(REFEREED RESEARCH)

EFFECTS OF SOLVENT MIXTURES ON THE MORPHOLOGY OF ELECTROSPUN THERMOPLASTIC POLYURETHANE NANOFIBRES

ÇÖZGEN KARIŞIMLARININ ELEKTROLİF ÇEKİM YÖNTEMİ İLE ÜRETİLMİŞ TERMOPLASTİK POLİÜRETAN NANOLİFLERİNİN MORFOLOJİSİNE ETKİSİ

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ABSTRACT

The effects of solvent mixtures on the electro-spinnability of the thermoplastic polyurethane (TPU) solutions and the morphological appearance of the electrospun thermoplastic polyurethane nanofibres were investigated qualitatively by means of a scanning electron microscope (SEM). N,N-dimethylformamide (DMF), tetrahydrofuran (THF) and ethylacetate (EA) were used as solvents. TPU-DMF/THF and TPU-DMF/EA solutions and the resultant nanofibres were compared to those produced by TPU-DMF system. Fibre diameters increased with the increasing THF volume fraction. At 50/50 and 40/60 DMF/THF mixtures fibres were fused to adjacent fibres and electrospinning is restricted due to low conductivity and low boiling point of the THF, and the high viscosity of the prepared solution. On the other hand, 90/10 and 80/20 DMF/EA solutions led to lower nanofibre diameters. Therefore, diluting TPU solutions with 10 or 20 % of EA had positive effect on electrospun nanofibres.

Keywords: Thermoplastic polyurethane, electrospinning, nanofibres, solvents.

ÖZET

Termoplastik poliüretan (TPU) çözeltilerinin elektrolif çekim yöntemine göre çekilebilirliklerine ve elde edilen termoplastik poliüretan nanoliflerinin morfolojik görünümlerine çözgen karışımlarının etkileri taramalı electron mikroskopu (SEM) ile nitel olarak incelenmiştir. Çözgen olarak N,N-dimetilformamid (DMF), tetrahidrofuran (THF) ve etilasetat (EA) kullanılmıştır. TPU-DMF/THF ve TPU-DMF/EA çözeltileri ve elde edilen nanolifler, TPU-DMF sistemi ile elde edilen nanolifler ile karşılaştırılmıştır. Lif çapları artan THF hacim oranı ile artmıştır. 50/50 ve 40/60 DMF/THF karışımlarında lifler birbirlerie yapışmıştır ve elektrolif çekimi THF'nin düşük iletkenliği ve kaynama noktası ve hazırlanan çözeltilerin yüksek viskozitelerine bağlı olarak zorlaşmıştır. Diğer taraftan, 90/10 ve 80/20 DMF/EA ile hazırlanan çözeltilerden daha ince lif çapı olan nanolifler elde edilmiştir. Bu nedenle TPU çözeltilerini %10 veya %20 EA ile seyreltmek elektrolif çekim yöntemine gore elde edilen nanolifler üzerine olumlu etki yapmaktadır.

Anahtar Kelimeler: Termoplastik poliüretan, elektrolif çekimi, nanolifler, çözgenler.

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1. INTRODUCTION

Electrospinning is a simple technique to produce nanofibres of polymers (1-18). A typical electrospinning set-up basically only requires a high voltage power supply, a syringe, a flat tip needle and a conducting collector (19). On the other hand there are many parameters that affect the electrospinning process and the resultant fibre morphology. Polymer solution has the most significant influence in the electrospinning process and the resultant fibre morphology (20), since viscoelastic and gravitational forces play a major role. Viscoelastic force depends on polymer solution concentration, average molecular weight of the polymer, final viscosity and surface tension of the solution (21).

Electrospinning solution properties are directly related to the solvent type. It involves stretching of the solution caused by repulsion of the charges at its surface, thus if the conductivity of the solution is increased, more charges can be carried by the electrospinning jet (19). As much as solution conductivity, the dielectric constant of a solvent has also a significant influence in electrospinning process. Higher dielectric property reduced the bead formation and the diameter of the resultant electrospun fibres (22). For instance, in the study made by Lee et al. (23), in which the electrospinning of poly(ε-caprolactone) was investigated, it has been found that the addition of N,N-dimethylformamide (DMF) into the electrospinning solution was beneficial to increase the dielectric property to improve the fibre morphology. In confirmation of this study, Hsu and Shivkumar (24) investigated that the addition of DMF led to extensive jet splaying, resulted in the reduction of fibre diameter. Similarly, Wannatong et al. (21) have reported that the productivity of the electrospinning of polystyrene (PS) nanofibres increased with increasing dielectric constant and dipole moment. On the other hand, as Jarusuwannapoom et al. (25) have pointed out that, interaction between the incorporated additional solvent and polymers is of importance in terms of resultant fibre morphology. As well as conductivity and dielectric property, the dipole moment and the boiling point of the solvents and the viscosity and the surface tension of the resultant electrospinning solution are of great importance and directly influence the resultant fibre properties.

