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Microstructure interpretation of macromechanical behaviour of poly urethane eletrospun nanofiber webs

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In this study, the effect of electrospinning duration, polymer concentration, solvent mixture and fiber orientation on stress-strain behavior of thermoplastic polyurethane (TPU) nanofiber web is investigated. The tensile behavior of PU network obeys nonlinear elastic that were interpreted in regard to the polymer molecular chain and network morphologies. With increasing electrospinning duration, polymer content and increasing of DMF in THF/DMF solvent, fiber diameter, thickness of fiber network and tensile strength increased but the behavior of elongation was different. Also, the results show that with increasing electrospinning duration, thickness of nano-fiber web increased nonlinearly.

For investigating the effect of fiber orientation, the stress strain curve of PU membrane is compared with PU yarn. The results show that initial hardness of stress-strain curve of PU mat is due to the fiber oriented normal to elongation direction.

The initial hardness of stress strain curve is the results of the fibers normal to the elongation direction.

Keywords: Electrospinning, Nanofiber, Mechanical properties, Polyurethane

INTRODUCTION

Investigation of the Stress-Strain Behavior of electrospun nanofibers is a very wide and popular research area, nowadays [1, 2, 3]. Due to the high surface area and interconnected porosity, electrospun nanofibrous webs are an important area in nanotechnology applications [4, 5, 6].

TPUs is considered as "bridging the gap between rubber and plastics", since TPUs not only offer mechanical performance characteristics of rubber, but also it can be processed as thermoplastics [7]. These randomly segmented copolymers composed of hard and soft segments form a two-phase microstructure. The hard segments, composed of polar materials, can form carbonyl to amino hydrogen bonds and thus tend to cluster or aggregate into the ordered hard domains, whereas the soft segments form amorphous domains resulting phase separation [7].

Tensile behavior of thermoplastic polyurethane elastomer (TPUE) is investigated by different researchers [1,8]. These works reported that electrospun TPUE fibre mats showed non-linear elastic and inelastic characteristics which may be due to the slippage of crossed nanofibers (i.e. non-bonding or physical bonding structure) and breakage of the nanofibers at junctions (i.e. point bonded or chemical bonding structure).

Some research showed that the mechanical properties of electro-spun nano fiber mat are affected by the nature of solvent that has been used [9]. With using DMF in electrospinning of TPU as solvent, the tensile strength is much more than the mat that used THF as solvent [10]. Other parameters that affect mechanical properties of nanofiber mat are the concentrations of polymer in electrospinning solution [11]. The fiber orientation also has important effect on mechanical properties of mat. Tensile strength increases through an increase in fiber orientation [12, 1]. In previous work, it has been shown that electrospun nanofibrous web has a good potential as membrane for using in protective clothing applications [1, 2, 4]. Although some researches have been carried out on studying the mechanical properties of the electrospun nanofibers, comprehensive investigations are necessary for studying the effects of micro structure on macro mechanic of PU electrospun nanofiber mat.

In this study the effect of solvent mixture, polymer concentration, fiber orientation and electrospinning duration has been studied on tensile behavior of TPU electrospun nanofibrous web. Also, the effect of these parameters on fiber diameter, web thickness, tensile strength and elongation has been investigated and interpreted. The stress-strain behavior of PU membrane has been interpreted with regards to polymer structure and web morphology.

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EXPERIMENTAL

Electrospinning

Electrospinning solution was prepared from 13,14 and 15 percent wt./vol of commercial TPU (Mw: 65,000, Bayer. Germany) which was dissolved in tetrahydrofuran (THF) and N,N- dimethylformamide (DMF) mixture (60:40, 55/45 ,50/50, v/v). In order to obtain different thickness and studding the effect of mesh thickness electrospinning process was done with different durations (2,4, and 6 hours).

