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The Effect of Salt on the Roller Electrospinning of Polyurethane Nanofibers

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Abstract: In this study, we investigated the effect of tetraethylammoniumbromide (TEAB) salt on the spinnability of polyurethane nanofibers via roller electrospinning method. At first, solution properties, spinnability and fiber properties were determined and then all the results were analyzed. According to the results, TEAB salt concentration has an important effect on the conductivity, viscosity, spinning performance, fiber diameter and morphology. It was found that all these parameters increased with salt concentration. Also it was indicated that viscosity decreased with shear rate. Polyurethane including 1.82 wt % TEAB gives the best spinning performance although 0.87 wt % TEAB is the optimum value related to fiber properties such as diameter, uniformity and morphology given the ideal polyurethane nano web structure.

Keywords: Polyurethane, TEAB, Solution, Electrospinning, Nanofiber

Introduction

Inventions in fiber science during the last part of 20th century are inclined to polymer fiber development. Particularly nanofiber technology has become the latest trend leading to many discoveries in available application areas of textile. In literature generally nanofibers term is called that the fibers have the diameter under one micron. These special fibers in nanometer size diameter have specific improved properties (very large ratio of surface area to volume, small and controllable pore size, superior mechanical performance) due to their nano size. These remarkable properties make nanofibers indispensable for many application's raw material such as medical areas [1-3], protective clothing [4-6], filtration [7,8], nanocomposites [9,10], membranes [11,12] nanosensors [13], electrical and optical [14,15] use.

The most outstanding method is the electrospinning process with needle to produce nanofibers has been known until 1600' years. The investigation of physical phenomena connected with electrospinning starts with William Gilbert [16]. Much more serious work has been done by Rayleigh in 19th century, who described the critical charge values needed for the disintegration of charged liquid droplets [17]. After Rayleigh's studies, Zeleny, Wilson and Taylor, Nolan, and Macky investigated about interaction between the liquids and electrostatic field [18-21]. With respect to these kinds of scientific work, Taylor contributed a theoretical description of liquid surface equilibrium shapes under the action of external electrostatic fields. This shape is a cone with semivertical angle called now as the Taylor cone [22]. Since this method is basically the drawing of a polymer fluids, there are many different types of polymers such as natural (collagen, DNA, silk), synthetic (acrylic, polyurethane, polyamid etc.), biodegradable polymers (poly(caprolactone), chitosan etc.) and polymer mixture have been used to obtain nanofibers [23-33].

Electrospinning process was patented first by Formhals in 1934 [34]. After Formhal's patent, various new methods have been developed to provide mass production of nanofibers [35-41]. Among these methods, Nanospider is the unique method which has been used in industry to produce nanofibers continuously. This method was invented by Jirsak in Technical University of Liberec (Czech Republic), 2003. Also this method is the first for all over the world, which was commercialized under the name of Nanospider from Elmarco Company in Liberec. In this work, we used Nanospider method to obtain polyurethane nanofibers [42].

Polyurethanes are one of the most widely used polymers in biomedical, filtration, protective clothes, composites, sensor, actuator and wound healing applications [1,5,6,10, 11,43,44]. Therefore it is very important to investigate the spinnability and properties of polyurethane nanofibers. There are several studies about polyurethane nanofiber production with needle electrospinning while there is very few work with roller electrospinning. Vlad and Oprea investigated the rheological behaviour of thermoplastic polyurethane solutions. They found that viscosity of polyurethane decreases with the increasing shear rate [45]. Demir *et al*. studied about the electrospinning of polyurethane fibers and determined viscosity, concentration and temperature are the dominant factors on the fiber morphology [27]. Khil *et al*. claimed that nanofibrous polyurethane membrane was prepared by electrospinning promoted fluid drainage for the healing of wound [1]. Lee *et al*. investigated the mechanical behaviour of electrospun fiber mats of poly(vinyl chloride)/polyurethane polyblends. They determined that point-bonded structures in the fiber web rose with polyurethane composition and also mechanical properties of the web was effected by these point-bonded structures [46]. Pedicini and Farris were also determined the

