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Beaded nanofibers formed during electrospinning

H. Fong, I. Chun, D.H. Reneker*

Maurice Morton Institute of Polymer Science, The University of Akron, Akron, OH 44325-3909, USA

Dedicated to Professor Ronald K. Eby on the occasion of his 70th birthday

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Abstract

Electrospinning is a straightforward method to produce polymer fibers from polymer solutions, with diameters in the range of 100 nm. Electrospun fibers often have beads in regular arrays. The viscoelasticity of the solution, charge density carried by the jet, and the surface tension of the solution are the key factors that influence the formation of the beaded fibers. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

It was known in the early 1900s that if molten sealing wax was electrified, solid fibers were ejected. Sealing wax is brittle, and no viable commercial development of this process for making fibers has resulted so far. Focus is now on the liquid jets created by electric fields, the distortion of liquid droplets in an electric field, the collapse of liquid jets into droplets, and the development of processes for electrospraying paint and other liquids. In the past century, electrostatic spinning and related phenomena, such as aerosol spraying, atomization in the charged droplets and the formation of particles, have received attention [1–5]. Baumgarten [6], working at Dupont in the 1970s, published high speed photographs and other data describing the formation of fibers of an acrylic polymer by electrostatic spinning. Reneker [7–9] and co-workers characterized the electrospinning process and the physical properties of electrospun nanofibers.

Electrospun fibers often have beads as ''by products''. The formation of beaded fibers has been observed widely [10]. The electrospun beaded fibers are related to the instability of the jet of polymer solution, which was studied by Yarin [11] and Entov [12]. They developed a mathematical model for the break-up of jets of polymer liquids, which did not include the effects of electric fields. In 1962, Magarvey and Outhouse [13] found that the break-up of water jets depended on the electrical current. The more current the water jet carried, the less likely it was to form droplets. Huebner [14] also considered such electrical phenomena. Fang [8] electrospun beaded DNA nanofibers. Jaeger [15,16] reported beaded fibers spun from aqueous solutions of poly(ethylene oxide) (PEO). He found that the bead diameter and spacing were related to the fiber diameter: the thinner the fiber, the shorter the distance between the beads and the smaller the diameter of the beads.

Characterization of the formation of electrospun beaded nanofibers shows that solution viscosity, net charge density carried by the electrospinning jet and surface tension of the solution are the main factors. Higher viscosity favors formation of fibers without beads, higher net charge density not only favors formation of fibers without beads, but also favors the formation of thinner fibers. Surface tension drives towards the formation of beads, hence reduced surface tension favors the formation of fibers without beads.

Changing the polymer concentration can vary the solution viscosity. The surface tension coefficient depends on the polymer and solvent. For example, changing the ratio of ethanol to water can change the surface tension coefficient of the PEO solution. Net charge density carried by the jet in the electrospinning process is primarily affected by the applied electrostatic field and to a lesser extent by the conductivity of the solution. For example, the addition of NaCl to a PEO/water solution is observed to increase the net charge density carried by the spinning jet. The use of the quantity charge per unit volume (C/l) does not imply that the net charge density is distributed uniformly throughout the jet. When the jet shape is changing rapidly, most of the net charge is found to be near the surface. The net charge density on the jet can be reduced to a low value, by ions

* Corresponding author. Tel.: + 1-330-972-6949; fax: + 1-330-972-5290.

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Table 1
The preparation and characterization of the solutions

Sample number	PEO (g)	Water (g)	Ethanol (g)	NaCl (g)	Solution viscosity (centipoise)	Solution surface tension (mN/m)	Solution resistivity (Ω m)
1	1.00	100			13	77.8	306
2	1.50	100			32	76.4	295
3	2.00	100			74	76.0	254
4	2.50	100			160	78.6	234
5	3.00	100			289	77.6	221
6	3.50	100			527	77.0	212
7	4.00	100			1250	76.6	204
8	4.50	100			1835	76.2	195
A	3.00	97		0.0015	375	76.2	83.4
B	3.00	97		0.0060	392	74.8	47.4
C	3.00	97		0.030	432	75.0	16.7
D	3.00	97		0.150	431	76.0	3.61
E	3.00	97		0.30	387	74.2	1.90
F	3.00	97		1.50	362	76.4	0.462
I	3.00	97	0		402	75.8	110
II	3.00	92	5		504	68.9	130
III	3.00	87	10		623	63.1	180
IV	3.00	77	20		889	59.3	269
V	3.00	67	30		1129	54.7	333
VI	3.00	57	40		1179	50.5	386

with polarity opposite to those carried by the jet, from a corona discharge in air.

