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ELECTROSPINNING OF POLYURETHANE NONWOVEN FIBROUS MATS

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Abstract: Electrospinning is a very simple and versitile nanofibrous production technique, very much utilized in the past decades. The current study concerns this process by presenting the production of polyurethane nonwoven fibrous mats. Three types of polyurethane samples were electrospun by setting up the primary technical parameters on the basis of polymer solution jet stability vizual detection. The electrospun fibers diameter, being the key factor that determines the functional characteristics of an electrospun end product, was evaluated for the polyurethane nonwoven fibrous mats. It was noted that the diameter range dstribution was narrower and fibers deformations disappeared as the applied voltage was increasing and the nozzle tip to collector distance was decreasing, but the lowest value of the measured fiber diameter was in the sample with the opposite operating technical parameters. The lower volume flow rate gave more uniform structure with no bead formations.

1. INTRODUCTION

1.1. The process of electrospinning

The fast spreading of the research in the field of nanotechnology in the past decades has conducted the need of an old fiber spinning technique, the electrospinning. Electrospinning is the process of uniaxial stretching of a viscoelastic solution under electrostatic forces for the purpose of nanoscale (diameter) fiber formation *(Teo et al., 2006.)*. Under the electric field the fluid elongates from a nozzle tip and its beeing ejected by increasing the field intensity *(Huang Z. M. et al. 2003.)*.

The process was first observed by Rayleigh in 1897. The basis were laid by Taylor in 1969., and various models of the set up were patented by Formahls 1934-1944. *(Bhardwaj et al. 2010.)* In the past years the investigation of nanoscaled materials has intensified the interest in this very simple and versatile process, but yet very complex in its pre-process and after analysis. What makes the electrospun fibers great candidates for the vast amount of applications is their high specific surface area and small pore sizes *(Frenot et al., 2003.)*. Today a wide range of polymers are electrospun for the purpose of different end applications, e.g. in the field of filter production, catalysis, protective textiles, nanocomposite materials, nanofibrous structures, storage cells for hydrogen fuel cells, cosmetics, tissue engineering, drug delivery systems etc. *(Subbiah T. et al. (2005.)*.

1.2. Processing parameters

Studies have reported on the significance of two groups of parameters that govern the final electrospun structure characteristics. The first group is related to the technical process parameters: the applied voltage, the nozzle tip to collector distance, needle size and the volume flow rate, and the second group is related to the polymer solution characteristics: the viscosity, molecular weight, concentration, conductivity and surface tension. Additionally the temperature, relative humidity and time dependence are also not to be neglected.

(Tan S. H. et al., 2005.) observed the processing parameters as the one that affect the mass of the polymer that is fed out from the nozzle, these were considered to be the volume flow rate, polymer concentration and applied voltage, and the other are those that affect the electrical force during electrospinning. If all: volume flow rate, polymer concentration and applied voltage are lower, will result in smaller diameter fibers when the effects of the mass polymer are dominant to determine the final fiber diameter or when all being higher if the effect of the jet elongation is the one that is dominant.

A study on the morphology of polyamide 6 electropsun fibers reported that the increasing viscosity and conductivity (salt content) increased the fibers diameter, and the smallest fibers were observed in the middle range of the applied voltage *(Heikkila P. et al., 2008.)*.

The fiber diameter decreased with the amount of NaCl content as investigated by *(Zhang C. et al. 2005.)*, in a study of the morphology of poly(vinyl alcohol). They also reported that the higher concentration of the polymer solution will result in fibers with no beads (deformations) and the nozzle tip to collector distance has no significant effect on the geometry of the fiber.

A model by *(Fridrikh S. V. et al., 2003.)* suggested on a certain limit of minimum fiber diameter formation resulting from the balance between surface tension and surface charge repulsion forces that are determined by the flow rate, electric current and the fluid surface tension. In this way the electrospun diameter can be controlled which is limited through the polymer concentration, due to the narrow window of spinnable solution concentrations.