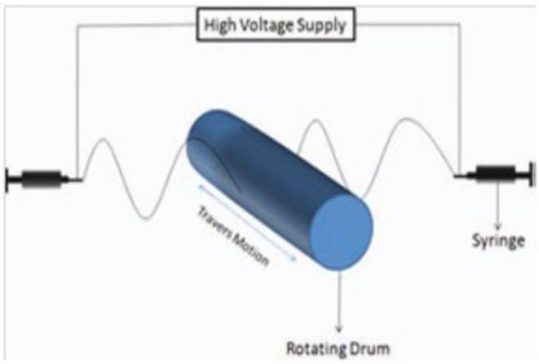

Fig. 1. Schematic diagram of double nozzle electrospinning machine with rotating drum**.**

In this research an electrospinning machine with 2 nuzzles has been used. In the electrospinning process, PU solution from two opposite needles was electrospun simultaneously on one rotating drum. The optimum distance between nozzle and collector was 13 centimetre. The rotation speed and traverse speed of drum and applied voltage was respectively 150 RPM, 400mm/min and 13KV. The average of 20 points is reported as thickness of mat with using a micrometer (Dial Thickness Gage, Mitotoyo, Japan). Morphology of electrospun polyurethane fibres was studied using scanning electron microscopy (SEM) and diameter of the nanofiber was measured from SEM image using Image analyzer software. Five dumbbell-shaped specimens in machine direction (MD) and five dumbbell-shaped specimens in transverse direction (TD) were examined for characterization of mechanical properties according to ASTM D-638. Figure 2 shows a typical SEM of electrospun PU web.

To study the effect of fiber orientation on tensile behaviour of electrospun web an aligned yarn was produced by the setup that is proposed by Najafi and Gharehaghaji [5]. For producing aligned nanofibers in yarn formation zone, two nozzles with opposite charge were used. These nuzzles were connected to 1 ml syringes that were fixed on the syringe pump. Polymer solution was electrospun and produced jets were moving towards each other and then were joined together on the surface of aluminum collector. The aluminum drum was used as a temporary collector. Consequently, twisting and winding units were used to align and twist the nanofiber strand. During this transformation, a tensile load was exerted on nanofibers and a spinning triangle was formed.

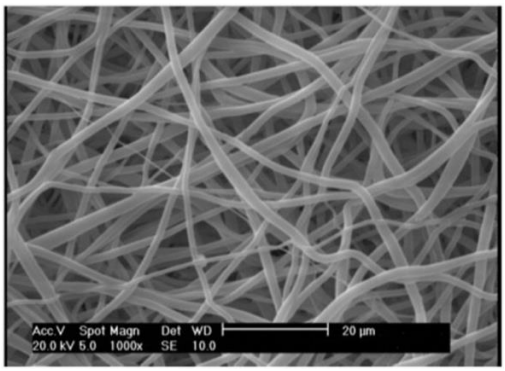

Fig. 2. A typical SEM of electrospun PU web.

The nanofibers orientation distribution was calculated by a program which was encoded in MATLAB Software (version 7.0.0.1920) as explained in previous work [1]. The summary of results is shown in Table 1.

RESULTS AND DISCUSSION

Stress–strain behavior of electrospun PU

The data from uniaxial tensile tests showed the perfectly non-linear elastic behavior of the electrospun PU nanofiber web. Figure 3 shows the typical stress-strain curve of PU nanofibrous webs. The load-elongation curve shows a high initial modulus that after approximately 15 mm elongation is followed with a slightly slope and around 150 mm elongation this slope increased again.

