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Electrospinning of polyurethane fibers

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Abstract

A segmented polyurethaneurea based on poly(tetramethylene oxide)glycol, a cycloaliphatic diisocyanate and an unsymmetrical diamine were prepared. Urea content of the copolymer was 35 wt%. Electrospinning behavior of this elastomeric polyurethaneurea copolymer in solution was studied. The effects of electrical field, temperature, conductivity and viscosity of the solution on the electrospinning process and morphology and property of the fibers obtained were investigated. Results of observations made by optical microscope, atomic force microscope and scanning electron microscope were interpreted and compared with literature data available on the electrospinning behavior of other polymeric systems. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Electrospinning; Nanofibers; Polyurethanes

1. Introduction

Electrospinning is a fiber spinning technique that produces polymer fibers of nanometer to micrometer size in diameters. Typically, a polymer solution or melt is placed into a container that has a millimeter size nozzle and is subjected to electric fields of several kilovolts, up to 40 kV. Under the applied electrostatic force, the polymer is ejected from the nozzle whose diameter is reduced significantly as it is transported to and deposited on a template, which also serves as the ground for the electrical charges. Such thin fibers provide unexpected high surface area to volume ratios and are of interest for many applications ranging from textile to composite reinforcement, sensors, biomaterials and membrane technology. In recent years, more than 20 different types of polymer fibers have been generated by elecrospinning. Their possible uses in different technologies, their history, patents received and the mechanisms of formation are discussed in detail by Reneker et al. [1].

The mechanism of jet formation in electrospinning is based on observations at a time resolution of approximately 0.0125 ms [1]. According to these observations, under Coulomb forces, a cone, called the Taylor cone, is formed at the nozzle, which then results in a straight fiber or jet. In a few centimeters after exiting the tip of the Taylor cone, the jet undergoes a bending instability, alternatively referred to as whipping instability [2] during which the jet rotates in a conical region, whose vertex is the end of the straight jet. The other end of the jet, which is highly stretched, and reduced in diameter, is deposited on the collector as a result of the fast whipping motions. Previous observations at coarser time resolution led to the mechanism where, instead of a single whipping fiber, a large number of smaller diameter fibers are formed at the end of the initial straight jet under the action of charges present, and are deposited independently on the collector [3,4].

An advantage of electrospinning is that it can be performed on polymers both in solution and in the melt. In earlier work [5], fibers from acrylic resins dissolved in dimethyl formamide were obtained. Bulk polyethylene and polyethylene dissolved in paraffin were electrospun by Larrondo and Manley [6]. In addition, Kim and Lee carried out the electrospinning of poly(ethylene terephthalate), poly(ethylene naphthalate) and their blends [7] in the molten state. Zacharides and Porter [8] obtained high modulus fibers from Kevlar and poly(*p*-phenylene terephthalamide). Polybenzimidazole [9], calf thymus Na-DNA [10], styrene–butadiene–styrene triblock copolymer [11] and carbon nanofibers [12] were electrospun by Reneker and co-workers. Poly(ethylene oxide), which is known as an easily soluble and crystallisable polymer in aqueous solution, has been used for setting the optimum conditions and characterization of fibers [3,4,13–15]. Conductive

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nanofibers were obtained from electrospinning of polyaniline/poly(ethylene oxide) blends [16]. Nylon [17], poly(vinyl alcohol) and cellulose acetate [4] fibers were electrospun in solution. A biocompatible protein thin film, a silk-like polymer, was processed using electrospinning by Buckho [18]. Bognitzki and co-workers have obtained nanofibers from poly-L-lactide, polycarbonate, polyvinylcarbazole [19], and polyvinylpyrolidone [20].

In the present work, we study the electrospinning properties of segmented polyurethaneurea copolymers in solution. We present the effects of instrument variables such as electrical field and solution variables such as temperature, conductivity and viscosity of the solution on the fiber forming process by electrospinning. We interpret results of observations made by optical and atomic force microscope (AFM) and scanning electron microscope (SEM), and compare with previous literature results on the electrospinning of other polymer solvent systems.

