafe) denenmiştir. Gerek elektrospining işleminin uygulanabilirliği gerekse de SEM görüntülerine dayanarak liflerin biçimsel durumları ve çap değişimleri analiz edilmiş ve çeşitli sonuçlara ulaşılmıştır. Elektrospining işleminin uygulanabilirliği bakımından Cyclohexane ın Toluene nazaran daha uygun olduğu görülmüştür. THF (Tetrahydrofuran) yerine DMF in (Dimethylformamide) kullanılması ile iğne ucundaki tıkanmalar azaltılmış olmakla birlikte, gerek vizkozitenin kısmen de olsa artması, gerekse de buharlaşma sıcaklığının yükselmesi sebepleri ile, elektrospinningden elde edilen lifin çapında artma görülmüştür. Elektrospining işlemi esnasında, voltaj değişiminin mesafe ve besleme hızına nazaran lif çapına daha tesirli olduğu görülmüştür. İstatistiksel t- testi sonuçlarına göre (0.05 seviye ve çift kuyruk), voltajın istatistiksel olarak önemli, besleme hızı ve mesafenin ise istatistiksel olarak önemsiz bir degişime sebep olduğu görülmüştür.

Anahtar Kelimeler: Elektrospinning, Nano lif ağı, Elastomerik polimer, SEM, Morfoloji-çap.

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1. INTRODUCTION

Electrospinning process yields a fiber which diameter is in the range from a few nanometers to a few micrometers. During production, it is also possible to get different fiber morphology by change of materials, environmental, setting, etc. such as smooth surface, porous surface, beaded structure, hollow structure, etc (1). Decrease of polymeric fibers's diameter from micrometers to sub-micrometers or even nanometers usually results to better structural properties such as high ratio of surface area to volume, improved mechanical properties, etc. Thus, nanofiber obtained from electrospinning technique can be used for very wide application area, such as drug delivery, blood vessel, wound dressings, surface modification, filtration, nano cable for microelectronic, etc (2).

In the literature, there are studies related with parameters affecting the morphology and diameters of electrospun fibers. For example, Baumgaten was among the first researchers who made a research on some electrospinning parameters of polyacrylonitril (PAN) fibers. He pointed out that an increase of solution viscosity results to an increase of diameter of fiber, while solution feed rate does not affect much the diameter of the fibers (2, 3).

For some application such as tissue engineering, wound dressing, filtration, etc. the elasticity of the fiber web is important. There are several studies related with the elastomeric polymer electrospun fiber. For example, Jarusuwannapoom, *et.al.*(4) studied the effect of solvents on electrospinnability of Polystyrene (PS). They pointed out that electrospinnability of PS improves when dipole moment and conductivity of both solvent and solution increase. Manee-in, *et.al.*(2), also produced nanofiber from Polystyrene and they pointed out that LiCl and KCl (1 % w/v) increase both the conductivity of the PS solution and the size of the fibers. They pointed out that an increase of electrostatic field strength and the concentration of the solution results to an increase of fiber diameter. An increase of applied potential or decrease of distance between collector and needle also result to a decrease of beads. Kim, *et.al,* (5), studied with PS and they concluded that the higher concentration of solution results fewer beads. Evaporation of the solvents affects a splitting and spraying of the fibers during production. Chen *et.al.* (6), produced core-shell type nanofiber by thermoplastic elastomer polyurethane (TPU) and thermoplastic stiff polymer poly (m-phenylene isophthalamide) (Nomex). Li, *et.al.* (7), used an elastomeric polyurethane and polyacrylonitrile for side-by-side electrospinning process. They could produce self-crimped bicomponent nanofibers. Borg, *et.al.*(8), used degradable poly (urethane urea) elastomer which was electrospun into scaffolds for tissue engineering. The diameter of fiber was in the range from 100 nm to a few micrometers. They pointed out that both film and electrospun mat have a similar elongation (about 200 %).