1.3. Polyurethane electrospinning

Polyurethanes are synthetic polymers made by a step-growth polymerization of isocyanates and an alcohol both with at least two functional groups *(Soljacic I. 1993)*. Polyurethanes have a vast range of applications in different industry fields, e.g. automotive, construction, furniture, footwear etc (*Introduction to polyurethanes*). Nowadays there are number of studies that reported on the successful electrospinning of polyurethane solutions, especially for the purpose of protective textiles and tissue engineering applications.

Study reported on polyurethaneurea solution electrospun into fibers with diameters in the range of 7 nm to 1.5 μm. Fibers spun at lower solution concentration were noted to have beads and at high concentrations resulted in curlyness. Hihger than room temperatures conditions improved the fibers imperfections *(Demir M. M. et al. 2002.)*.

Another study reported on polyurethane/collagen electrospun fibers through coaxial spinneret as well as both pure polymers separately *(Chen R. et al. 2010.)*. It was observed that a range of solution concentration between 3-6 wt% of the core PU structure provided smooth fibers, higher concentration increased the fibers diameters. Improving solution conductivity obtained smaller diameters.

2. PROCEDURE

2.1. Electrospinning apparatus

The electrospinning apparatus implemented in this study is part of the advanced technological devices at the Faculty of Textile Technology of Zagreb**,** Department of Fundamental Natural and Engineering Sciences. High voltage electrospinning system NT-ESS-300 consists of: high voltage power supply, web winding system, electrospinning nozzle, syringe pump and a control unit.

Figure 1 presents the electrospinning set-up scheme. The high voltage power supply unit operates normally with an electric voltage of 5 to 25 kV (max 60 kV). The web winding system is a metal cylinder covered with an aluminium foil that performs both rotation and horizontal migration, governed by the control unit. The syringe pump, model KDS 100 series, operates with a volume flow rate of 0.1 to 120 cm^3 / h. Crocodile electrode is attached to the tip of the syringe nozzle in order to establish the electric field between the nozzle and the collector. Prepared polymer solution comprised in a plastic syringe is injected from the tip of the nozzle under the electrostatic force that ovecomes the fluid surface tension forces.

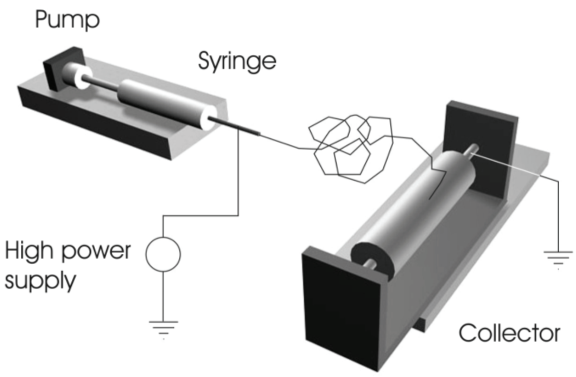


Fig. 1. Electrospinning apparatus

2.2. Materials and process parameters

The polymer material used in this study was polyurethane (PU), dissolved in a mixture of two solvents: N,N-dimethylformamide (DMF) and tetrahydrofuran (THF) by weight ratios of 2:3 respectively. The polymer solution was made at room temperature and stirred over night to obtain a homogenious solution. Prepared solution was electrospun into polyurethane nanofibers nonwoven mats by the varriation of the initial technical parameters of the electrospinning process at room temperature of 20°C and a relative humidity of 40%.

The electrsopsun fibrous mats processing conditions are given in Table 1. All the samples were electrospun with only horizontal winding system migration (31 moves / min), to obtain random fiber collection with an uniform deposition over the surface. In order to make sure that the residual solvent is removed the samples were dried at room temperature for 24 h at least. The crucial factor that can affect the final quality of the electrospun material, as reported in literature, is actually the forth mentioned solvent evaporation.