2. Experimental

2.1. Materials

Cycloaliphatic diisocyanate, bis(4-isocyanatocyclohexyl)methane (PICM) was obtained from Bayer AG, Leverkusen, Germany and had a purity better than 99.5% as determined by the back titration of isocyanate end-groups [21]. Poly(tetramethylene oxide) glycol (PTMO) with a number average molecular weight of 2000 g mol^{-1} was received from Du Pont, USA. Reagent grade 2-methyl-1,5-diaminopentane (DAP), dibutylamine (DBA), dimethylformamide (DMF) and isopropanol (IPA) were obtained from Aldrich. Dibutyltindilaurate (DBTDL) catalyst and polydimethylsiloxane fluid (Witco l-7602) were obtained from Witco. Water contents of PTMO and DMF were determined by Karl Fisher titration and were found to be less than 300 ppm. All chemicals and solvents were used as received.

2.2. Synthesis of polyurethaneurea copolymer

A two-step procedure was followed during the preparation of segmented polyurethaneurea (PUU) copolymers. First step was the formation of isocyanate terminated prepolymer, followed by the addition of DBA to control the molecular weight (aimed at 25 000 Da). The second step was the chain extension with DAP to form high molecular weight copolymers. Typical procedure for the preparation of PUU was as follows. A four-neck, flat bottomed 1000 ml pyrex reaction kettle fitted with an overhead stirrer, addition funnel, thermometer and dry nitrogen inlet, was charged with 26.80 g of PICM (102.2 mmol) and 65.10 g of PTMO (32.6 mmol). The system was heated up to 80 °C and stirred. Reaction was started by the addition of 0.005 g of DBTDL catalyst in 1 ml of toluene. The reaction was followed by FTIR spectroscopy, monitoring the disappearance of sharp isocyanate peak at 2270 cm^{-1} and broad hydroxyl peak at 3400 cm^{-1} and formation of strong urethane (C=O) and (N–H) peaks at 1750 and 3300 cm^{-1}, respectively, using a Nicolet Impact 400D spectrometer. Prepolymer formation was completed in 2 h. Isocyanate content of the prepolymer was determined [21]. This was mostly around 96–98% of the theoretical amount. Remaining isocyanate was lost due to side reactions, which are typical in these systems [22]. The prepolymer was dissolved by adding 250 g of DMF into the reaction kettle and the solution was cooled down to room temperature. At this point, 1.02 g of DBA (7.9 mmol) in 10 g DMF was added to control the molecular weight of the polymer to be formed. For chain extension, 7.60 g DAP (65.4 mmol) was dissolved in 50 g of DMF and introduced into the addition funnel. DAP solution was added dropwise into the reactor, at room temperature and high molecular weight polymer was obtained. Towards the end of the chain extension process as the viscosity of the reaction medium increased, 10 g DMF and 20 g IPA were added for dilution. A representative chemical structure of the polyurethaneurea synthesized is given in Fig. 1.

Polymer content of the polyurethaneurea solution was determined by gravimetric methods. Solvents were first evaporated at room temperature and then in a vacuum oven at 50 °C until a constant weight was reached. The solid content of the polymer solution was determined to be 21.2 wt%.

For electrospinning experiments, original polymer solution was diluted with DMF to prepare several new solutions with concentrations ranging from 2.5 to 17.7 wt%. The solutions were prepared the same day of electrospinning at room temperature and stirred gently for at least 3 h. Special care was taken to avoid any contact with humidity since polyurethaneurea solutions coagulate easily in aqueous media.