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mechanical behaviour of electrospun polyurethane. They compared the stres-strain behaviour of electrospun polyurethane and bulk material and found that molecular orientation of electrospun fibers leads to reduction in elongation to failure of electrospun mat [47]. Adomaviciüte *et al*. determined that the time of sulfonation improves the uniformity of the polyurethane nano webs for the sulfonated polymers [48]. Hong *et al*. observed that electrospun polyurethane nano web has improved the young modulus and tensile strength of composites [10]. Xu *et al*. studied the dielectric strength of thermal interface material produced with electrospun nanofiber. They found the adequate dielectric strength value (5.82 kV/mm) for microelectronics applications [49]. And recently, Lee and Obendarf developed a protective textile material with polyurethane for agricultural workers. They improved the barrier performance of the material with electrospun polyurethane nanofibers [6].

There has been very few work in the literature about the spinnability of polyurethane nanofibers with roller electrospinning in industrial scale that's why we focused on this subject.

Experimental

Materials

In this study, polyurethane (PUR, Larithane LS 1086, aliphatic elastomer based on 2000 g/mol, linear polycarbonated diol, isophorone diisocyanate and extended isophorone diamine), was used as a polymer and tetraethylammonium-bromide (TEAB) was used as a salt.

All the solutions were prepared at 15 wt % concentration with dimethylformamide (DMF) solvent. The value of 15 wt % polyurethane concentration was preferred to consider of the previous roller electrospinning experiments. It was prepared five different polyurethane solutions include different percent of TEAB salt such as, 0-0.1-0.3-0.87 and 1.82 wt % respectively. The concentration of the salt was performed electrospinning up to 1.82 wt %, because of the saturated value in dimethylformamide solvent. Polyurethane was obtained from Larithane Company, dimethylformamide and tetraethylamoniumbromide were purchased from Fluka and Sigma Aldrich Company.

Methods

A series of solutions was prepared containing;
15 wt % polyurethane
x wt % TEAB (x = 0, 0.1, 0.3, 0.87, and 1.82)
(100 – 15 – x) wt % DMF

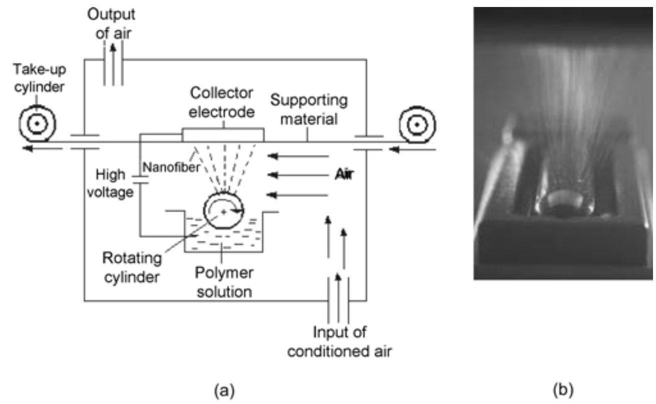


Figure 1. (a) Schematic diagram of nanospider method and (b) the rotating cylinder [50].

Solution properties such as conductivity, surface tension and viscosity were determined, then solutions were electrospun into nanofibers and fiber properties were analyzed. Conductivity and surface tension properties were determined by a conductivity meter (Radelkis, OK-102/1) and Du Nouy Ring method (Krüss) using a platinium ring and a highly precise electronic balance respectively. Rheological properties of polyurethane solutions were measured using Rheometer HAAKE Roto Visco 1 at 25 ^{o}C.

Roller electrospinning method (Nanospider) with high voltage power supply was used to spin nanofibers (Figure 1). Nanospider consists of rotating cylinder to spin fibers directly from the polymer solution [42]. The polyurethane polymer solution was filled into a polypropylene dish and the bottom of aluminium rotating cylinder body is partially immersed into the polymer solution. High voltage is connected to the rotating roller. The collector electrode is usually grounded to create potential difference (Figure 1(a)). Many Taylor cones [22] are created as the cylinder rotates along the top part of the cylinder (Figure 1(b)). As the solvent evaporates, the jets of polymer solutions are transformed and the solid nanofibers are obtained before reaching to the collector electrode.

In this work, optimum process parameters of the roller electrospinning which were determined previous experimental works were applied during the spinning experiments (Table 1).