In addition to the aforementioned studies, a series of papers have been published on the effects of the solvents on the morphology of nanofibres. Theron et al. (26) have investigated the effects of physical parameters of a number of polymer solutions. In this study, the effects of the addition of ethanol into the poly(ethylene oxide) electrospinning solution in which water was used as solvent, has also been reported. They have concluded that the main positive effect of ethanol incorporation was the increase in the solution evaporation rate that facilitates nanofibre solidification, although the volume charge density decreased. Again for poly(ethylene oxide) nanofibres, Son et al. (22) have tested chloroform, ethanol, DMF and water as solvents. They have observed that the increase in the dielectric constant of solvent decreased the diameter of the resultant fibres. Lee at al. (23) have characterized poly(ε-caprolactone) nanofibres by using methylene chloride, toluene and DMF as solvents. Methylene chloride, toluene and DMF has been found to be good, poor, and nonsolvent for poly(ε-caprolactone) respectively and electrospinning enhanced with the mixture of methylene chloride and DMF. Megelski et al. (27) have investigated the electrospinning of four different polymers electrospun from various solvents. They have observed pore formations on the nanofibres, which was thought to connected to the formation of water droplets from atmosphere due to the rapid solvent evaporation. In the study of Song et al. (28) in which the electrospinning of gelatine nanofibres was investigated, it has been reported that the replacement of acetic acid with ethyl acetate as solvent has improved the electrospinnability of gelatine due to the lover surface tension and higher pH of the solution. The effects of the solvent system on the properties of cellulose acetate nanofibres have been investigated by Tungprapa et al. (29). They have reported that the cellulose acetate-acetone solution was difficult to electrospun because of the low boiling point of acetone and it could be improved by addition of a co-solvent like N,N-dimethylacetamide.

Combination of biocompatibility, non-toxicity, toughness and functionality has led to the widespread use of thermoplastic polyurethanes (TPUs) (30). With regards to nanofibrous TPUs, some commercial products have been appeared on the market for skin decontamination (31). TPU nanofibres are believed to have a potential to substitute breathable polyurethane films and TPU wound care products thanks to their nanofibrous structures. Besides drug release properties of electrospun TPU nanofibers were investigated by Akduman et al. (32) and considered as a medical textile application. The effects of several solution and process parameters such as material composition, concentration, rheological properties, applied voltage, tip to collector distance on the resultant TPU nanofibres have been investigated by several authors (33-36). Ketones such as acetone, methyl ethyl ketone, cyclohexanone are partial solvents for TPUs. Aliphatic esters such as ethylacetate and butylacetate strongly cause severe swelling of TPUs. Highly polar organic solvents such as dimethylformamide (DMF), dimethylsulfoxide (DMSO), N-methylpyrrholidon and tetrahydrofuran (THF) dissolve TPU (37). On the other hand, investigation of the effects of solvents in TPU electrospinning systems has only appeared in the study of Mondal (38), in which four different solvents (tetrahydrofuran, N,N-dimethyl formamide, N,N-dimethyl acetamide, and dimethyl sulfoxide) had been used. It has been reported that the morphology of the resultant nanofibres has been changed significantly with the solvent selection. Solvent conductivity and vapour pressure of the solvents has been found to be the important factors.

In the present study, the effects of the incorporation of ethyl acetate or tetrahydrofuran into TPU/DMF solvent system were investigated in terms of resultant fibre morphology and diameters. To the best of the authors' knowledge, the incorporation of the ethyl acetate into the solvent system of electrospun TPU nanofibers is the preliminary study in the literature.

2. EXPERIMENTAL

2.1. Materials

A commercial TPU, Pellethane 2103-80AE Velox (Lubrizol Advanced Materials), based on 4,4'-methylene bis (phenylene isocyanate) (MDI), polytetramethylene oxide (PTMO) and 1,4 butanediol was used. N,N dimethylformamid (DMF), tetrahydrofuran (THF) and ethyl acetate were used as received from Sigma Aldrich. All of these solvents were analytical research grade and used without further purification. Some basic properties of the solvents were summarized in Table 3.

2.2. Preparation of thermoplastic polyurethane solutions

TPU solutions were prepared by dissolving 8% (w/v) of TPU plastic granulates in each solvents systems as summarized at Table 4, at room temperature. Thus eight types of solutions were prepared.