2.3. Electrospinning setup

Polymer solution was held in a glass capillary. The diameters of the capillary and the tip were 5 and 1 mm, respectively. The electrical field was provided by a high voltage (HV) power supply (CPS HV power supply), Model 2594, which can generate voltages of up to 50 kV with 500 μA direct current. The output voltage and the

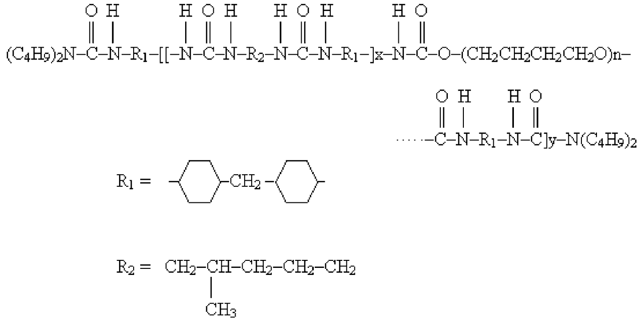


Fig. 1. Chemical structure of polyurethaneurea copolymer. $x = 2$, $y = 8$ and $n = 28$.

current between grounded aluminum sheet and the copper probe were measured from an external connection of the power supply with multimeter. The jet diameter was determined by shining a 632.8 nm laser light beam on the jet which led to a diffraction pattern on a screen. The diameter of the jet was calculated from the distance between the first maxima of the diffraction pattern [23].

The potential difference between the pipette and the ground used to electrospin varied in the range 0–35 kV. The copper probe of the HV generator was inserted into the capillary and electricity was conducted through the solution. The capillary was tilted approximately 10° from the horizontal to maintain a droplet of solution at the tip of the pipette [10]. A grounded aluminum sheet was positioned opposite and perpendicular to the tip of the pipette into which the fibers were deposited. After solvent evaporation, fibers were ready for characterization.

2.4. Measurements and characterization

The morphology of the electrospun elastic fibers were examined by optical microscopy, atomic force microscopy and scanning electron microscopy. Optical micrographs were taken with an Olympus SZ-STUZ optical microscope (OM). A JVC TK-C1381 camera was attached to the microscope to investigate the presence of electrospun fibers on the aluminum sheets. AFM measurements were carried out with a Nanoscope III (Digital Instruments, Inc., Santa Barbara, CA, USA) in tapping mode in air with etched Si probe. E-type scanner was employed with a probing area of $17 \times 17\ \mu m^2$.

Two different makes of SEMs were used for characterizing electrospun fibers. They were FEG (Gemini/Leo) SEM (LEO, Oberkochen, Germany) and XL30 SFEG SEM (FEI, Eindhoven, The Netherlands).

3. Results and discussion

3.1. Jet forming concentrations

Different concentrations of polyurethaneurea solutions in DMF, varying in the range 2.5–21.2 wt% were prepared. Jet formation was not observed for solutions above 12.8 wt% at room temperature. At concentrations below 3.8 wt%, electrospraying took place where the jet broke into droplets. Continuous fibers formed between 3.8 and 12.8 wt% solutions, called lower and upper concentration boundaries of electrospinning, respectively. The viscosity corresponding to the successful concentration range was between 0.015 and $1.63\ N\ s\ m^{-2}$. The surface tension was around $0.032\ N\ m^{-1}$, and the conductivity was in the range 0.4×10^{-3}–$0.76 \times 10^{-3}\ A\ V^{-1}\ m^{-1}$. Fig. 2 shows an electron micrograph of electrospun fibers of polyurethaneurea from high concentration. Fibers are distributed randomly in the form of a nonwoven mat. The scale bar shown on the lower left corner corresponds to 20 μm.

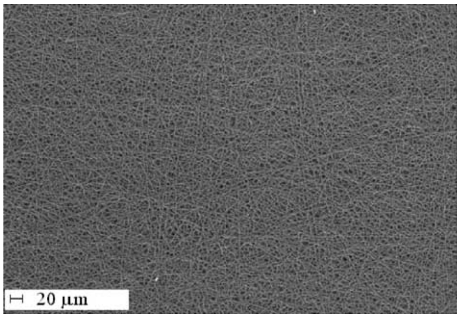


Fig. 2. Electron micrograph of electrospun polyurethaneurea fibers. The fibers were spun from 21.2 wt% solution in DMF with the help of temperature and an electrical field of $4.6\ kV\ cm^{-1}$.