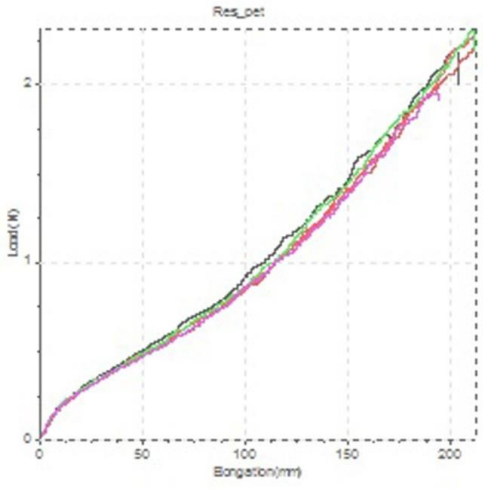

Fig. 3. The typical stress-strain curve of PU webs

Table 1. Characterization of produced sample

Sample Code**	Mat thickness (mm)		Tensile at break (N)				Elongation at break (%)			
	Mean	S. D.	Machine Direction		Cross Direction		Machine Direction		Cross Direction	
			Mean	S. D.	Mean	S. D.	Mean	S. D.	Mean	S. D.
III 2h 13%	0.039	0.010	1.46	0.272	2.19	0.144	200.30	14.52	206.10	8.03
III 2h 14%	0.031	0.002	1.12	0.35	1.57	0.32	194.60	8.59	184.40	24.87
III 2h 15%	0.040	0.006	1.54	0.30	2.09	0.16	197.90	0.09	204.00	9.52
II 2h 13%	0.029	0.003	0.82	0.10	1.20	0.09	135.30	6.56	153.3	12.05
II 2h 14%	0.039	0.008	1.05	0.20	0.90	0.08	140.40	11.10	100.20	8.10
II 2h 15%	0.038	0.004	1.19	0.57	0.70	0.05	144.6	10.28	105.8	8.02
I 2h 13%	0.039	0.014	1.33	0.213	1.53	0.30	198.5	6.02	198.00	12.16
I 2h 14%	0.044	0.011	0.66	0.09	8.84	0.15	96.02	12.86	170.70	14.81
I 2h 15%	0.056	0.014	1.34	0.17	1.92	0.15	156.80	8.11	182.40	11.16
III 4h 13%	0.077	0.014	1.99	0.70	2.51	0.08	166.9	17.00	154.20	6.81
III 4h 14%	0.092	0.005	1.97	0.30	3.37	0.2	0.213	13.13	180.10	7.42
III 4h 15%	0.114	0.019	1.93	0.37	2.41	0.12	260.70	4.27	187.30	10.80
II 4h 13%	0.080	0.014	1.43	0.53	1.86	0.10	126.80	19.28	128.70	7.03
II 4h 14%	0.087	0.007	0.87	0.15	1.23	0.18	135.50	10.12	164.00	14.05
II 4h 15%	0.082	0.015	3.35	0.90	3.96	0.27	191.40	12.57	191.60	8.71
I 4h 13%	0.090	0.013	2.15	0.70	3.41	0.22	156.30	15.44	177.30	9.22
I 4h 14%	0.095	0.005	2.00	0.32	2.95	0.20	183.70	15.30	189.90	9.63
I 4h 15%	0.070	0.011	2.92	0.33	3.66	0.44	124.70	13.94	134.90	6.09
III 6h 13%	0.112	0.015	3.58	0.39	5.53	1.12	163.50	0.35	169.60	40.29
III 6h 14%	0.142	0.004	4.72	0.44	6.35	0.76	230	16.12	226.30	21.06
III 6h 15%	0.085	0.019	4.61	1.14	6.21	0.72	234.60	9.47	221.00	13.73
II 6h 13%	0.099	0.010	2.84	0.61	3.66	0.39	145.20	15.63	153.40	18.00
II 6h 14%	0.114	0.034	2.92	0.96	3.51	0.14	139.1	25.74	131.70	6.09
II 6h 15%	0.113	0.020	3.60	1.14	3.32	0.11	153.50	16.50	139.80	4.02
I 6h 13%	0.136	0.016	3.13	0.48	4.29	0.48	153.9	8.02	154.10	16.38
I 6h 14%	0.153	0.029	3.42	0.50	5.31	0.81	189.30	18.35	200.70	25.02
I 6h 15%	0.160	0.027	0.02	0.52	2.58	0.19	97.98	9.40	120.90	9.45

** Sample coding: solvent mixture (I=60/40, II=55/45 and III=50/50(THF/DMF)),Electrospinning duration (2h=2hours, 4h= 4hours and 6h= 6hours) and Polymer content.