During electrospinning, many of parameters such as concentration, viscosity, conductivity, molecular weight, moisture and temperature of environment, applied potential, solution feed rate, collector material, and collection type, etc. affect the morphology and diameter of electrospun fiber. Last two decades, studies related with electrospun fiber are made extensively. However, it is necessary to make many others of studies to get more knowledge about electrospun fiber for more controllable production and also for more contribution to the literature. Thus, in this study elastomeric polymer which can be important for some area such as wound dressing, filtration, etc. has been used for electrospinning process. Three different elastomeric polymer, different solvent type and different production parameters (applied voltage, distance, and feed rate) have been tried. Electrospinibility and morphology/ diameter of the electrospun fiber have been analyzed.

2. MATERIALS AND METHODS

Three commercial elastomeric polymer have been used, i.e., Polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene-graft-maleic anhydride from Sigma Aldrich (it was called as MAH-PS), Polystyrene-*block*-polyisoprene-*block*-polystyrene from Sigma Aldrich (it was called as PS-ISOPRENE) and Styrene-butadine block copolymer from BASF (it was called as SBS). Their concentration in the solvent has been shown by percentage of weight. As a solvent, Cyclohexane, Tetrahydrofuran (THF), Dimethylformamide (DMF), Asethone, Toluen from Merck have been used. Each component of solvent have been mixed and shown by A/B/C; for example Cyclohexane, DMF, Asethone (80/15/5) means that 80 % Cyclohexane, 15 % DMF, 5 % Asethone (percentage is weight ratio). Viscosity of the solutions has been measured by model Fungilab, Type: Smart Series. Other information about the solution has been given in Table 1.

Scanning Electron Microscopy (SEM, JEOL, Model JSM-5910LV) was used to obtain microphotographs of electrospun fiber (accelerating voltage 20 kV, an approximately 5nm layer of gold/palladium, Au/Pd-80-20%).

Nanofiber has been produced by conventional electrospinning system shown in Figure 1. Solution fed by syringe pump (Sıno mdt, sn-50c6/c6t) was forced by high power supply (Matsusada). Aluminum collector and steel needle (gauge 0.8 x 38 mm) was used. All experiments were carried out at the room temperature in air. In Table 1, production parameters (electrospinning set up) have also been given.

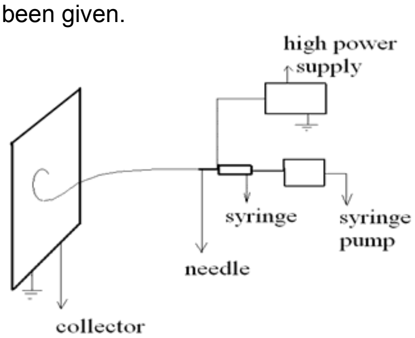

Figure 1. Schematic illustration of electrospinning unit

3. RESULTS AND DISCUSSION

As seen from Figure 2-6 and Table 1 (sample 1,2,3,4), solutions consisted of Toluen (boiling point 111 ^{o}C, dielectric constant 2,38) generally resulted with fail, since formation which contain very fine fibers together with beads and balls (sample 2,3) or spraying (sample 1,4) could be obtained. However, when these three sample (sample 1,2,3) are compared with each other, it can be said that result in terms of fiber formation can