An electrically driven jet of a low molecular weight liquid will form droplets [2] (electrospraying). The formation of these droplets is due to the capillary breakup of the spinning jet by surface tension [11]. For polymer solutions, the pattern of the capillary breakup is changed radically. Instead of breaking rapidly, the filaments between the droplets are stabilized and a stable beads-on-string structure is formed. The reason for this is that the coiled macromolecules of the dissolved polymer are transformed by the elongational flow of the jet into oriented, entangled networks that persist as the fiber solidifies. The contraction of the radius of the jet, which is driven by surface tension, causes the remaining solution to form beads.

As the viscosity of the solution is increased, the beads become bigger, the average distance between beads longer, the fiber diameter larger, and the shape of the beads changes from spherical to spindle-like. As the net charge density increases, the beads become smaller and more spindle-like, while the diameter of fibers become smaller. Decreasing the surface tension make the beads disappear gradually. Neutralization of the charge carried by the jet favors the formation of beads, because the tension in the fiber depends on the net charge repulsion and the interaction of the net charge with the electric field.

2. Experimental

PEO, with an average weight molecular weight of 9×10^5 (g/mol), was obtained from Scientific Polymer Product Company and used without further purification. Distilled water was used. The solutions were prepared at room temperature, and gently stirred to speed dissolution. The PEO solution was held in a hemispherical metal spoon, which had an orifice of 0.3 mm diameter in its bowl. The diameter of the spoon was about 2.0 cm and the thickness about 1.0 mm. The spoon was connected to a high-voltage supply, which is capable of generating positive DC voltages up to 30 kV. A flat piece of aluminum foil, placed 21.5 cm below the orifice, was used to collect the electrospun material. Currents were measured with a 100 μA meter attached between the aluminum foil and ground. Neutralizing ions were generated by using a negative 30 kV supply attached to a bundle of fine copper wires ($d = 0.4$mm) to create a corona discharge. The bundle of copper wires was put in a plastic tube that was connected with an air blower. The airflow rate was about 0.1 l/s. The outlet of the tube was 10 cm below and 40 cm to the side of the metal spoon. The concentration of the neutralizing ions was controlled by adjusting the negative voltage between 0 and 18 kV.

The morphology of the electrospun nanofibers was observed with a Scanning Electron Microscope (Model No. JSM-5310) manufactured by Japan Electron Optical Laboratory.

3. Results and discussion

Three series of solutions were prepared for the study: (1) PEO with distilled water only, (2) PEO and NaCl with