Table 1. Process conditions of the PU electrospun samples

	Electrospun nanofibrous webs		
Conditions	PU-1	PU-2	PU-3
Polymer concentration	10 wt %	10 wt %	10 wt %
Volume flow rate	0.5 cm^3 / h 1 cm^3 / h	0.5 cm^3 / h 1cm^3 / h	0.5 cm^3 / h 1cm^3 / h
Tip to collector distance	18 cm	15 cm	12 cm
Electrical voltage	13 kV	16 kV	19 kV
Needle size	21 gauge	21 gauge	21 gauge

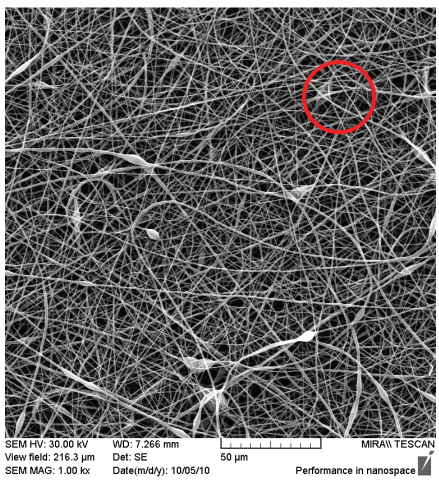
Some preliminary experiments were carried out regarding the solvent selection. At first polyurethane was dissolved in N,N-dimethylformamide (DMF) only, with different concentrations of 4, 6, 8 and 10 wt %. The elecetrospun fibrous webs resulted in a non uniform structure which was evident by the nonwoven breakage in the shape of small holes. The electrospun web surface nonuniformity was decreased as the polymer concentration was increasing (some improvments were observed on the samples made of PU with 10 wt%). The second solvent was chosen to be added in the solution in order to avoid the droplet formation during the electrospinning, which was noted visually. As later on discussed the electrospun structure deformation was removed by the solvents mixture and the selection of the highest polymer concentration.

3. RESULTS AND DISCUSSION

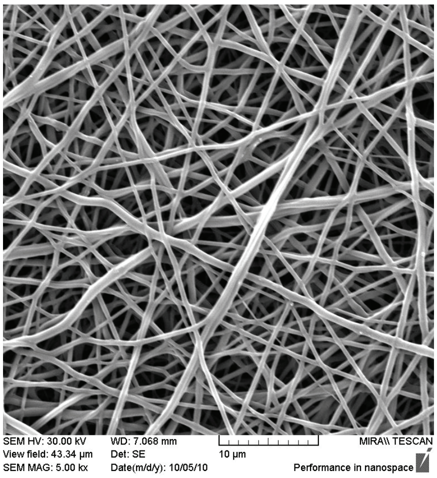
The electrospun polyurethane fibrous mats were studied with scanning electron micoscope type: SEM-FE MIRA II LMU. The samples were Pt / Au coated, with 4 series / 180 seconds. The study was focused on the electrospun surface uniformity, fibres morphology, with the accent on the fibres diameter and fibers deformations. As already well known the electrospun fibers diameter is the main parameter observed when studies of these type are carried. That is why the same is of paramount importance for the end product characteristics, whether it is a filtration membrane, permeable textile, scaffold for biological engineering etc. From this point of view the control over the fiber diameter is still a technological bottleneck.

Within this study three types of polyurethane fibrous webs were electrospun, variating two technical parameters, the applied voltage and the tip to collector distance. Three different values of the two parameters were chosen on behalf of visual identification of: jet stability, no droplet formation and no mats surface breakage. The highest jet instability was observed when the tip to collector distance was chosen to be over 18 cm, as was evident from the splashing polymer solution all over the winding system surface. The minimun instability was detected when the chosen tip to collector distance was 12 cm with the highest applied voltage of 19 kV. The jet instability was observed to be time dependent as well. This was evident after 5 h of electrospinning, when the stretched polymer solution in the shape of a filament fiber was heading towards peripheral surfaces and by the very slow web winding system movement (rotation). Such phenomena can be explained with the off rotation of the winding system, since the drum surface after a certain time is covered by the electrospun mat, which is non conductive, and the jet itself is attracted by the conductive aluminium foil on the opposite drum side, similarly *(De Vrieze S. et al., 2007.),* have reported that after some hours the jet of the polymer solution alignes towards the edges of the (flat) collector which is free of nanofibers.