3.2. Effects of instrument variables

The voltage needed to eject a charged jet from the drop at the nozzle depends mainly on the solution viscosity. The threshold voltage to start the jet formation is plotted as a function of concentration in Fig. 3. As concentration, or equivalently, the viscosity increases, higher electrical forces are required to overcome both the surface tension and the viscoelastic force for stretching the fiber.

Jet current is proportional to the transport of electrons, which is a measure of mass flow from the tip of the pipette to the grounded sheet. The spinning process was run for 50 s for each voltage value. Mass of the conductive sheet was recorded before and after the experiment. The mass difference was considered as the amount of deposition of fibers within 50 s. Results for the 3.8 wt% polymer solution are presented in Fig. 4. The spinning distance was 8 cm. The filled circles represent the flow rate from tip to target. The open circles display the current measured during the experiment. Results of measurements exhibit a power law dependence between flow rate and applied voltage, and the measured current and flow rate as:

$$\text{Flow rate} \sim (\text{Voltage})^3, \qquad \text{Current} \sim (\text{Voltage})^{2.7}$$

Considering the similarity of the two scaling relations, we concluded that the flow rate and current are linearly related. It is to be noted that the amount of polymer solution reaching the anode was usually less than the ejected amount of

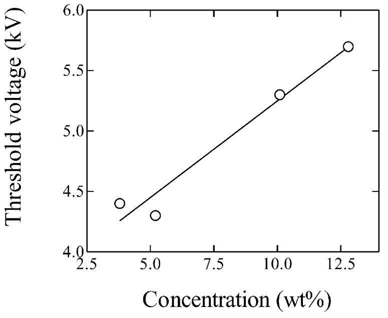


Fig. 3. Threshold voltage as a function of concentration.

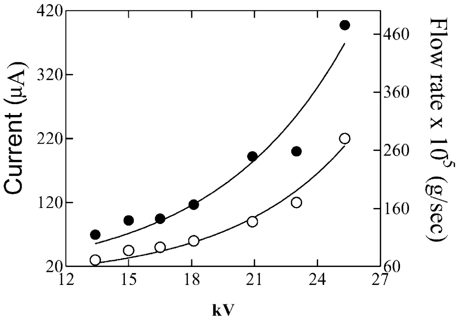


Fig. 4. Comparison of jet current with flow rate.

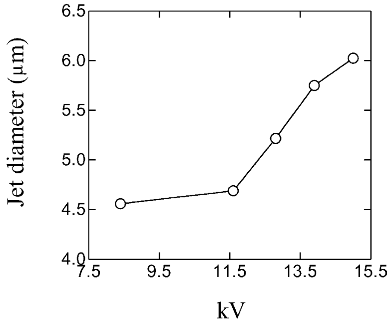


Fig. 6. Diameter of the jet as a function of voltage.

solution from the drop due to the various losses as the jet moved towards the anode. In our experiments, the system was assumed ideal and the flow rate was considered as the deposition rate.

3.3. *Effect of salt addition*

Conductivity of the solution is the key factor determining the spinning current. In order to see the extent of the effect of charge carriers, a salt was added (triethylbenzylammonium chloride) into the solution. The change in mass flow with salt concentration is shown in Fig. 5, where the addition of a small amount of salt is observed to dramatically increase the mass flow.

3.4. *Jet diameter*

The jet diameter becomes smaller as it travels to the ground due to: (i) solvent evaporation, and (ii) continuous stretching due to electrical force [3]. In Fig. 6, the jet diameter is shown as a function of the applied voltage. The diameter of the jet was determined by laser diffraction as explained earlier. The jet diameter seems to increase in a sigmoidal manner with increasing voltage.