Table 1. Materials and electrospinning set-up parameters

Sample	Polymer	Polymer Concentration (%) Viscosity (cP)	Solvents (% ratio)	voltage(KV) feed rate(ml/h) distance (cm	Result
1	MAH-PS	15 % 370 cP	80%Toluen 15%DMF, 5%Aseton	20 KV 1,5 ml/h 15cm	spraying
2	PS-ISOPRENE	15 % 58 cP	80%Toluen 15%DMF 5%Aseton	20 KV 1,5 ml/h 15cm	fibers together with beads and balls and spraying
3	SBS	15 % 63 cP	80%Toluen 15%DMF 5%Aseton	20 KV 1,5 ml/h 15cm	very fine fibers together with beads and balls and spraying
4	MAH-PS	15 %	80%Toluen, 10% THF 10% Aseton	20 KV 1,5 ml/h 15cm	distinctly spraying that could be observed during electrospinning process
5	MAH-PS	15 % 132 cP	80%Cyclohexane 10%THF 10% Aseton	20 KV 1,5 ml/h 15cm	Electrsopun fibers which diameters is in the range from few micron to nanometer. Occasionally clogging of needle's tip because of solvent evaporation
6	MAH-PS	17 %	80%Cyclohexane 10%THF 10% Aseton	20 KV 1,5 ml/h 15cm	electrospinning could not be carried out
7	MAH-PS	15 %	80%Cyclohexane 15%THF 5% Aseton	20 KV 1,5 ml/h 15cm	Excessive solvent evaporation leading to clogging of needle's tip (thus, electrospinning could not be carried out)
8	MAH-PS	15 % 186 cP	80%Cyclohexane 15%DMF 5% Aseton	20 KV 1,5 ml/h 15cm	Electrsopun fibers which diameters is in the range from few micron to nanometer.
9	MAH-PS	15 %	70%Cyclohexane 30%DMF	--	Solution at tip of needle could not be drawn towards collector between 20 KV-30 KV
10	MAH-PS	15 %	70%Cyclohexane 20%DMF 10%THF	20 KV 1 ml/h 15cm	Often, clogging of needle's tip
11	MAH-PS	13 %	70%Cyclohexane 30%DMF	20 KV 1 ml/h 15cm	Often, clogging of needle's tip
12	MAH-PS	10 % 33 cP	70%Cyclohexane 20%DMF 10%THF	20 KV 1 ml/h 15cm	Electrospun fibers which diameters is in the range from few micron to nanometer.
13	MAH-PS	10 % 33 cP	70%Cyclohexane 20%DMF 10%THF	25 KV 1 ml/h 15cm	Electrospun fibers which diameters is in the range from few micron to nanometer.
14	MAH-PS	10 % 33 cP	70%Cyclohexane 20%DMF 10%THF	20 KV 0.5 ml/h 15cm	Electrospun fibers which diameters is in the range from few micron to nanometer.
15	MAH-PS	10 % 33 cP	70%Cyclohexane 20%DMF 10%THF	20 KV 1 ml/h 20cm	Electrospun fibers which diameters is in the range from few micron to nanometer.

be classified from the best to the worst as PS-ISOPRENE, SBS and MAH-PS. Thus, it can be said that different elastomeric polymer type can have a different results even though all other experimental conditions (concentration, solvents, set-up) are kept constant and also Toluen is not very suitable solvent for electrospinning process due to low dielectric constant and high boiling point. This result can also be seen from the sample 4, 5 (Table 1)

When Cyclohexane (boiling point 81 ^{o}C, dielectric constant 2,02) was used instead of Toluen, fibers which diameters is in the range from few micron to nanometer could be produced successfully at the same experimental condition, this may be due to low boiling point of cyclohexane. Thus, it can be said that solvent are very important factor for electrospinibility.

During electrospinning process, clogging of needle's tip has been occasionally observed; this may be resulted from rapidly evaporation of solvent at the needle's tip during process. Although electrospun fiber could be obtained by 15 % MAH-PS (sample 5, Table 1), when 17% MAH-PS (sample 6, Table 1) was used, it could not be possible to produce fiber because of viscosity of solution and evaporation of solvent. To decrease evaporation, the ratio of Aseton (boiling point 56 ^{o}C, dielectric constant 21) has been decreased from 10 % to 5 % while the ratio of THF (boiling point 66 ^{o}C, dielectric constant 7,5) has been increased from 10% to 15% (sample 7, Table 1). However, it has been observed that electrospinning could not have been done because of excessive solvent evaporation leading to clogging of needle's tip. When DMF(boiling point 153 ^{o}C, dielectric constant 38) was used instead of THF, electrospun fiber could be obtained. This can be due to the fact that the dielectric constant and boiling point of DMF is higher than those of THF. However, as seen from Table 2, when DMF(sample 8, Table 1) was used instead of THF, the diameter of electrospun fiber obtained from 50 measurement is higher than that's of THF (sample 5, Table 1) , due to higher viscosity resulted from use of DMF and high boiling point leading less evaporation. This difference is significant according to statically t –test (0.05 level, two tailed).