Table 3. Properties of selected solvents (20, 39)

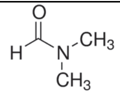
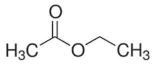
Solvent	Chemical formula		Molecular weight (g/mol)	Boiling point (^oC)	Density (g/ml)	Dipole moment (Debye)	Solubility Parameter (δ) $(cal/cm^3)^{1/2}$	Dielectric Constant (ε)
N,N Dimethyl-formamide (DMF)	C_3H_7NO		73.09	153	0.944	3.86	12.1	37
Tetrahydrofuran (THF)	C_4H_8O		72.1	65-67	0.889	1.75	9.1	7.5
Ethylacetate (EA)	$CH_3COOCH_2CH_3$		88.11	76.5-77.5	0.902	1.78	18.3	6

Table 4. Solvent mixture ratios of TPU solutions

	DMF	DMF/THF	DMF/THF	DMF/THF	DMF/EA	DMF/EA	DMF/EA	DMF/EA
Solvent (v/v)	100	60/40	50/50	40/60	90/10	80/20	70/30	60/40

2.3. Solution properties

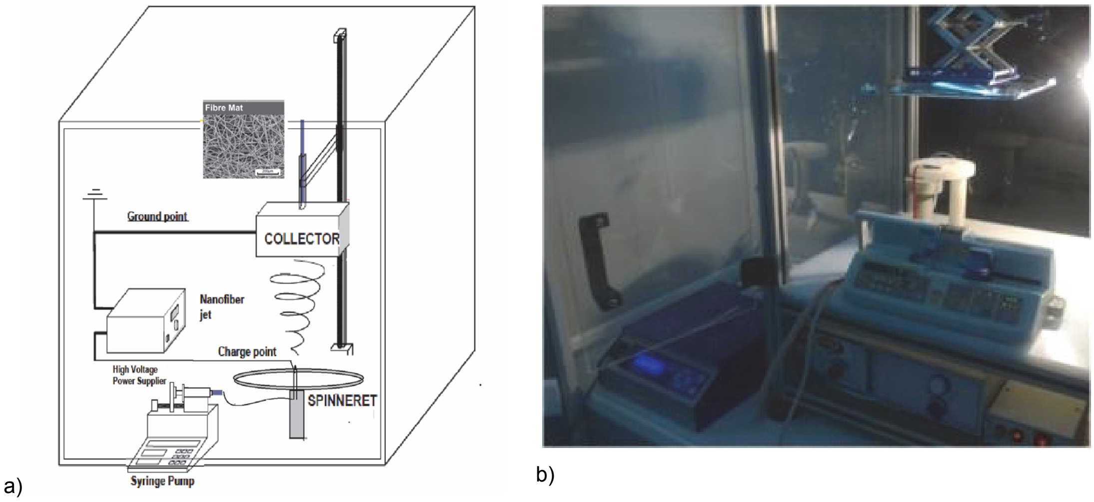
The viscosity of the polymer solutions was measured at 20 ^oC by using Brookfield DV-III Rheometer using the spindle type SC4-21 at 30 rpm. The viscosity measurements were repeated two times or more to ensure consistent viscosity readings. Surface tension of the solutions was characterized by using a Krüss Easy Dyne analyzer by Plate Method. Conductivity of the solutions was tested using a J.P. Selecta Conductivity meter, CD-2004 at room temperature.

2.4. Electrospinning set-up

In the electrospinning set-up (Figure 1), each of the solutions was stocked in a 10 ml syringe. A 2.5 cm long, 22 gauge stainless steel needle with a flat tip and a cone angle of 90^o was used as a spinneret. The tilt angle of the syringe was 90^o from a horizontal baseline. Besides the effects of solvent and its properties on electro-spinnability of the solutions and morphological appearance of the obtained TPU fibres, the effects of the tip to collector distance on the morphological appearance of the resulted fibres was also investigated. To observe the collection distance of 20 and 25 cm, a fixed applied potential of 13kV was applied with feeding rate of 3 ml/h and 5 ml/h respectively and collection time for each spinning condition was fixed at around 5 minutes.

2.5. Morphological observation

The morphological appearance of TPU nanofibres were visually investigated from scanning electron micrographs obtained using a FEI Quanta250 FEG scanning electron microscope (SEM). Each sample was coated with thin film of gold using Emitech K550X ion sputtering device at 15 milliamper and 8x10^{-2} mbar vacuum.



a)

b)

Fig. 1. Electrospinning set-up (a) schematic and (b) photo of the electrospinning device

2.6. Statistical evaluation

All results were expressed as mean ± standard deviation (SD). Data were analyzed by one-way ANOVA followed by Duncan post-hoc test. Differences of $p < 0.05$ were considered statistically significant.