At high fields and low viscosities, more than one jet was ejected from the drop at the tip. Increase of the voltage favors the formation of several jets. Multiple jet formation is plotted as a function of the electrical field in Fig. 7. The different fibers repel each other due to the flowing charge on their surface as a result of which the fibers distribute themselves at a larger area on the collector. Jets are observed to rotate in clockwise direction in going from the nozzle to the collector. Fig. 7 expresses the multiple jet formation, when a 3.8 wt% polymer solution is electrospun at 8 cm. The circles represent the average of two measurements. For the most concentrated solution, 12.8 wt%, a single jet was formed at each experiment.

3.5. *Fiber diameter and morphology*

3.5.1. *Fiber diameter*

Fig. 8 shows a series of AFM height images of the nanofibers obtained from electrospinning of polyurethaneurea solutions with four different concentrations, which are: (a) 3.8, (b) 5.2, (c) 10.1, and (d) 12.8 wt%. An increase in solution concentration results in fibers with larger diameters. The dependence of the average fiber diameter (AFD) on solution concentration is shown in Fig. 9, which leads to a power law relationship of

$$\mathrm{AFD} = (\mathrm{Concentration})^3$$

indicating that solution concentration plays an important role in determining the fiber diameter. However, this observation is based on polymer solutions of only one molecular weight. An accurate measurement of the electrospun fiber diameter with AFM requires a rather precise procedure. The fibers appear larger than their actual diameter because of AFM tip geometry [24]. For a precise measurement, two fibers crossing each other on the surface was chosen. The upper horizontal tangent of the lower fiber was taken as reference, and the vertical distance above this reference

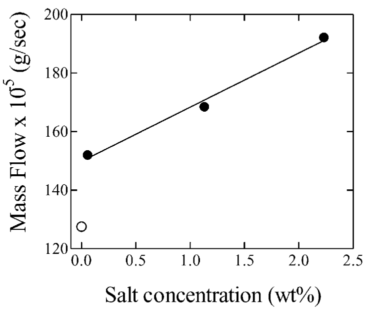


Fig. 5. Effect of salt concentration on jet current.

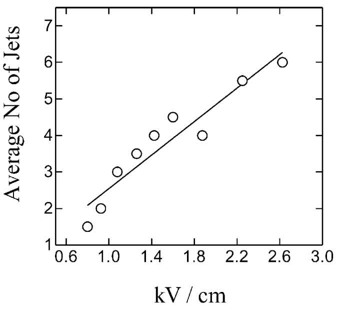


Fig. 7. Multiple jet formation as a function of electrical field.

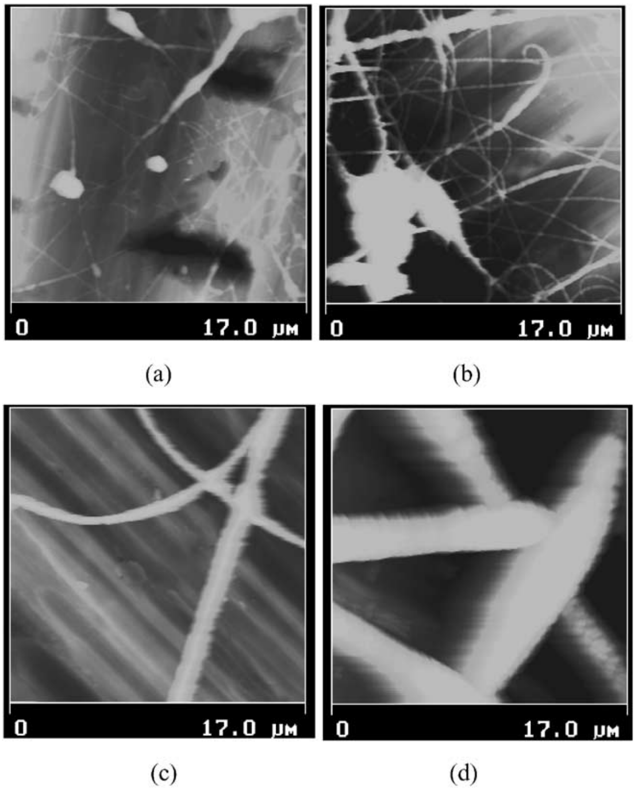


Fig. 8. AFM images of nanofibers obtained from four concentrated solutions: (a) 3.8, (b) 5.2, (c) 10.1, and (d) 12.8 wt%.

was considered to be the exact diameter of the upper nanofiber.