The PU web gives a characteristic response to elastomeric materials -sigmoidal in shape-, with strain hardening resulting from molecular orientation at high degrees of strain. This behaviour can be interpreted with regards to two sources; firstly fiber polymer's molecular structure and secondly network morphology.

The segmented polyurethanes are consisted of hard and soft segments. Hard domains act as physical crosslinks and impart the material's elastomeric behavior. At room temperature, soft domains are above their glass transition temperature and impart the material its rubber-like behaviour; hard domains are below their glass or melt transition temperature and are thought to control and regulate the high modulus and tensile strength [7].

The electrospun PU mesh has stress–strain responses resulting from molecular orientation within the fibres as a result of electrospinning, and a strain-induced orientation of the electrospun fibre mat. When a strain is applied to the electrospun mat, fibers oriented in the direction of cross-head displacement are stretched uni-axially, while fibers oriented at some angle relative the principal strain direction experience a rotation. As the strain in the electrospun mat increases and more fibers become oriented in the direction of strain, the relative number of fibers stretched in comparison to the fibers rotated, increases and the stress in the electrospun mat increases. The electrospun mat is globally isotropic, the individual fibers comprising the web have a certain degree of molecular orientation prior to stretching. The strain applied to the electrospun mat serves to orient both fibers and molecules within the fibers. The apparent molecular orientation in the electrospun fibers also leads to the pronounced reduction in elongation to failure of the electrospun mat.

In the beginning of the tensile process the electrospun nanofiber mesh has Hookian behavior, and structural morphology does not change. After a critical level of stress the weaker fibre breaks or the bonding between the fibres where fibres cross each other, break up and nanofibers slip on each other. Because the breaking force of fibre is significantly higher than the forces needed for breaking the bonding between fibre, this point bonding starts to break up at an average extension of 20 %, then the slope of graph decreases. Because of the bonding break up stress, quality of the bonding between fibres and fibre diameter deviation, a long transition is observed in graph.

Federico and Gasser [13] in studding the nonlinear elasticity of biological tissues with statistical fiber orientation showed that the comparison potential terms with the fibres allowed to resist compression, are convex with the isotropic fibre distribution, for all deformation states tested, and non-convex with the anisotropic fibre distribution, for most of the deformation states tested. In contrast, the anisotropic ensemble potential terms with tension-only fibres is convex for all tested combinations of fibre orientation and deformation state. Their result suggests that the assumption of fibres having asymmetric behaviour in tension and compression is not only more realistic, but also needed from the point of view of mathematical consistency, in order to achieve convexity. In the other words, when the nanofibrous web is loaded the fiber in the other direction resist to buckle and this imparts a convexity to tensile behavior (This is the reason of initial high moduli), and after overcoming to this resistance (when fiber in perpendicular direction is buckle) the curve continue with smaller slope. The comparison between load-elongation of electrospun nanofiber web with fiber oriented in different directions (fig. 3) and load-elongation of aligned nanofiber yarn with fiber aligned in loading direction (fig. 4) confirms this assumption.

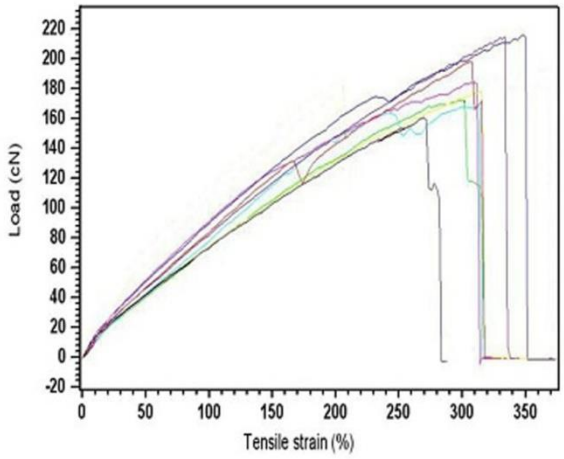

Fig. 4. The typical stress-strain curve of PU webs.