3. RESULTS AND DISCUSSION

The polymer solution properties are known to be the most important parameters that affect the resultant fibre properties. Table 5 summarizes the properties of the solutions (surface tension, conductivity and viscosity) used in this study. Polymer solutions with DMF had the highest surface tension. The addition of THF or EA along with DMF led to a decrease in the surface tension of the solutions. Correspondingly, the conductivity of the solutions was decreased by the addition of THF or EA into the solvent systems. On the other hand, it was observed that the viscosity of the solutions increased by the use of THF or EA along with DMF.

3.1 Nanofibres obtained from TPU-DMF solutions

TPU granulates form a semi-transparent solution after dissolving in DMF and it was observed that 6 h stirring was adequate. Electrospinning of TPU solutions in DMF was found to be quite controllable, possibly due to the relatively high dipole moment and relatively high conductivity of the solvent. Figure 2(a) illustrates frequency distribution of fibre diameter and Figure 3(a) illustrates the scanning electron micrographs of resultant fibres from TPU solutions in DMF. The mean fibre diameter was observed to be around 1074 nanometers for 20 cm tip to collector distance with 3 ml/h feeding rate. When the distance of tip to collector increased to 25 cm, feeding rate has to be increased to 5ml/h in order to produce stable jets. Accordingly, as in the previous studies which were presented elsewhere (40), increasing the tip to collector distance led thinner fibres, however in this case increase of the feeding rate from 3 to 5 ml/h has a drastic effect on the fibre diameters. This increase also caused the increase of the jet length to a great extent which led to shorten the tip to collector distance as well. Combination of these two effect led to thicker fibres (41) (1295 nm) in diameter compared to 20 cm tip to collector distance.

3.2 Nanofibres obtained from TPU-DMF/THF solutions

Figure 2(b-d) shows frequency distribution of fibre diameters and Figure 3(b-d) shows the scanning electron micrographs of TPU nanofibres obtained by various DMF/THF mixture ratios. It was observed that as increasing THF volume fraction, electrospinning is strictly restricted due to high viscosity and low conductivity. The resultant fibre diameters increased and at 50/50 and 40/60 DMF/THF mixtures fibres were fused to adjacent fibres, although THF has a lower boiling point. This could be explained due to relatively low dipole moment, dielectric constant and relatively low conductivity of THF and higher viscosity of TPU-DMF/THF solutions. At higher THF concentration it was difficult to electrospin the TPU-DMF/THF solution because of the higher viscosity and the solution often clogged at the tip of the nozzle. Clogging by the solution was obviously because of the low boiling point of the THF compared to DMF (see Table 3). It was also observed that the increase in the feeding rate increased the diameter of the resultant fibres. Mean diameters of resultant fibres were summarized in Table 6. There was a statistically significant difference between the mean diameters of four groups as determined by one-way ANOVA ($p<0.05$) for both the distance and feeding rate of 20 cm- 3 ml/h and 25 cm - 5ml/h ($F(3,76) = 179.061$, $p < .001$, $F(3, 76) = 80.145$, $p < .001$ respectively). A Duncan post-hoc test revealed that the mean diameter of the TPU fibers was found to be statistically significantly higher when THF is added into DMF.

Table 5. Surface tension, conductivity and viscosity of pure solvents and TPU solutions

Solvent System	Surface Tension (m/Nm)		Conductivity (µS/cm)		Viscosity (cp)
	Pure Solvent	8% PUR (w/v)	Pure Solvent	8% TPU (w/v)	8% TPU (w/v)
TPU-N,N Dimethylformamide (DMF)	36.7	39.6	0.51	0.94	653
Tetrahydrofuran (THF)	27.2	-	0.15	-	-
Ethylacetate	23.7	-	0.13	-	-
TPU-DMF/THF (60/40)	31.9	35.6	0.44	0.89	893
TPU-DMF/THF (50/50)	31.1	34.3	0.29	0.80	1040
TPU-DMF/THF (40/60)	30.2	33.3	0.25	0.58	1160
TPU-DMF/Ethylacetate (90/10)	34.5	37.0	0.45	0.87	720
TPU-DMF/Ethylacetate (80/20)	32.8	35.5	0.40	0.81	733
TPU-DMF/Ethylacetate (70/30)	31.1	34.3	0.37	0.72	853
TPU-DMF/Ethylacetate (60/40)	30.1	32.5	0.32	0.65	867

Table 6. Mean fiber diameter of electrospun TPU-DMF/THF fibres

Solvent System	*Mean Fibre Diameter ± S.D (nm)*	
	20 cm,13 kV, 3 ml/h	*25 cm,13 kV, 5 ml/h*
TPU-DMF	*1074.24 ±234.66* ^{a}	*1295.80 ±171.83* ^{a}
TPU-DMF/THF (60/40)	*1392.91 ±148.97* ^{b}	2373.09 *±240.26* ^{b}
TPU-DMF/THF (50/50)	*2272.83±295.15* ^{c}	2190.76 *±275.26* ^{b}
TPU-DMF/THF (40/60)	*3365.26 ±553.53* ^{d}	3596.64 *±855.69* ^{c}