The effects of solution properties on fiber diameter have previously been discussed for other polymeric systems [25]. In order to investigate the effect of solution properties on fiber diameter of polyurethaneurea, the polymer solution was mixed with: (a) a tertiary ammonium salt, and (b) a silicone (PDMS) polymer. Tertiary ammonium salt is an organic material known for its effects for increasing the solution conductivity and surface tension. As explained earlier, addition of the salt into the solution increased the conductivity. PDMS polymer, which has a very low surface tension, was mixed at concentrations of 1–3.7 wt% into original solution. Dramatic changes in fiber diameter were not observed in neither of the cases.

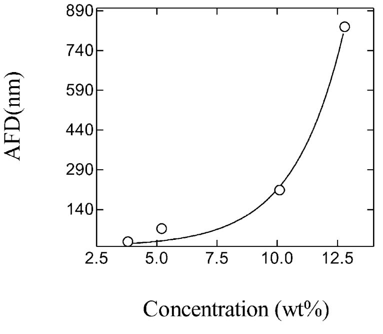


Fig. 9. AFD as a function of concentration.

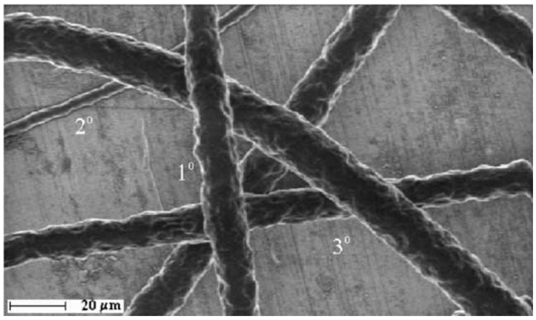


Fig. 10. Electron micrographs of size distribution in AFD. Fibers obtained from electrospinning of 12.8 wt% polyurethane urea belonging to primary, secondary and tertiary populations are demonstrated.

3.5.2. Fiber morphology

Electrospun fibers were not uniform in diameter and morphology. Concentration and temperature both have significant roles in determining the fiber size distribution and morphology. At high concentration, electrospun fibers exhibit three different populations with respect to diameters. In the electron micrographs shown in Fig. 10, approximately a trimodal distribution in fiber diameter is observed for fibers obtained from 12.8 wt% polyurethaneurea solutions. The three different sized fibers are denoted as primary (1°), secondary (2°) and tertiary (3°). The diameter of the primary population of fibers is approximately 1 μm. The second population is nearly one-third of the primary one, which is approximately 0.4 μm, whereas the tertiary population is approximately 1.4 μm in diameter.

A bimodal distribution has been reported to occur in electrospinning of 10 wt% PEO in aqueous solution [13]. In Fig. 11, the distribution of diameters observed in electrospinning of 12.8 wt% polyurethaneurea fibers is shown. In addition to the primary and the secondary peaks noted on the curve in Fig. 11, a small tertiary peak is also observed. The size of the primary population is larger than the total size of the secondary and tertiary population.