From the preliminary experiments, optimum values of relative humidity and temperature are 27 % and 23 ^{o}C respectively, inside the chamber to spin polyurethane nanofibers via roller electrospinning. The nanofibers were collected on the polypropylene (PP) spunbond nonwoven antistatic material.

The fiber morphology and diameter of the polyurethane nanofibers were determined using a scanning electron

Table 1. Process parameters of the roller electrospinning

Roller length (cm)	Roller diameter (cm)	Roller speed (rpm)	Take-up cylinder speed (m/min)	Distance between the electrodes (cm)	Voltage (kV)
14	2	3.2	0.12	11	81.2

microscopy (SEM). TESCAN Digital Microscopy Imaging SEM using an accelerating voltage of 30 kV was employed to take the SEM photographs. Then, the average fiber diameter was calculated from the SEM photos with the aid of Lucia 32G computer soft ware.

And recently, fiber uniformity was determined using the number and weight average calculations. Number average has been known as an arithmetic mean in mathematics science. And the method which was used to calculate uniformity coefficient has the same principle with molar mass distribution in chemistry science. We calculated both of these values using the formulas 1 and 2 were given below.

$$A_n = \frac{\sum n_i d_i}{\sum n_i} \text{ (number average)} \quad (1)$$

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

d_i: fiber diameter
n_i: fiber number

The fiber uniformity coefficient was determined by ratio A_n/A_w and optimum value should be very close to 1 for uniform fibers.

Results and Discussion

Determination of Polymer Solution Properties

In this study, at first we determined the changing of conductivity and surface tension values with various TEAB salt concentration (Table 2). As it is seen from Table 2, solution conductivity increases with TEAB salt concentration. On the other hand there is not any noticable change in surface tension values with TEAB salt concentration. As it has been known from the literature, it is important to understand the role of surface tension in a fluid [51].

Time-dependence of viscosity at 10 1/s shear rate was shown in Figure 2. During viscosity experiments we used low shear rate because of less noticeable time-dependence of the solution at high shear rate [52]. It can be explained that polymer chains are oriented immediately at high shear rates.

The viscosity has been measured for 10 minutes and each curve consists of 600 different values. It can be seen from Figure 2, viscosity values of polyurethane increase with TEAB salt while the time does not effect the viscosity noticably. It can be explained that salt seems to increase the solubility of polyurethane in DMF. This leads to more entanglements in the polymer network and makes the network stronger.

Table 2. The changing of conductivity and surface tension values with TEAB salt concentration

Solution properties	TEAB wt % concentration				
	0	0.1	0.3	0.87	1.82
Conductivity (mS/cm)	0.0915	0.46	1.145	2.97	5.3
Surface tension (mN/m)	37.04	36.89	36.92	37.16	37.54

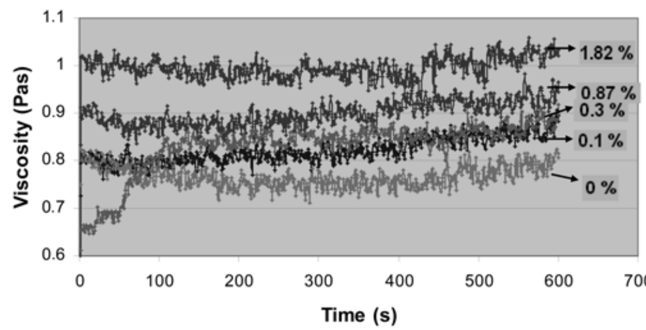


Figure 2. The variation of viscosity with time for polyurethane at 25 °C, shear rate=10 1/s.

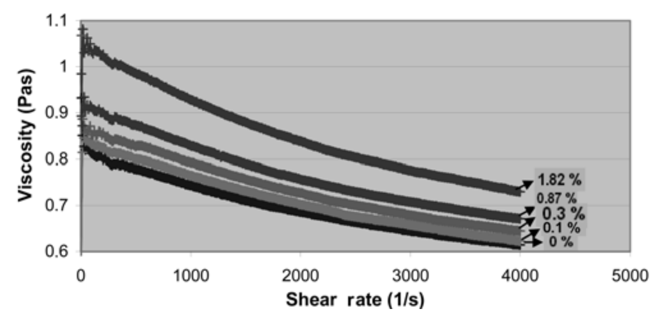


Figure 3. The variation of viscosity with shear rate for polyurethane at 25 °C.