As it can be seen from figure 4, the initial slope in nanofiber yarn stress-strain curve is smaller than figure 3 that is because of fiber orientation distribution in PU electrospun nanofibrous web.

Stress softening (Mulins effect)

Figure 5 shows the softening behavior during the cyclic loading. In cyclic tests, the stress-strain curve in the second cycle is far more compliant than that of observed in the first cycle. The stress-strain behavior tends to be stabilized after four cycles and most softening occurring during the first cycle. As the strain upon reloading approaches the maximum strain achieved in prior cycles, the stress tends to approach to the stress level of a first cycle

test at that strain and unloading paths after a given strain all follow the same curve, independent of cycle number. Softening depends on strain history, where larger strain produces greater softening and the residual strain occurs predominantly after the first cycle, and no significant height changes are observed after the additional cycles. Stable curves are typically observed after only 4 cycles.

The stress-strain elastic nonlinear behaviour and stress softening of electrospun nanofibrous PU web are similar to the bulk behaviour of thermoplastic polyurethane that reported by Qil and Boyce [7].

The domain structure of segmented polyurethane is responsible for the softening effect. It is found that the stress inhomogeneity in the soft domains could lead to the rotation of hard domains in order to minimize the overall energy of deformation. It is also found that at large stretch the hard domains would break down to further accommodate stretch. To achieve the high degree of hard block orientation, it was necessary that hard domains undergo the plastic deformation, which was accompanied through the breakage and reformation of hydrogen bonds [7].

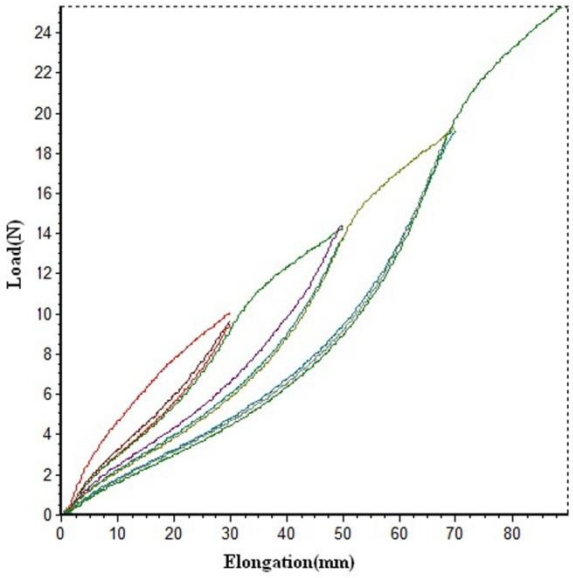

Fig. 5. Cyclic uniaxial tension test.

On the other hand, the network microstructures can cause the stress softening effect. Electrospun fibers are held together through connecting sites such as crossing and bonding between fibres [8]. The point-bonding and physically crossed structure occurred for electrospun PU. The relatively weak non-bonded structures tend to break or slip-apart, under loading resulted in the stress-softening behaviour in cyclic loading-unloading tests. It is stated that the non-bonding structures do not contribute effectively for carrying the load in comparison with the point-bonded structures [14]. It can consider that the point bonding and the non-bonding (physical crossed structure) in electrospun fibrous network play the role of the hard segment and soft segment in the PU molecular chain, respectively.