$^{a,b,c\ d}$, ** **p<0.05.** One Way ANOVA, Duncan post hoc test*

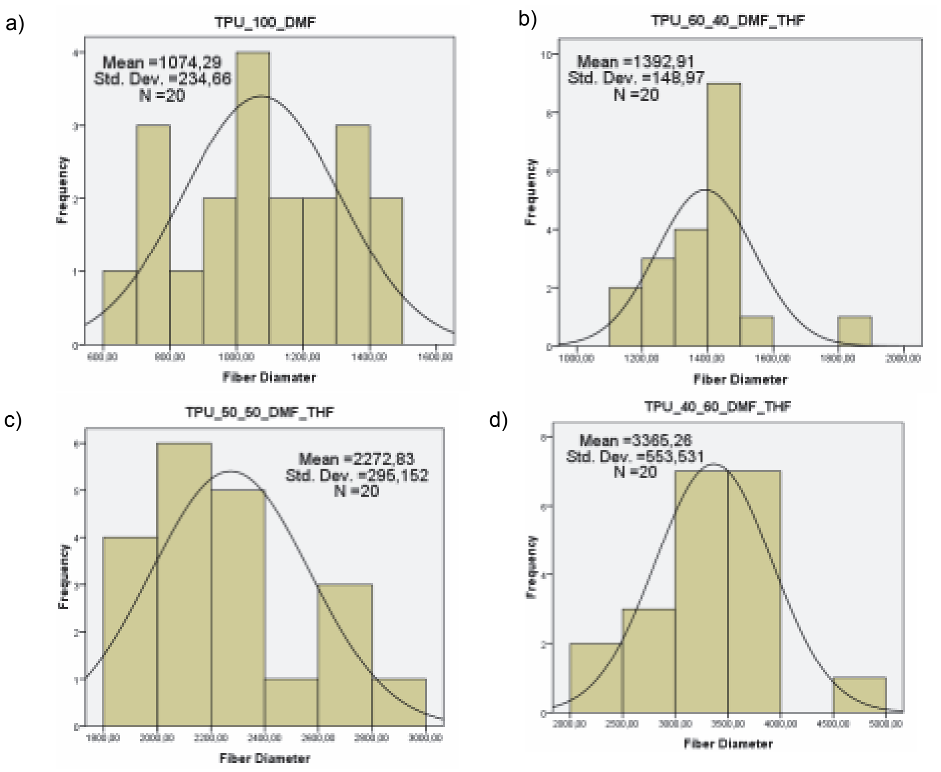


Figure 2. Frequency distribution of fibre diameters of electrospun TPU nanofibres obtained by the solvent mixture of DMF/THF (a) 100/0, (b) 60/40, (c) 50/50, (d) 40/60 (v/v) at 13 kV, 20 cm, 3 ml/h