There is a variation of viscosity with shear rate in Figure 3. This experiment was achieved for 5 minutes and 300 different values were measured for each sample. It is very clear to see that viscosity decreases with increasing shear rate for all samples of polyurethane. Similar results were reported in previous works [41].

Spinning and Analysis of Fiber Properties

After measurements of solution properties, the solutions were electrospun and the spinning performance (throughput) was determined.

As it can be seen from Figure 4, it was not possible to spin any nanofibers with the solutions containing 0 and 0.1 wt % TEAB salt. The solution of polyurethane having 1.82 wt % TEAB gives the highest spinning performance approximately 1.6 gram nano web per minute per one meter roller length (g/min/m). It is very clear to see that spinning performance increases with TEAB salt for polyurethane solution.

Average fiber diameter was calculated with Lucia 32G computer soft ware and 200 different diameter values were used for each sample. Then we determined the effect of TEAB salt on the fiber diameter of polyurethane (Figure 5). It can be seen that fiber diameter increases with TEAB salt and also it was observed high linear regression between the

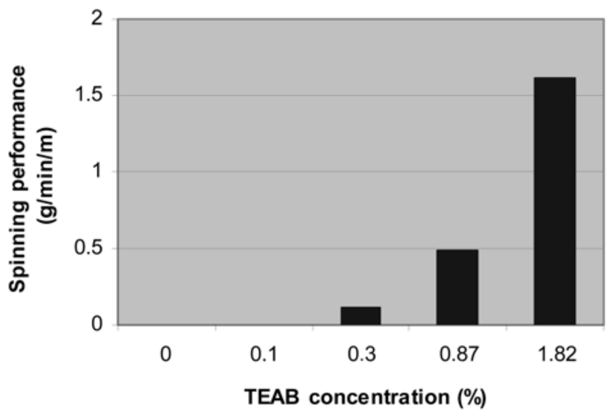


Figure 4. The effect of TEAB salt on the spinning performance of polyurethane.

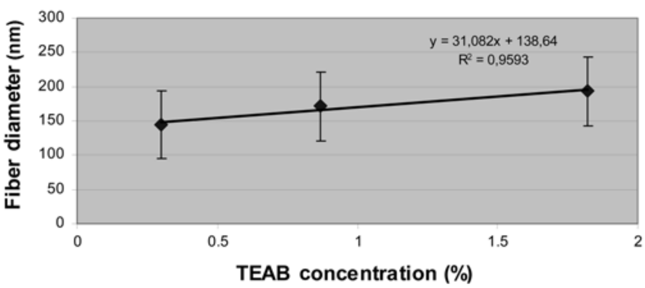


Figure 5. The effect of TEAB salt on the diameter of polyurethane nanofiber.

fiber diameter and TEAB salt concentration.

In Figure 6, there are SEM images of various polyurethane nanofibers having 0.3, 0.87 and 1.82 wt % TEAB, respectively. From these images, it can be seen that fiber diameter increases with TEAB salt concentration.

Also we analyzed fiber diameter histograms as it is shown in Figure 7, 8, and 9.

We found that the finest fibers with average diameter 144 nm were obtained by using polyurethane solution of concentration of 0.3 wt % TEAB salt while from polyurethane solution of

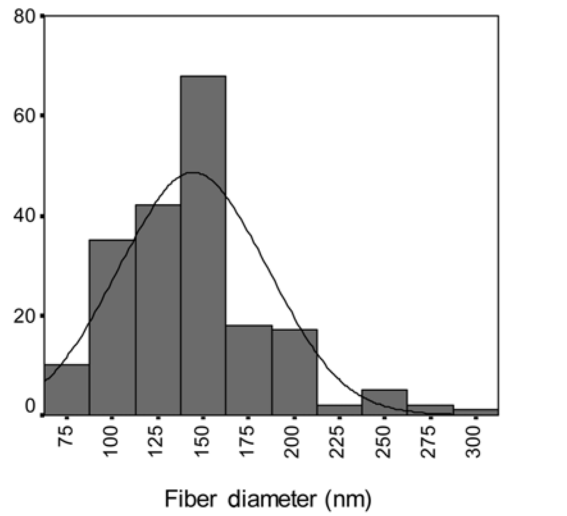


Figure 7. The fiber diameter distribution of polyurethane (0.3 % TEAB).