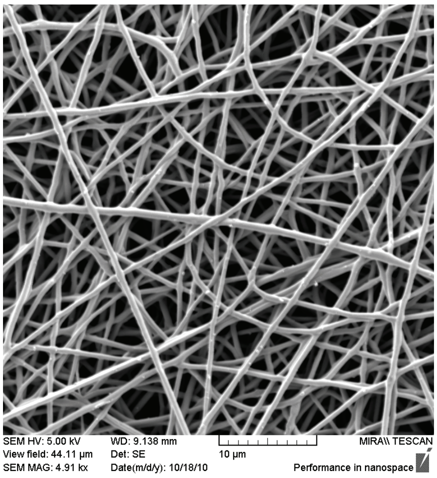
Figure 2 presents the SEM images of the three electrospun fibrous mats, PU type 1, PU type 2 and PU type 3 under a, b, and c respectively, spun with volume flow rate of 1 cm^3 / h. All the SEM images were taken after several hours of electrospinning, which explains the quite dense mats structure (at this point the end product purpose was not in the scope of this study). The first image under a). indicates the electrospun fibres deformations in the shape of beads on PU type 1 electrospun mats, which is noted to be decreased within the second type of PU, image under b). and was no present within sample PU type 3, visible on image under c).
The electrospun mats with the volume flow rate of 0.5 cm^3 / h did not showed fibrous structure deformations.



a).



b).



c).

Fig. 2. SEM images of the PU electrospun fibrous webs:

a). PU type 1; b). PU type 2 and c). PU type 3.

In the following figures 3-8 the fiber diameter distribution in each of the electrospun samples is given. The diameters were measured from SEM images of 5.0 Kx magnifications and the statistical analysis were made from over 300 measurements obtained for each of the three types of electrospun samples. In figure 3 and 4 the diameter fiber distribution is given for the samples made with two different

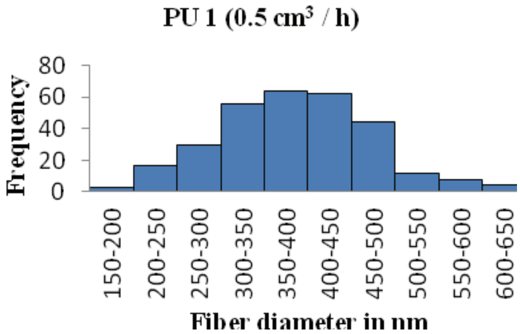


Fig. 3. Fiber diameter distribution of electrospun polyurethane, type 1

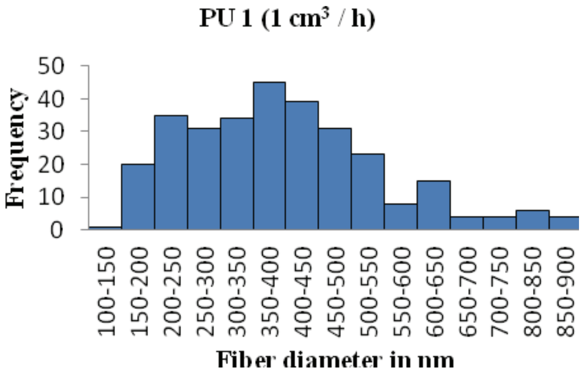


Fig. 4. Fiber diameter distribution of electrospun polyurethane, type 1

flow rates, 0.5 cm^3 / h and 1 cm^3 / h respectively, for polyurethane type 1, showing that the lower volume flow rate gave smaller varriations in the diameters values, the most frequent diameter for both was at 350-400 nm, but the smaller fibers diameters were at the sample spun with volume flow rate of 1 cm^3 / h. In the case of samples PU type 2 and 3 (figures 5 and 6, and figures 7 and 8) higher variations of the diameters were as well at volume flow rate of 1 cm^3 / h, but smaller diameters ranging from 150-200nm and 100-150nm were at 0.5 cm^3 / h.