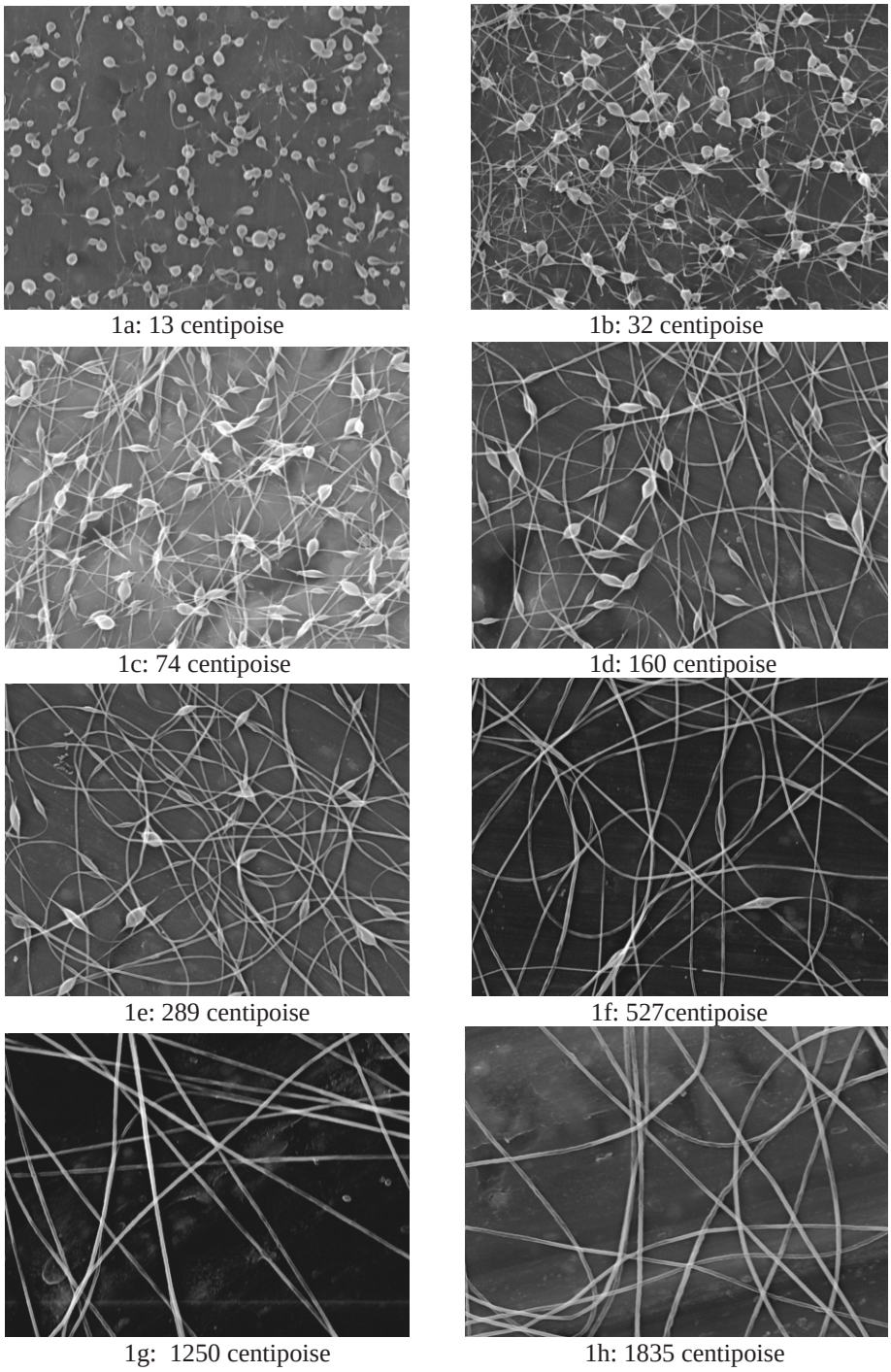
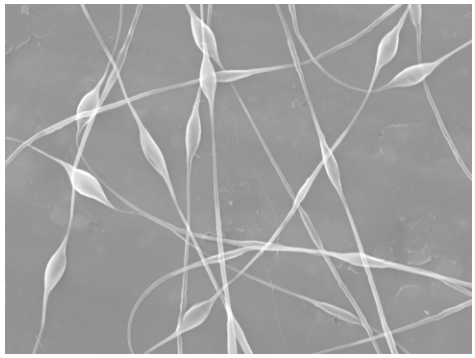


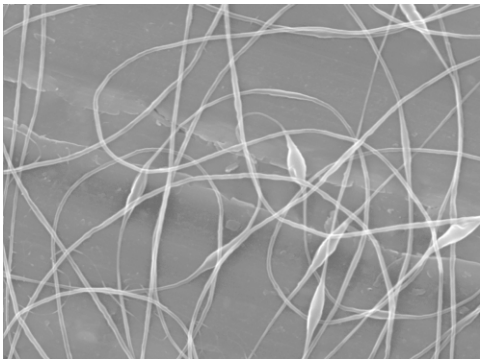
Fig. 1. The morphology of beaded fibers versus solution viscosity. Electric field is 0.7 kV/cm. The horizontal edge of each image is 20 microns long.

distilled water, and (3) PEO with distilled water and ethanol. The preparation and characterization of these solutions are summarized in Table 1. The water used for samples 1–8 was distilled twice and the resistivity was 1629 Ω m. For other samples, the water was distilled only once and the resistivity was 165 Ω m. The resistivity increased as alcohol was added, because alcohol has a resistivity that is at least two orders of magnitude greater than that of water.