Fiber morphology of polyurethaneurea fibers varies with the concentration of solution subjected to electrospinning. Different fiber morphologies occur at different concentrations and have significant effects on surface area to volume ratio of the fibers. At high concentrations, fibers exhibit curly, wavy, and straight structures. The fiber indicated

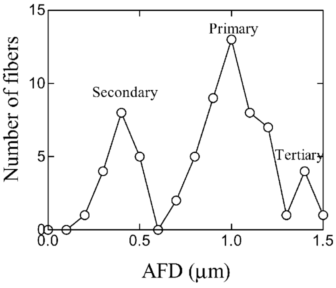
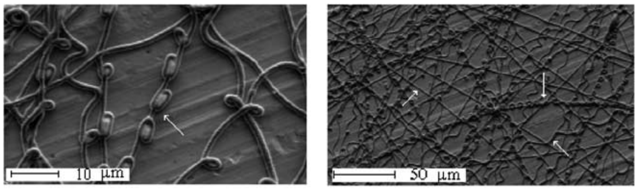


Fig. 11. Diameter distribution of fibers obtained from 12.8 wt% concentrated polyurethaneurea solution.

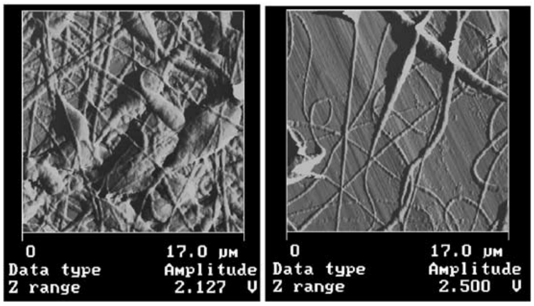


(a) (b)

Fig. 12. Electron micrographs of curly, wavy and straight nanofibers. These images demonstrate the morphology of fibers at high concentration.

with the white arrow in Fig. 12(a) has identical knots with regular distance. The same fiber can be seen in Fig. 12(b), which has five times larger scan area than the first one. Fig. 12(b) shows that the fiber structures are not uniform. In addition to the curly structures, wavy and straight structures indicated with white arrows are observed on the same sample. On the other hand, fibers obtained from low concentration (5.2 wt%) solutions exhibit 'beads on string' morphology. The average bead length was 700 nm. Lower viscosity solution favors the formation of beads and also favors the formation of thinner fibers [14]. Beads are known as defect structures because they disturb the unique property of electrospun fibers and decrease the surface area to volume ratio. The occurrence of the bead formation stems mainly from the high electrical field applied to the system. Increasing the distance or decreasing the electrical field, decreases the bead density. The nanofibers in the first image of Fig. 13 were generated with an electrical field of 2.35 kV cm^{-1}, whereas nanofibers in the second image were obtained at 0.52 kV cm^{-1}. To this end, the morphology of electrospun polyurethaneurea fibers changes from curled, at high concentration, to one containing beads, at low concentration. Both morphological properties have negative influence on surface area to volume ratio of electrospun fibers. It is, therefore, desirable to generate fibers without beads or curled structures, in other words without any 'by products'.

Solution temperature is a key parameter that affects fiber morphology and spinnability. At room temperature, the highest concentration that yielded fibers was 12.8 wt%. In Fig. 14, the electron micrograph of a 21.2 wt% solution electrospun at approximately 70 °C is shown, and compared with Fig. 10 with those obtained from a 12.8 wt% solution at room temperature. At the high temperature, several jets were developed from the drop at the tip with a large angle between each other. Unlike the fibers generated from the 12.8 wt% solution at room temperature, fibers produced at high temperature were surprisingly uniform in diameter, approximately 1 µm, Fig.14. In addition, although the fiber concentration is higher, the fiber diameter distribution is uniform, as can be seen from the figure.



(a) (b)

Fig. 13. AFM images of fibers obtained from low concentration (5.2 wt%) polymer solution.

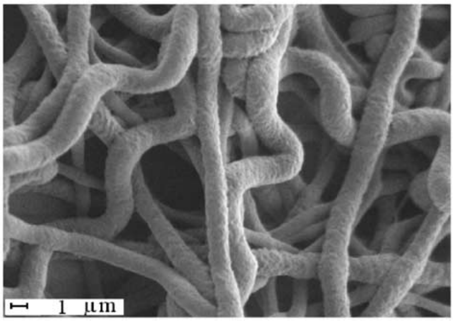


Fig. 14. Electron micrograph of fiber morphology of polyurethaneurea fibers obtained from solutions 21.2 wt% at 70 °C.