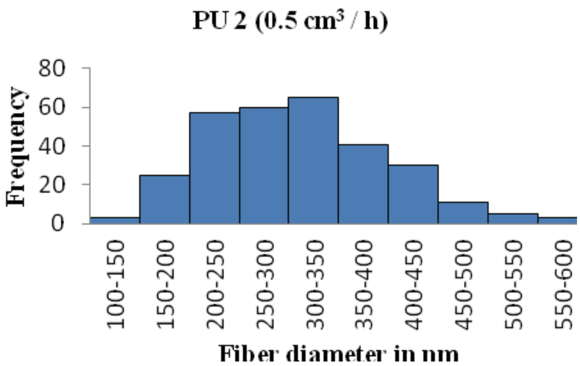


Fig. 5. Fiber diameter distrbution of electrospun polyurethane, type 2

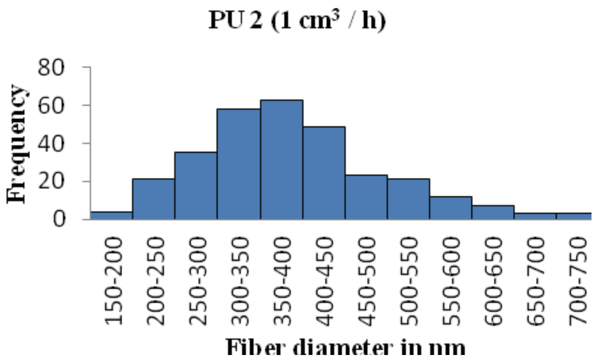


Fig. 6. Fiber diameter distribution of electrospun polyurethane, type 2

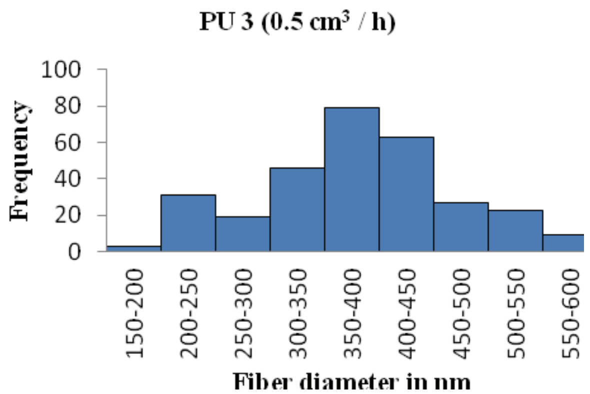
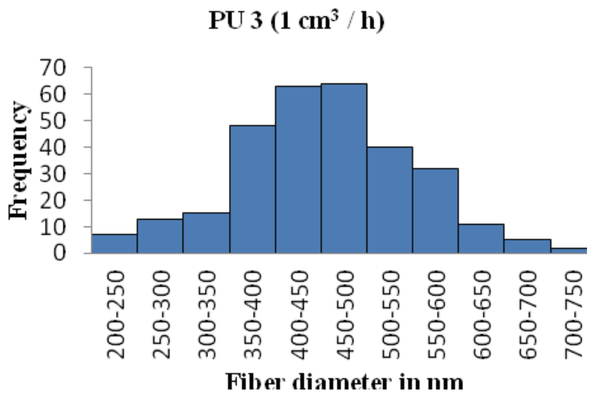