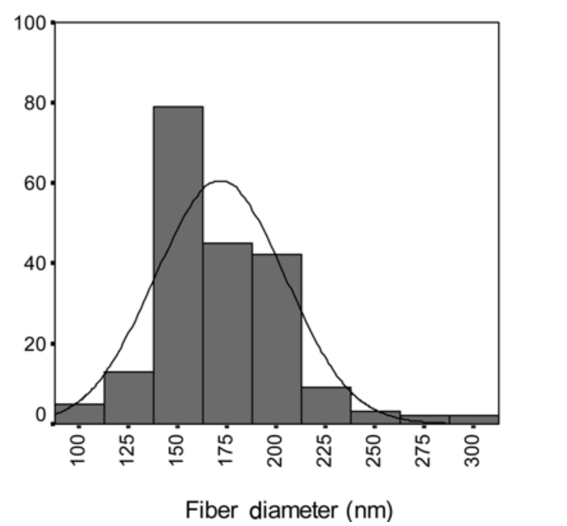


Figure 8. The fiber diameter distribution of polyurethane (0.87 % TEAB).

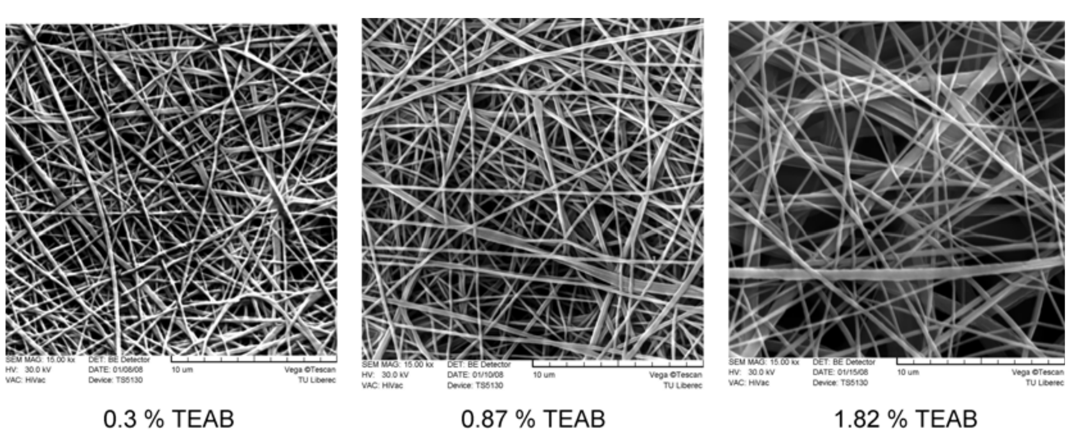


Figure 6. SEM images of nanofiber samples of polyurethane includes various percent of TEAB salt, 27 % RH (15.000×).

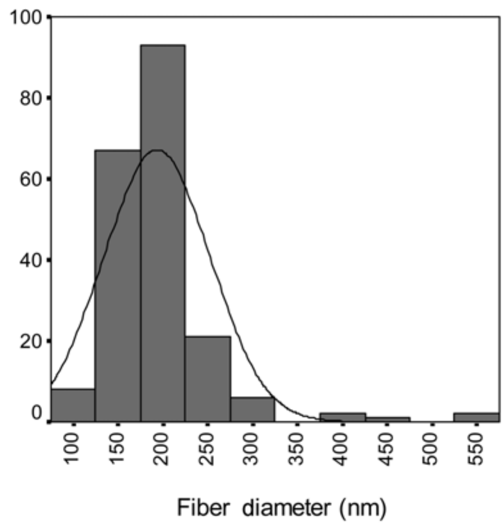


Figure 9. The fiber diameter distribution of polyurethane (1.82 % TEAB).

concentration 1.82 wt % of TEAB were generated nanofibers with average diameter 193 nm.

Then fiber uniformity was determined using the number and weight average calculations. According to the results, number average and weight average of fiber diameter increase with TEAB salt. When we analyzed standard deviation and uniformity coefficient of polyurethane nanofibers, the value of 0.87 wt % TEAB is the best. It was also determined about there has been a significant difference between the uniformity coefficient results statistically.