It is also observed that the deposition rate increased as a function of temperature. Regardless of the applied electrical field, the deposition rate of fibers at high temperature is significantly higher as compared to that of fibers at room temperature, at equal deposition times. As a result, the film thickness (thickness of nonwoven fabric) is significantly affected by the solution temperature.

3.6. Comparison with wet-spun fibers

Fig. 15 displays the significant diameter difference between the fibers obtained by wetspinning and electrospinning techniques. In the figure, a wet-spun monofilament is spread over the electrospun fibers. The electrospun fibers are one or two orders of magnitude smaller in diameter than wet-spun monofilament but they are in the form of nonwoven fabric. Chaotic deposition with nanoscale porous structure makes the electrospun fibers excellent candidates for membrane technology. However,

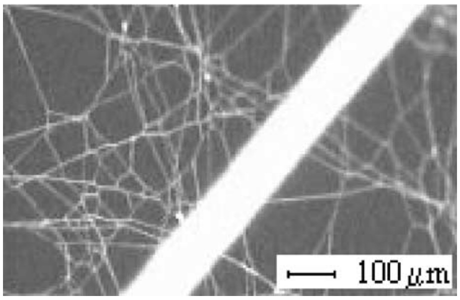


Fig. 15. OM image of polyurethane urea fibers. The diameter of the big fiber is 100 µm.

Table 1
Roughness of fiber surfaces. Wet-spun fibers were produced in our laboratory. Their surface is heterogenous. Roughness of electrospun fibers was compared for all morphologies. Roughness is given in terms of the current measured on an area of 975×975 nm^2

Fiber type	Morphology	Roughness (mV)
Wet-spun	Disordered	35.6
Wet-spun	Fibrillar	26.0
Wet-spun	Flat	15.0
Electrospun		74.0

this property hinders the collection of electrospun fibers in the form of a yarn. In an earlier work, the deposition pattern was investigated in detail for controlling the form of the electrospun fibers [26].

Although the wet-spun fibers are known to have a high degree of surface roughness compared to fibers spun by other conventional techniques [27], our AFM measurements of the surface roughness of the electrospun fibers show that the latter are more than two times rougher than the wet-spun fiber of the same polymer, as shown in Table 1. The roughness measured by the AFM depends on the size of the area selected. In our work, this area was kept constant, 975×975 nm^2, for all measurements. The roughness value reported here is the arithmetic average of the deviations of height from the central horizontal plane, given in terms of millivolts of measured current. The contribution from the cylindrical curvature of the fibers was subtracted out, using the options of plane fit and flatten filters available in the Nanoscope software.

4. Conclusions

In the present work, ultra fine elastic fibers with submicron diameters have been successfully produced by electrospinning of polyurethaneurea solutions. Fiber diameters in the range 7 nm to 1.5 μm were obtained by varying the solution concentration. Fiber diameters increase as the third power of solution concentration. Viscosity, i.e. the concentration of the solution and temperature, is the dominant factor among the other solution properties. Concentration effects on the electrospinning process and final product were investigated and expressed here but a systematic study of the effect of temperature was not performed. A trimodal distribution of fibers in diameter has been found in electrospinning of highest concentration. The morphology of electrospun fibers is strongly correlated with viscosity, equivalently concentration and temperature. Low concentration solutions drive towards the formation of fibers with beads, whereas increased concentration favors the formation of curly fibers. Both morphological imperfections result in decreasing the surface area to volume ratio of electrospun fibers. We find that it is possible to improve the fiber morphology by increasing the solution temperature. Fibers spun at high temperature are uniform unlike those obtained at room temperature. Moreover, high temperature makes the electrospinning process quick, so it is an important advantage from the aspect of industrial applications.

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