The effect of electrospinning duration

Statistical analysis shows a significant difference between mean diameters of fibre among different levels of electrospinning duration (2, 4 and 6 hours). The results show that with increasing electrospinning duration that resulted in increasing web thickness the diameter of fiber increased (fig 6). It seems that with increasing fiber on collector drum, the charge carrying capacity of the jet decreases, thereby subjecting it to lower tension when the electric field is applied. Lower tension resulted in decreased elongation forces exerted on the jet, yields a coarser fiber.

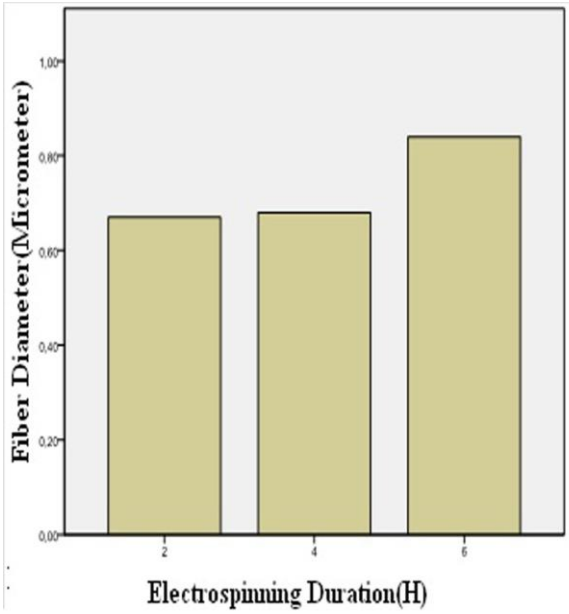

Fig.6. The effect of electrospinning duration on diameter of fibers.

One of the most important factors that affect the mechanical properties of fibrous material is the thickness of structure. The test result shows that with increasing process duration the weight and thickness of layers increase linearly but the increase in slope of thickness is larger than weight. It is described that as the fibers reach the collector the charge intensity decreased and this caused that next fiber with a lower speed moved in distance between nuzzle and collector and the thicker web produced. On the other hand the as spun fibers have some electrical charged ions that repel other fiber that yielded to more voluminous network.

With increasing electrospinning duration, the tenacity of layers increased and elongation of them

decreased. The results indicate that these layers have good strength as a result of point bonding due to the residual solvent.

As figure 7 show a nonlinear relation is governing between strength at break (N) and electrospinning duration (H). The regression model (R^2=98%) is as below:

$$\text{Tenacity (N)} = 0.562+0.\ (036\text{Electrospinning Duration(h)}^2)$$

This regression equation suggests that the rate of strength increasing is being increasing with increasing electrospinning duration (web thickness). This is due to this fact that with increasing the web thickness the residual solvent should pass a longer way to leave the nanofibrous web and the nanofibers have more time to connect each other by residual solvent and produce network have more chemical connection and strength.

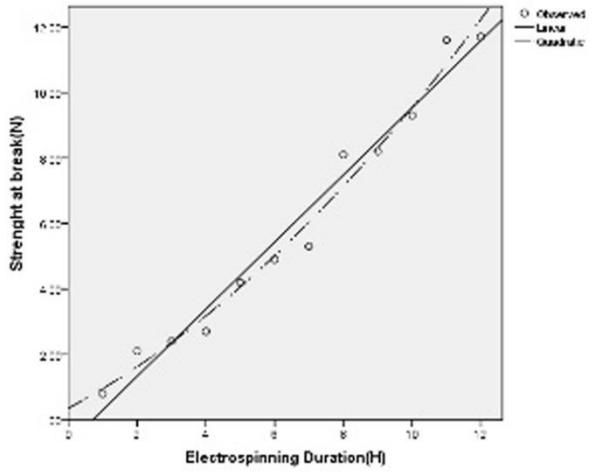

Fig. 7. Strength at break versus electrospinning duration

The effect of fiber orientation distribution

The results of this experiment show that tenacity in cross direction (CD) is about 28% more than the machine direction (Fig.8) but no significant difference occurred in elongation at break. Figure 9 shows typical fibres orientation in different directions of samples. As this figure demonstrates, the fibres are more oriented in cross direction than machine direction.