Table 3. The results of parameters about polyurethane nanofiber uniformity

PU solutions	Fiber uniformity properties			
	Number average (A_1) (nm)	Standard deviation	Weight average (A_2) (nm)	Fiber uniformity coefficient (A_2/A_1)
0.3 % TEAB	144	40.95	156	1.08
0.87 % TEAB	171	32.87	177.6	1.04
1.82 % TEAB	193	59.25	211.2	1.09

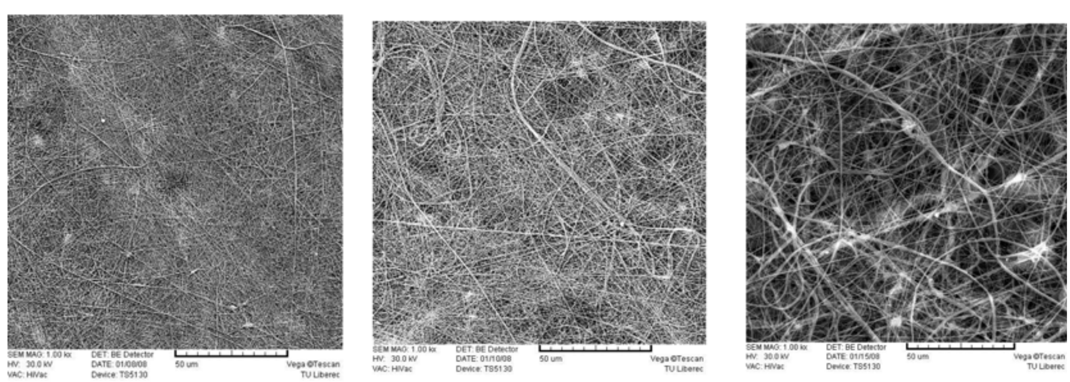
According to the all results, we obtained very fine and uniform polyurethane nanofibers (Table 3).

There have been SEM images of nanofibers with 1.000× magnification from various polyurethane solutions having 0.3, 0.87 and 1.82 wt % TEAB respectively in Figure 10.

Fiber morphology is getting worse with the TEAB salt concentration increases (Figure 10). As the TEAB salt concentration increases, more non-fibrous bodies appear in the nanofiber layer.

All of the results about solution, fiber and nano structure properties obtained from our study were given in Table 4 below.

The TEAB does not influence surface tension of



0.3 % TEAB 0.87 % TEAB 1.82 % TEAB

Figure 10. SEM images of nanofiber samples of polyurethane includes various percent of TEAB salt, 27 % RH (1.000×).

Table 4. All the results of solution and fiber properties of polyurethane samples

PU solutions	Properties						
	Conductivity (mS/cm)	Surface tension (mN/m)	Viscosity (Pas)	Spinning performance (g/min/m)	Fiber diameter (nm)	Fiber diameter uniformity coefficient	Fiber morphology
0 % TEAB	0.09	37.04	0.76	0	No fiber	No fiber	No fiber
0.1 % TEAB	0.46	36.89	0.82	0	No fiber	No fiber	No fiber
0.3 % TEAB	1.14	36.92	0.83	0.11	144	1.08	Smoothest
0.87 % TEAB	2.97	37.16	0.89	0.49	171	1.04	Smooth
1.82 % TEAB	5.3	37.54	0.99	1.61	193	1.09	With beads

polyurethane solutions considerably. On the other hand, it brings increase in electric conductivity, changes rheologic behaviour and considerably influences spinnability.

The question arises whether electric conductivity or rheologic behaviour are primary variables influencing spinnability. Shenoy *et al*. found that increasing solution conductivity can significantly aid fiber formation. The authors see the reason in stabilizing effect of increased electrical energy [53]. In another work there are several examples showing that increased solution conductivity by the addition of a salt leads to smaller fiber diameters [54]. Chaoi *et al*. and You *et al*. also determined the addition of salt caused a significant increase in conductivity and decrease in fiber diameter [55, 56]. Hovever, the result of addition salt leads to smaller fiber diameter was not supported in our experiments. Zong *et al*. found salt addition have larger effects on the fiber diameter than the other parameters [57]. According to the another work's results; it is possible to determine productivity and morphological properties can be predicted without a knowledge of viscosity, surface tension and conductivity [58]. On the other hand, number of polymer solutions showing low values of conductivity were successfully electrospun.