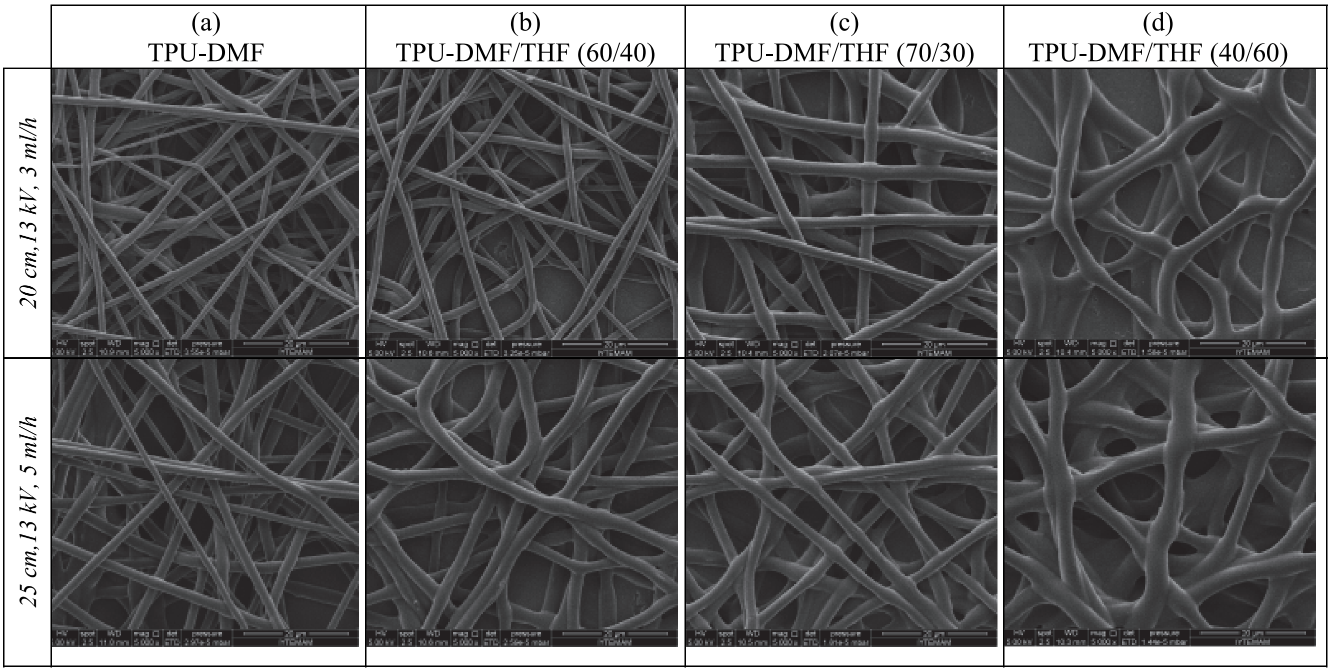


Figure 3. Scanning electron micrographs of electrospun TPU nanofibres obtained by the solvent mixture of DMF/THF (a) 100/0, (b) 60/40, (c) 50/50, (d) 40/60 (v/v) at 13 kV, 20 cm- 3 ml/h and 25 cm-5ml/h

3.3 Nanofibres obtained from TPU-DMF/EA solutions

EA mainly used in diluting TPU solutions (42, 43). The proportion of these diluents (EA) can be increased, if the solubility is needed to be improved. Figure 4 shows frequency distribution of fibre diameters and Figure 5(b-e) shows the scanning electron micrographs of TPU nanofibres obtained by various DMF/EA mixture ratios and mean diameters of resultant fibers of these DMF/EA mixtures were summarized in Table 7. There was a statistically significant difference between the mean diameters of five groups as determined by one-way ANOVA (p<0.05) for both the distance and feeding rate of 20 cm- 3 ml/h and 25 cm - 5ml/h (F(4,95) = 87.840, *p* < *.001*, F(4, 95) = 28.417, *p* < *.001* respectively). A Duncan post-hoc test revealed that the mean diameter of the TPU-DMF/Ethylacetate (90/10) fibres was statistically significantly thinner than TPU-DMF fibres. It may be the reason of the high solubility parameter (20), swelling (37) and diluting behaviour of the ethyl acetate. However, increase in EA ratio to 30 and 40 resulted in larger fibre diameters compared to pure DMF, 90/10 and 80/20 DMF/EA mixtures. There was not a statistically significant difference between TPU-DMF/Ethylacetate (80/20) and TPU-DMF fibres but mean diameter of the TPU-DMF/ Ethylacetate (70/30) and (60/40) fibres were statistically significantly higher than other TPU-DMF and 90/10 and 80/20 DMF/EA mixtures. EA has the ability to swell the TPU molecules followed by the absorption but it has a very low dielectric constant which limits the electrospinnability (20). Depending on the EA portions the capacity of separating and breaking of intermolecular forces will be different and less at lower DMF concentrations. This caused higher viscoelastic force of the solution to be stretched (44). Effect of the low boiling point of EA at higher concentration was also more significant and triggered the fast drying of the solution at the tip of the nozzle as well.

Table 7. Mean fibre diameter of electrospun TPU-DMF/EA fibres

Solvent System	*Fiber Diameter ± S.D (nm)*	
	20 cm,13 kV, 3 ml/h	*25 cm,13 kV, 5 ml/h*
TPU-DMF	*1074.24 ±234.66*^{b}	*1295.80 ±171.83*^{b}
TPU-DMF/Ethylacetate (90/10)	*890.97 ±230.55*^{a}	*1020.21±310.98*^{a}
TPU-DMF/Ethylacetate (80/20)	*951.48 ±252.27*^{ab}	*1167.29 ±467.19*^{ab}
TPU-DMF/Ethylacetate (70/30)	*1849.33±298.85*^{c}	*1793.71 ±334.20*^{c}
TPU-DMF/Ethylacetate (60/40)	*1930.99 ±180.29*^{c}	*2086.76 ±505.88*^{d}