Strength in different directions of electrospun nanofiber webs is due to the orientation distribution of the nanofibers in various directions [15]. In this work traverse motion of the drum causes the fibre bundle get more oriented in cross direction.

The results obtained by Pedicini and Farris[16] indicate that molecular orientation is induced by the electrospinning process and is a contributing factor to the 'stiffer' stress–strain behaviour of the eletrspun PU mat.

They showed that the molecular orientation function (f = [3cos2α -1]/2 where α is mean molecular angle) for oriented electrospun PU fibers is an order of magnitude larger than *f* for the isotropic electrospun fibers and PU film. This means that in cross direction oriented mat not only the fiber get more oriented in a cross direction but also the molecular chain is more oriented in cross direction and these two factors increased the strength in this direction.

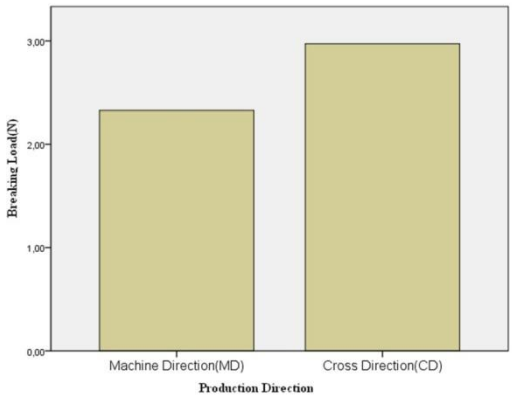

Fig. 8. The effect of production direction on load at break

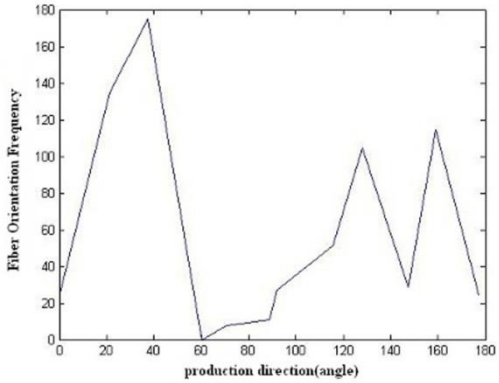

Fig. 9. Typical fibre orientation distribution.

The effect of polymer concentration

Solution concentration plays an important role in the fiber diameter. ANOWA analysis shows the significant effect of polymer content on tensile behavior of PU web (tab. 2). The result shows that with increasing polymer content, tenacity and elongation was increased (Fig. 9).

The polymer concentration that controls solution viscosity is one of the biggest determinants of fiber diameter and morphology when spinning polymeric nanofibers. Increasing the solution viscosity by increasing the polymer concentration caused that fiber diameter, web thickness, tenacity and elongation of PU electrospun web increased as shown in Table 3.

Table 2. Analysis of variance for the effect of polymer content and solvent mixture on load and elongation at break.

Source	Dependent Variable	Type III Sum of Squares	df	Mean Square	F	Sig.
Polymer Content (P.C)	Maximum Load	7.123	2	3.562	14.170	.000
	maximum elongation	3755.813	2	1877.906	9.958	.000
Solvent Mix-ture(S.M)	Maximum Load	37.741	2	18.870	75.072	.000
	maximum elongation	101033.576	2	50516.788	267.867	.000
P.C * S.M	Maximum Load	14.774	4	3.694	14.694	.050
	maximum elongation	2247.130	4	561.783	2.979	.065
Error	Maximum Load	41.224	164	.251		
	maximum elongation	30928.578	164	188.589		
Total	Maximum Load	1965.974	213			
	maximum elongation	6161941.690	213			
Corrected Total	Maximum Load	447.620	212			
	maximum elongation	292769.327	212			

Table 3. The effect of polymer content on morphology and tensile behaviour of PU mat