Fig. 7. Fiber diameter distribution of electrospun polyurethane, type 3

Fig. 8. Fiber diameter distribution of electrospun polyurethane, type 3



In overall the smallest fibers diameter are present in sample type 2 for both volume flow rates. It is to be noted that the diameter of the electrospun fibers is affected also by the coating Pt / Au layer, that was estimated to be arround 20 nm thickness. This could also be a disadvantage since the layer masks the „real“ fiber surface characteristics. As given in table 2, the most frequent electrospun fiber diameter would be in the range of 350 to 500 nm which is of submicron scale. The smallest fiber diameter (112 nm) was observed in sample type PU 1 with the flow rate of 1 cm^3 / h, but with the biggest diameter (900 nm) as well, due to the widest value ranges noticed. For the same flow rate as the applied voltage was increasing and the nozzle tip to collector distance was decreasing the smallest diameter was bigger (180.5 nm or

Table 2. Process parameter and electrospun fibrous mats characteristics dependance

	Samples					
Process parameters	**PU 1**		**PU 2**		**PU 3**	
Applied voltage, kV	13		16		19	
Distance, cm	18		15		12	
Flow rate cm^3 / h	0.5	1	0.5	1	0.5	1
Fibers diameter						
Highest frequensy at	400 nm (>60)	400 nm (<50)	350 nm (>60)	400 nm (>60)	400 nm (>80)	500 nm (>60)
Min diameter, nm	180.5	112	150	180.5	158	212
Max diameter, nm	610.5	900	600	743.5	590	732.5
Electrospun webs						
Structure uniformity	high	less	high	average	higher	higher
Bead formation	none	randomly present	none	less	none	none

The greater varriation of the fiber diameters in the case of the higher volume flow rate of 1 cm^3 / h is ranging from >200->750 or >250->750, figure 6 and 8 respectively. The most frequent fiber diameter is smaller (>350 nm or >400 nm) in the case of the lower volume flow rate, figures 5 and 7 respectively. From the view point of different sample comparison regarding different applied voltage and nozzle tip to collector distance in the case of the volume flow rate of 0.5 cm^3 / h (figures 3, 5 and 7), in between the three types of samples, the fibers diameter varriatios was the lowest within sample type 3., in the case of volume flow rate of 1 cm^3 / h (figures 4, 6 and 8) the fiber diameter value range is wider within sample PU type 1, and is decreasing as the tip to collector distance is smaller and applied voltage is higher, sample PU type 2. The wider the range of diameter values is, the more the electrospun fibrous mats structure uniformity is affected, but on the other hand it is an advantage as in sample PU type 1, fibres having their diameters arround 150 nm were formed and the frequency of the most present fiber diameter arround 400-500 nm is much lower, less than 50. Fibers with diameters slightly below 1 micrometer present in the electrospun samples, were observed directly on top of the strucutre surface, it was assumed to be formed by the end of the electrospinning process, when the electrical field is getting weaker.
212 nm), but at the same time the highest measured diameter was much less than 1 micrometer.

In the case of 0.5 cm^3 / h volume flow rate, the minimum fiber diameter value was noticed in sample PU type 2 (150 nm) with the middle range of applied voltage and nozzle tip to collector distance. Concerning the structure uniformity, positive result was observed within sample type PU 3, where no bead formation was noticed, for both volume flow rates. Smaller volume flow rate gave smaller fibers diameters and less diameters ranges varriations, in the combination with the higher applied voltage and smaller nozzle tip to collector distance.

4. CONCLUSION

In overall, regarding the correlation between the primary process parameters, and the electrospun fibrous mats (the fiber morphology), diameter range distribution was narrower and fibers deformations disappeared as the applied voltage was increasing and the nozzle tip to collector distance was decreasing, the lowest value of the measured fiber diameter was in the sample with the opposite operating technical parameters. Better structure characteristics and smaller fiber diameters are present with the lower volume flow rate.

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