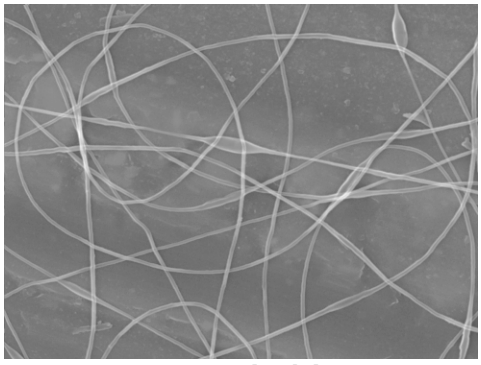
To characterize the SEM images of the beaded nanofibers shown in Figs. 1–4, the following measurements were made: average bead length along the fiber axis (BL), average bead width perpendicular to the fiber axis (BW), average fiber diameter (FD), average fiber length between beads (FL), and the approximate ratio of bead volume to fiber volume (AR). These are summarized in Table 2.



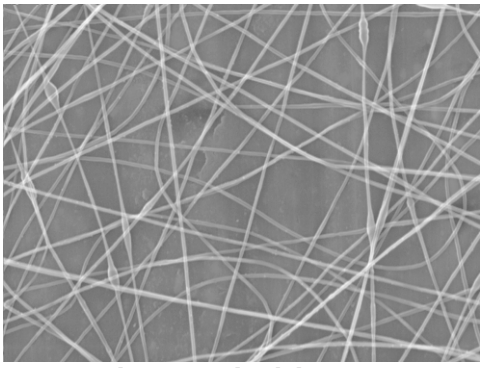
2a: 1.23 Coulomb/liter



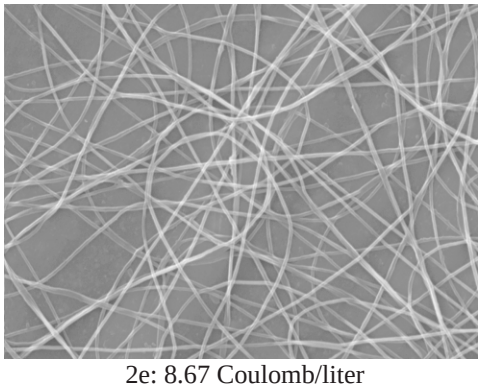
2b: 1.77 Coulomb/liter



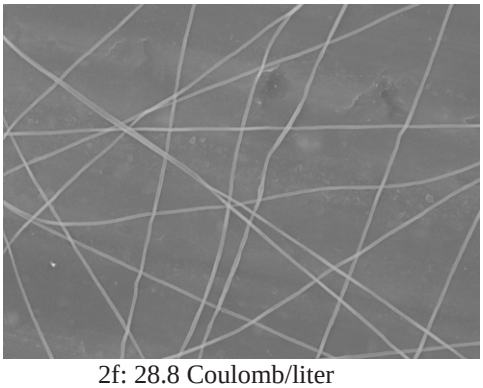
2c: 3.03 Coulomb/liter



2d: 6.57 Coulomb/liter



2e: 8.67 Coulomb/liter



2f: 28.8 Coulomb/liter

Fig. 2. Variation of beaded fibers as net charge density changes due to the addition of NaCl. Electric field is 0.7 kV/cm. Weight fraction of PEO is 3.0%. The length of the horizontal edge of each of the images is 20 microns long.

3.1. Viscosity

Fig. 1 shows the representative images of beads and beaded fibers for solutions with a range of viscosity (samples 1–8). Beads and beaded fibers are less likely to be formed for the more viscous solutions. The diameter of the beads become bigger and the average distance between beads on the fibers longer as the viscosity increases. Meanwhile, the shape of the beads gradually changes from spherical to spindle-like.