When the ratio of Cyclohexane is decreased from 80% to 70 % and the ratio of DMF is increased from 15% to 30 % (sample 8, 9 Table 1), the solution at the end of needle could not be drawn towards collector at the voltage between 20 KV-30 KV. However, at the same experimental condition, the solution at the tip of the needle could be drawn towards collector for solution with 70 % Cyclohexane, 20 % DMF, 10 %THF (sample 10, Table 1), even though clogging of needle's tip is observed frequently. It has been observed that the solution with 15 % MAH-PS (70 % Cyclohexane, 30 %DMF, sample 9) is too viscose to be drawn, may be due to low solvent (Cyclohexane) and high DMF ratio. Thus, concentration of sample 9 has been decreased from 15 % to 13 % (sample 11, Table 1). Thereby, solution at the tip of needle could be drawn towards collector.

In order to see the effect of the voltage, feed rate and distance, four sample (sample 12, 13, 14,15) have been produced. As seen from Table 1, Table 2 and Figure 7, an increase of applied voltage (sample 13) results to an increase of diameter, may be, because more solution is drawn from the tip of needle to the collector by higher voltage. An increase of distance (sample 15) and decrease of feed rate (sample 14) result to a decrease of diameter, compared to reference sample (sample 12). Increase of distance cause to an increase of time for evaporation and drawing, leading to decrease of diameter. Each parameter can be ordered as voltage, distance, feed rate, in terms of the effect of parameters on diameter. When t test is applied, it has been seen that the effect of voltage on diameter is statistically significant (0.05 level, two tailed), whereas the effect of distance and feed rate is not statistically significant (0.05 level, two tailed).

Table 2. The effect of set-up parameters on diameters of the electrospun fiber

Sample	Average diameter (micron) %CV	Minimum diameter (micron)	Maximum diameter (micron)
Sample no: 5 10%MAH-PS, 70%Cyclohexane 20%DMF, 10%THF 20 KV , 1,5 ml/h , 15cm	1,52 38 %	0,425 (425 nanometer)	2,87
Sample no: 8 10 % MAH-PS, 70%Cyclohexane 20%DMF, 10%THF 20 KV, 1,5 ml/h , 15cm	2,68 35 %	1,05	5,63
Sample no: 12 (reference) 10 % MAH-PS ,70%Cyclohexane 20%DMF, 10%THF 20 kV, 15 cm, 1 ml/h	0,645 (645 nanometer) 52 %	0,22	2,02
Sample no: 13 10 % MAH-PS, 70%Cyclohexane 20%DMF, 10%THF 25 kV, 15 cm, 1 ml/h	1,13 45%	0,34	2,04
Sample no: 14 10 % MAH-PS, 70%Cyclohexane 20%DMF, 10%THF 20 kV, 15 cm, 0.5 ml/h	0,636 52 %	0,11	1,36
Sample no: 15 10 % MAH-PS, 70%Cyclohexane 20%DMF, 10%THF 20 kV, 20 cm, 1 ml/h	0,603 45 %	0,27	1,22