$^{a,b,c\ d}$, *** $p<0.05$.** *One Way ANOVA, Duncan post hoc test*

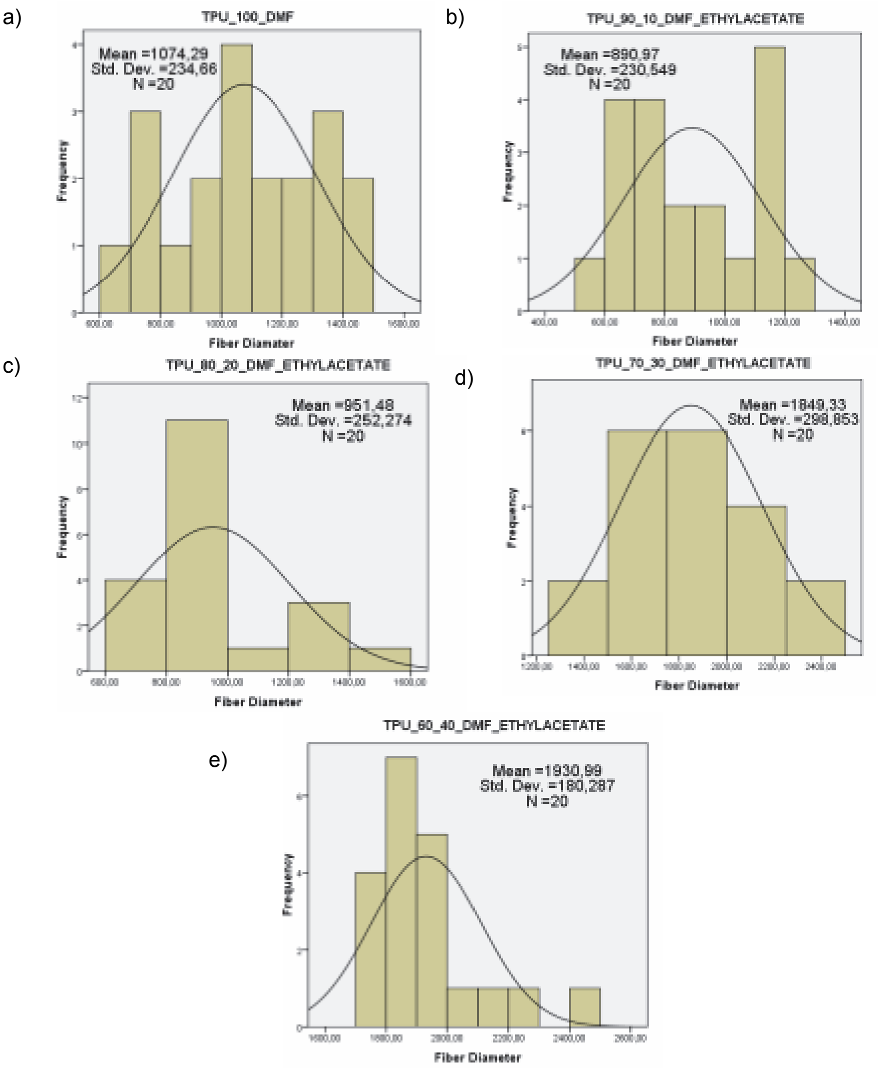


Figure 4. Frequency distribution of fibre diameters of electrospun TPU nanofibres obtained by the solvent mixture of DMF/EA (a) 100/0, (b) 90/10, (c) 80/20, (d) 70/30, (e) 60/40 (v/v) at 13 kV, 20 cm, 3 ml/h