Polymer content (%)	Fiber diameter (nm)	Mat thickness (mm)	Tensile at break (N)	Elongation at break (%)
13	610	0.075	2.53	159.95
14	810	0.086	2.68	167.41
15	950	0.102	2.76	169/66

Table 4. The effect of polymer mixture on morphology and tensile behaviour of PU mat

solvent mixture (THF/ DMF)	Fiber diameter (nm)	Mat thickness (mm)	Tensile at break (N)	Elongation at break (%)
50/50	920	0.095	3.00	195.90
55/45	850	0.077	2.56	157.36
60/40	710	0.080	2.35	159.96

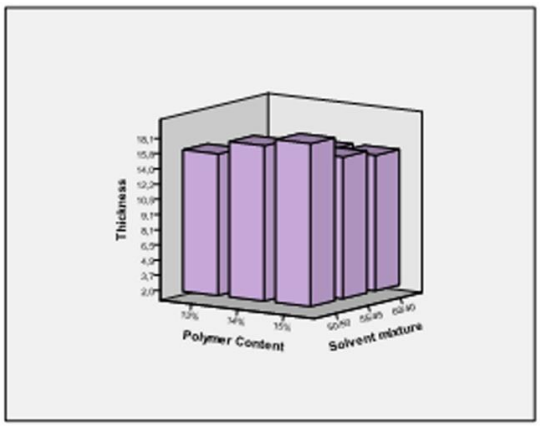

Fig. 10. The effect of polymer content and solvent mixture on strength of PU web.

The elongation of electrospun sample with 13%wt. polymer content had smaller value than two other samples but no significant difference between elongation of sample with 14% and 15% polymer concentration was observed.

The effect of solvent mixture

Rapid solvent evaporation and phase separations due to alternation of the jet are a common phenomenon in electrospinning process. Solvent volatility plays a major role in the formation of nanostructures through influencing the phase separation process. Also the electrolytic nature of the solvent is an important parameter in electrospinning [6].

As Table 2 shows, the solvent mixture has also significant effect on tensile behaviour of PU mat. It can be seen from Table 4 and figure 10 that with increasing DMF in THF/DMF mixture the strength and elongation of electrospun nanofibrous web increased.

With increasing THF content fiber diameters and web thickness increased. Data indicate that the mat tensile strength is sensitive to the fiber diameters and web thickness.

On the other hand, since the volatility of DMF is less than THF, the electrospun nanofiber by more DMF have a more time for connect to each other by residual solvent and this resulting to increasing strength.

It should be noted that increasing the DMF in THF/DMF content not only increased the web strength but also significantly increased the elongation of PU webs. Increasing in elongation is due to the more point bonded created by residual solvent as a result of less volatility of DMF. Then the sample with 50/50% THF/DMF solvent mixture can be considered as optimum condition having the best elongation and strength.

CONCLUSIONS

Because of the wide application of electrospun PU membrane, the stress strain behaviour as a key factor in macro mechanical properties of electrospun membrane is investigated with regards to some micro structures parameters like nanofiber diameter, web thickness and fibre orientation.

In the present work, ultrafine elastic fibers with submicron diameters have been successfully produced through electrospinnig the polyurethane solutions. This research investigated some important production parameters (electrospinning duration, polymer concentration and solvent mixture) on stress-strain behaviour of poly urethane nanofiber. It has shown that nonlinear elastic and stress softening in electrospun PU nanofibrous mat is arised of two source; PU molecular chain and network microstructures. Fibre diameters increase with increasing electrospinnig duration, polymer content and DMF content in THF/DMF mixture. The results of this study show that some mechanical properties of PU mat such as breaking load increase linearly with increasing electrospinning duration. These results also show that with increasing THF content tenacity and elongation of layers decrease.

This research showed that mechanical properties of PU membrane is mainly effected by morfological properties of mat that changed with changing production parameters and structures.

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