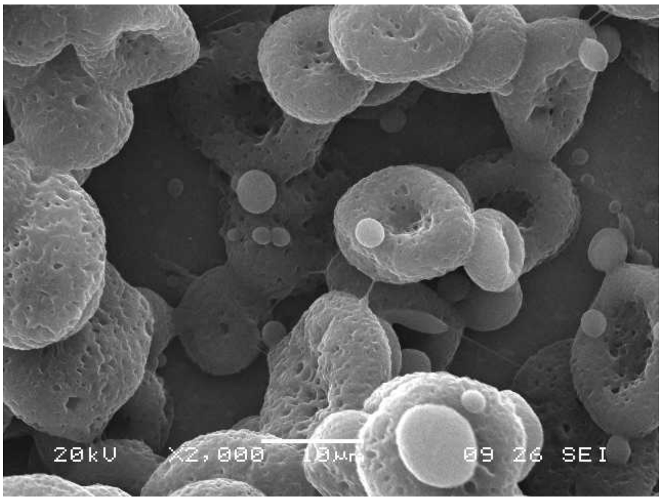

Figure 2. 15 % MAH-PS, 80-15-5 %Toluen-DMF-Aseton, 20 KV, 1.5 ml/h, 15cm

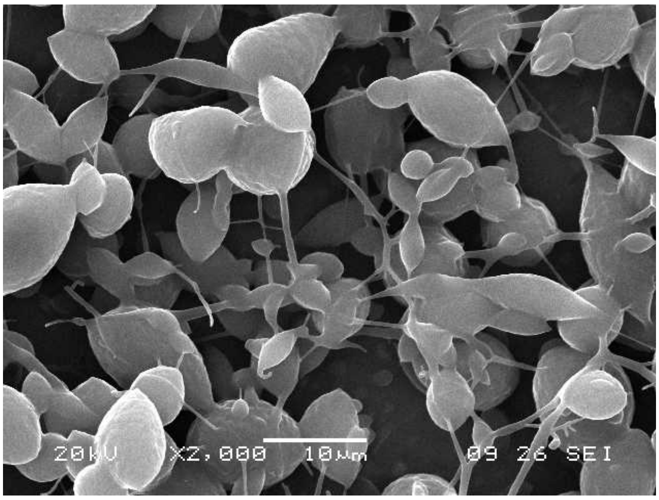

Figure 3. 15 % PS-ISOPRENE, 80-15-5 % Toluen-DMF-Aseton, 20 KV, 1.5 ml/h, 15 cm

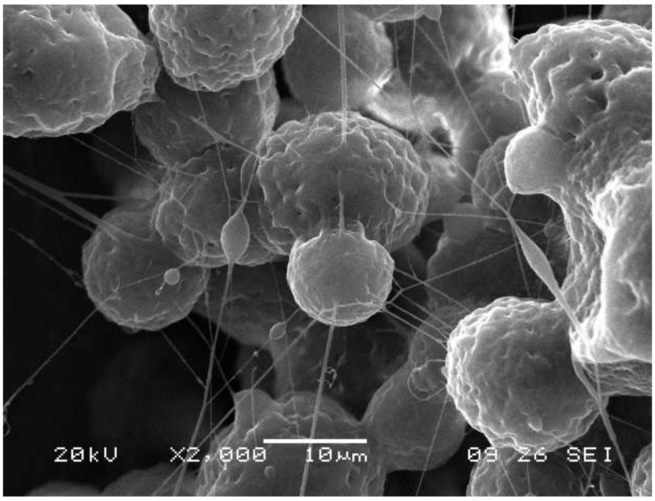

Figure 4. 15% SBS, 80-15-5 % Toluen-DMF-Aseton, 20 KV, 1.5 ml/h, 15 cm

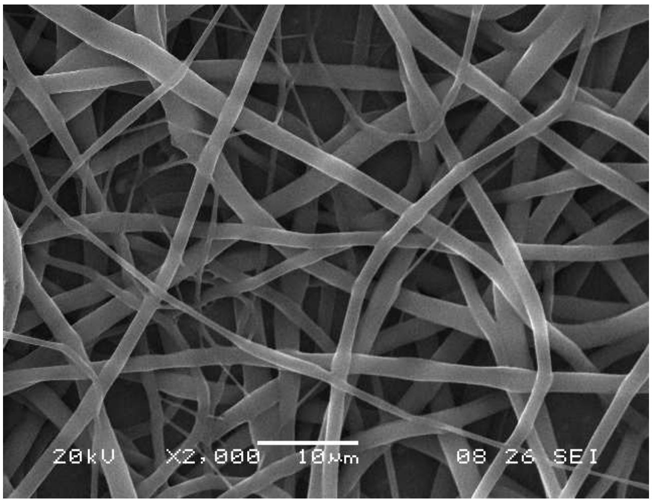

Figure 5. 15 % MAH-PS, 80-10-10 % Cyclohexane-THF-Aseton, 20 KV, 1.5 ml/h, 15 cm

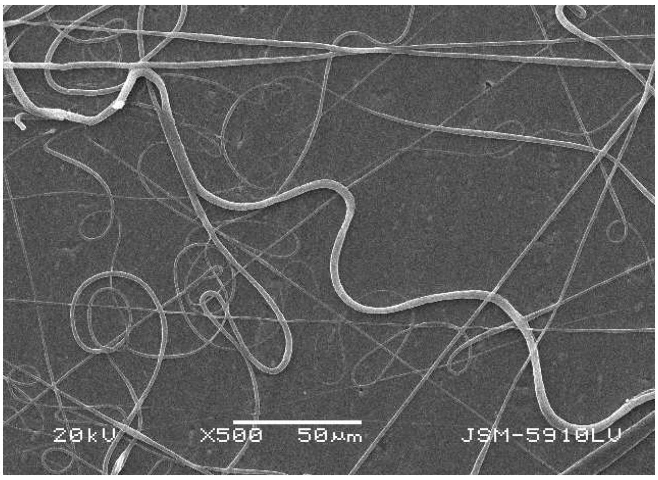

Figure 6. 15% MAH-PS, 80-15-5 % Cyclohexane-DMF-Aseton, 20 KV, 1.5 ml/h, 15 cm

4. CONCLUSIONS

Following results have been obtained:

Generally, Toluen is not very suitable solvent for electrospinning process due to low dielectric constant and high boiling point. When Toluen is used as a solvent, in three different elastomeric polymers, it can be said that a result in terms of fiber formation can be classified from the best to the worst as PS-ISOPRENE, SBS and MAH-PS. Thus, it can be said that different elastomeric polymer type can have a different results even though all other experimental conditions (concentration, solvents, set-up) are kept constant.

When Cyclohexane (boiling point 81 ^{o}C, dielectric constant 2,02) was used instead of Toluen, electrospun fiber could be produced, this may be due to low boiling point of Cyclohexane. Thus, it can be said that solvent are very important factor for electrospinibility.

During electrospinning process, sometimes, clogging of needle's tip has been observed; this may be resulted from rapidly evaporation of solvent at the needle's tip during process

In some trials, clogging of needle was decreased, when DMF was replaced with THF. However, diameter of electrospun fiber increased because of high viscosity resulted from use of DMF and high boiling point of DMF.

Another important parameter is the concentration of the solution. In some trial, when the concentration of sample has been decreased from 15 % to 13 %, solution at the tip of needle could be drawn towards collector.

An increase of applied voltage (sample 13) results to an increase of diameter, may be, because more solution is drawn from the tip of needle to the collector by higher voltage

An increase of distance and decrease of feed rate result to a decrease of diameter. Increase of distance cause to an increase of time for evaporation and drawing, leading to decrease of diameter

Each parameter can be ordered as voltage, distance, feed rate, in terms of the effect of parameters on diameter. When t test is applied, it has been seen that the effect of voltage on diameter is statistically significant (0.05 level, two tailed), whereas the effect of distance and feed rate is not statistically significant (0.05 level, two tailed).