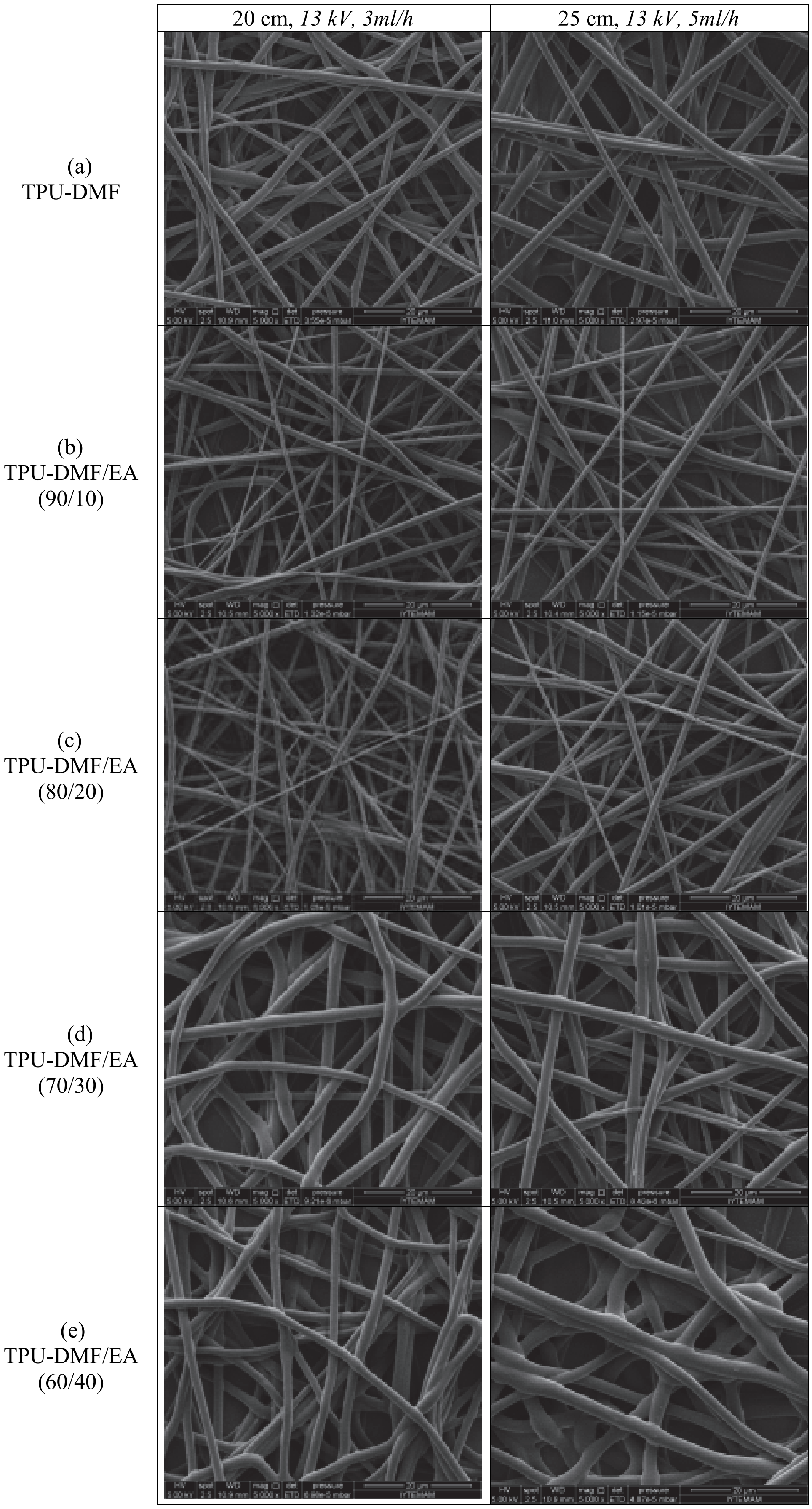


Figure 5. Scanning electron micrographs of electrospun TPU nanofibres obtained by the solvent mixture of DMF/EA (a) 100/0, (b) 90/10, (c) 80/20, (d) 70/30, (e) 60/40 (v/v) at 13 kV, 20 cm- 3 ml/h and 25 cm-5ml/h

3.4 Further Discussion

Six types of force may be considered for electrospun polymer solution; they are *(i)* body or gravitational force, *(ii)* electrostatic force which carries the charged jet from the tip to the collection plate, *(iii)* Coulombic force which tries to push apart the jet segment and is responsible for the stretching of the solution during its flight to the collection plate, *(iv)* viscoelastic force which resist the stretching of the solution, *(v)* surface tension which also acts against the stretching, and *(vi)* drag force from the friction between the charged jet and the air (21).

To explain the effect of the solvent type and concentration on the diameters of the electrospun fibres, these forces may be considered. According to Table 5, an increase in THF and EA part in the solution markedly increased the viscosity value of the polymer solution, while it made a little change in the surface tension. For a given solution system, an increase in the solution viscosity resulted in an increase in the viscoelastic force. Since the applied electrostatic field was fixed to be 13kV, both the electrostatic and the Coulombic forces acting on a jet segment should depend significantly on the amount of charge carriers being present in the jet segment. In case of DMF/THF mixtures, by the increase in solution viscosity, the higher viscoelastic force should prevent the jet segment from being stretched by the constant Coulombic force, resulting in the obtained fibres having larger diameters (Table 10). But in case of DMF/EA mixtures, diluting effect and severe swelling behaviour of ethyl acetate led to thinner fibres at 90/10 and 80/20 DMF/EA concentrations.

4. CONCLUSIONS

THF or EA were mixed with DMF as solvent systems for the production of TPU nanofibres and the results were compared to the nanofibres obtained by TPU/DMF solutions. The solutions of TPU in pure DMF and DMF/EA were found to be easily electrospinnable. Based on the results observed, the values of the solubility value, evaporation character due to their boiling point, dipole moment of the solvent, the conductivity and viscosity of the electrospinning solutions were important factors determining the electrospinnability of the solutions.

DMF seemed to be the best solvent to dissolve TPU pellets but diluting TPU solutions with 10 % or 20 % of EA ensured positive effect on fibre diameter by means of achieving thinner fibres. On the other hand, incorporation of THF led to thinner fibres compared to TPU/DMF solutions. With the increasing of THF volume fraction, electrospinning is restricted due to high viscosity and low conductivity. Also, at higher concentrations of THF, fibres were observed to be fused to adjacent fibres.

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