Certain value of electric conductivity of polymer solution is needed so that the surface is supplied with sufficient amount of charge. The charge is transported from surface towards the collector electrode in two ways: together with transported polymer and through ionized air. The measurement has shown that electric current corresponding to one jet is around 1 microAmpere [54]. Current moving through air can reach values even hundred times greater (per area corresponding to one Taylor cone).

Let us consider a 2 mm thick layer of polymer solution on the surface of a metal roller which is linked with the source of high voltage 20 kV. One Taylor cone may typically occupy the area of 0.2 cm^2. It is easy to calculate from these data that minimum required electric conductivity of polymer solution allowing electrospinning is approximately 10^{-8} Siemens $\cdot$ cm^{-1}. All the used solution in this work showed considerably greater values of electric conductivity. Therefore, the conductivity itself cannot be considered as ruling value in electrospinning provided it exceeds the above value. Many polymer solutions have been electrospun in previous experiments and electric conductivity was usually measured in the experiments. Significant influence of conductivity on electrospinning was never observed. Usually, the conductivity as well as surface tension are the secondary effect of additives but do not effect the process in particular.

According to the rheometric data shows, TEAB increases viscosity of polyurethane solutions. This can be caused by better solubility of polyurethane in the presence of TEAB which leads to more extensive entanglement of macromolecules. Polymer network is then more solid.

To explain strong dependence of polymer throughput on the concentration of salt, it is necessary to consider roller (surface) electrospinning mechanism.

There is a significant difference between the needle and roller (surface) electrospinning process. In the hollow needle, the polymer solution is moved ahead by mechanical forces. When leaving the needle, the solution is formed by electric field into the droplets or fibers, depending on polymer solution properties. In the roller electrospinning, Taylor cones are created on the surface of polymer solution as described by Lukas *et al*. [59]. If the Taylor cone is stable, it moves together with the surface of rotating roller and produces a jet.

Generally, there are two conditions for maintaining a stable Taylor cone. First, the jet must be strong enough to stabilize Taylor cone by mechanical forces as it is pulled towards the collector electrode. The life of Taylor cones is influenced by the stability of jets. As soon as the jet breaks, Taylor cone disappears. A droplet or non-fibrous particle may be created in this moment. Nevertheless, the spinning process does not continue. Thus, non-stable formation of solution which is typical for low molecular weight polymers and for electrospraying in the needle process does not start any process on the roller.

The second condition for a stable Taylor cone is the ability of the solution to feed it with fresh material from surroundings. This requires limited solution viscosity and suitable rheological behaviour. A stable Taylor cone is able to yield a jet during several seconds to tens of seconds. The number of Taylor cones per area of spinning roller is increase with concentration on the surface of the roller and throughput of the process.

Taylor cones appear by the mechanism described by Lukas *et al*. [59]. Their life time is very short unless they are stabilized by the polymer jet. Polymer jet is pulled towards collector electrode in the electric field. If the jet breaks or if it is easily deformable, the lifetime of Taylor cone is short. Salt makes the jet stronger.

Conclusion

This study was carried out to investigate the effect of TEAB salt on the spinnability of polyurethane nanofibers with roller electrospinning. At first solution properties and then spinnability, fiber and nano web structure properties were determined. According to the results, TEAB salt concentration has an important effect on the conductivity, viscosity, spinning performance, fiber diameter and fiber morphology. We found that polyurethane having 1.82 wt % TEAB gives the best result about spinning performance. However when we considered the other fiber properties such as diameter, uniformity and morphology, the optimum value is the 0.87 wt % TEAB to obtain ideal polyurethane nano structure. We also investigated the effect of shear rate on the viscosity and found viscosity decreases with shear rate.

Consequently, TEAB salt has an important role on the spinnability of polyurethane nanofibers with roller electrospinning. It was not fully cleared up in this work whether the salt influences electrospinning through increased electric conductivity or entanglement. Nevertheless, the authors prefer the latter explanation.

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