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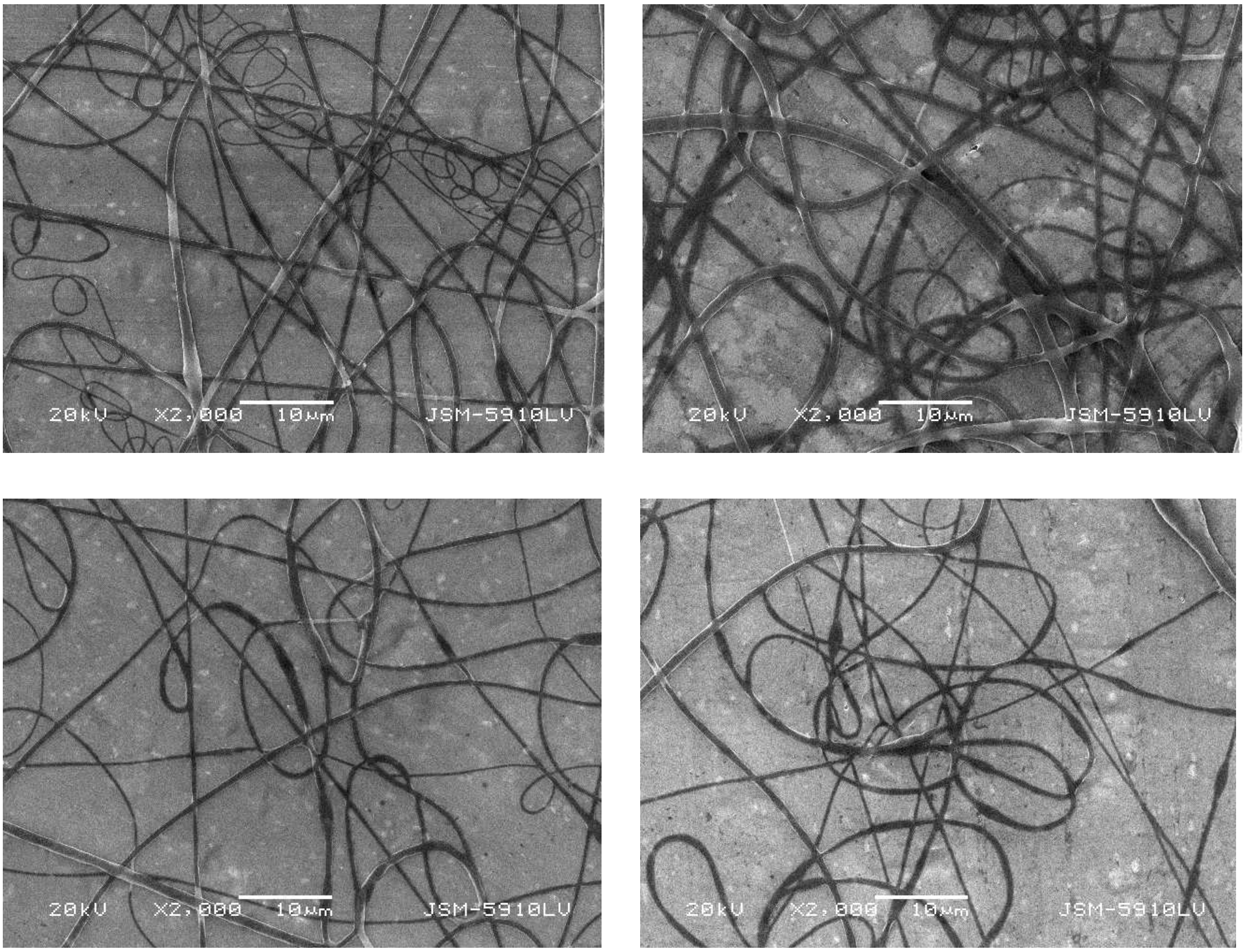

Figure 7. 10 % MAH-PS, 70-20-10 % Cyclohexane-DMF-THF, a- 20 kV, 1 ml/h,15 cm, b- 25 kV, 1 ml/h, 15 cm, c-, 20 kV, 0.5 ml/h, 15 cm, d- 20 kV, 1 ml/h, 20 cm

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