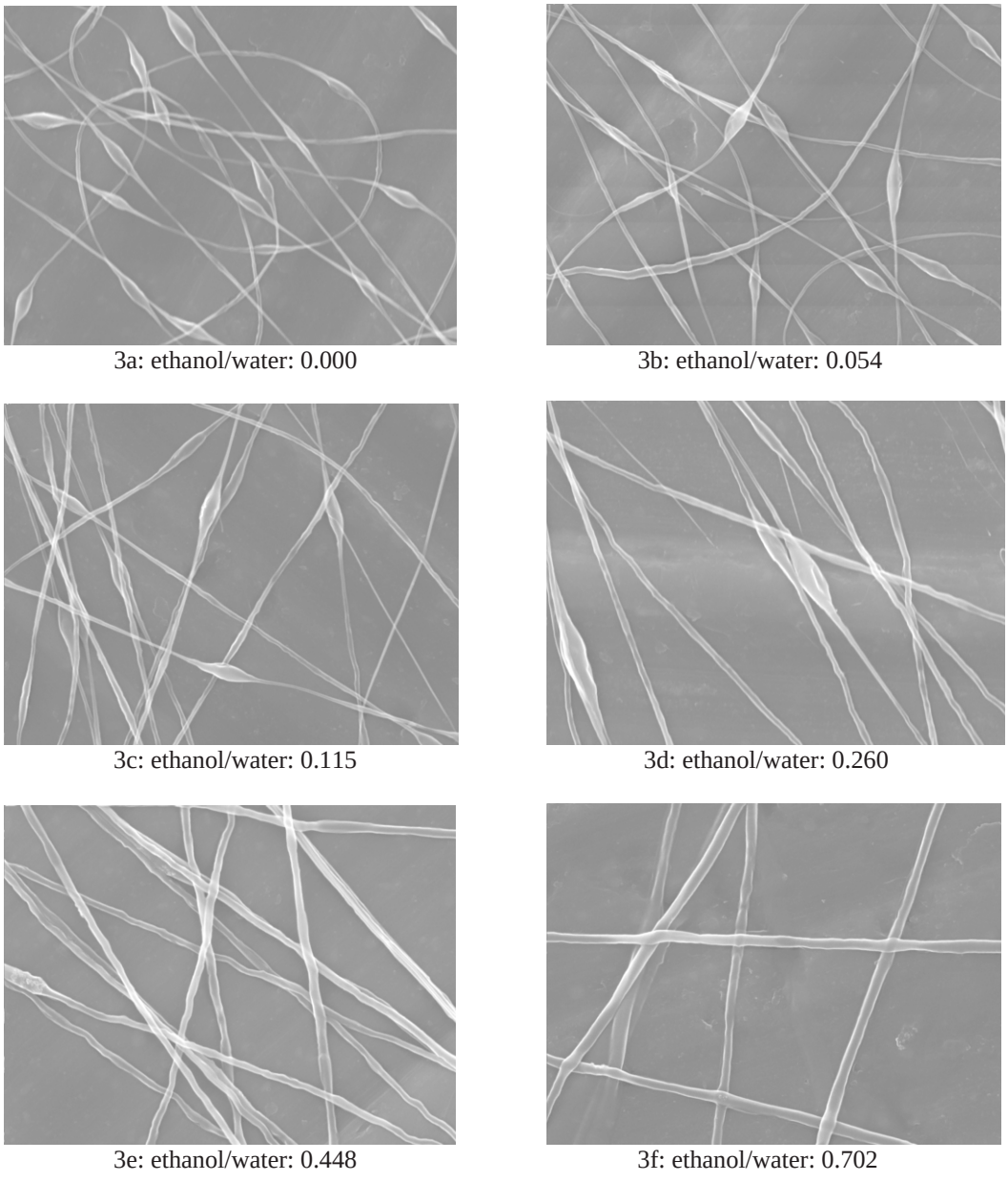
3.2. Net charge density

The net charge density carried by the moving jet (C/l), was determined from the electrical current and the mass of dry polymer collected on the aluminum foil as follows:

Net charge density = (jet current) × (collecting time) × (PEO concentration) × (solution density)/(mass of dry polymer)

The net charge density correlates with the formation of beaded fibers in a way that is similar to increasing the solution viscosity, as shown in Fig. 2. The net charge density was inversely proportional to the resistivity in this experiment.

Experimental results show that the addition of NaCl to the PEO solution increases the net charge density carried by the moving jet. The decrease in the resistivity of the solution is



3a: ethanol/water: 0.000 3b: ethanol/water: 0.054

3c: ethanol/water: 0.115 3d: ethanol/water: 0.260

3e: ethanol/water: 0.448 3f: ethanol/water: 0.702

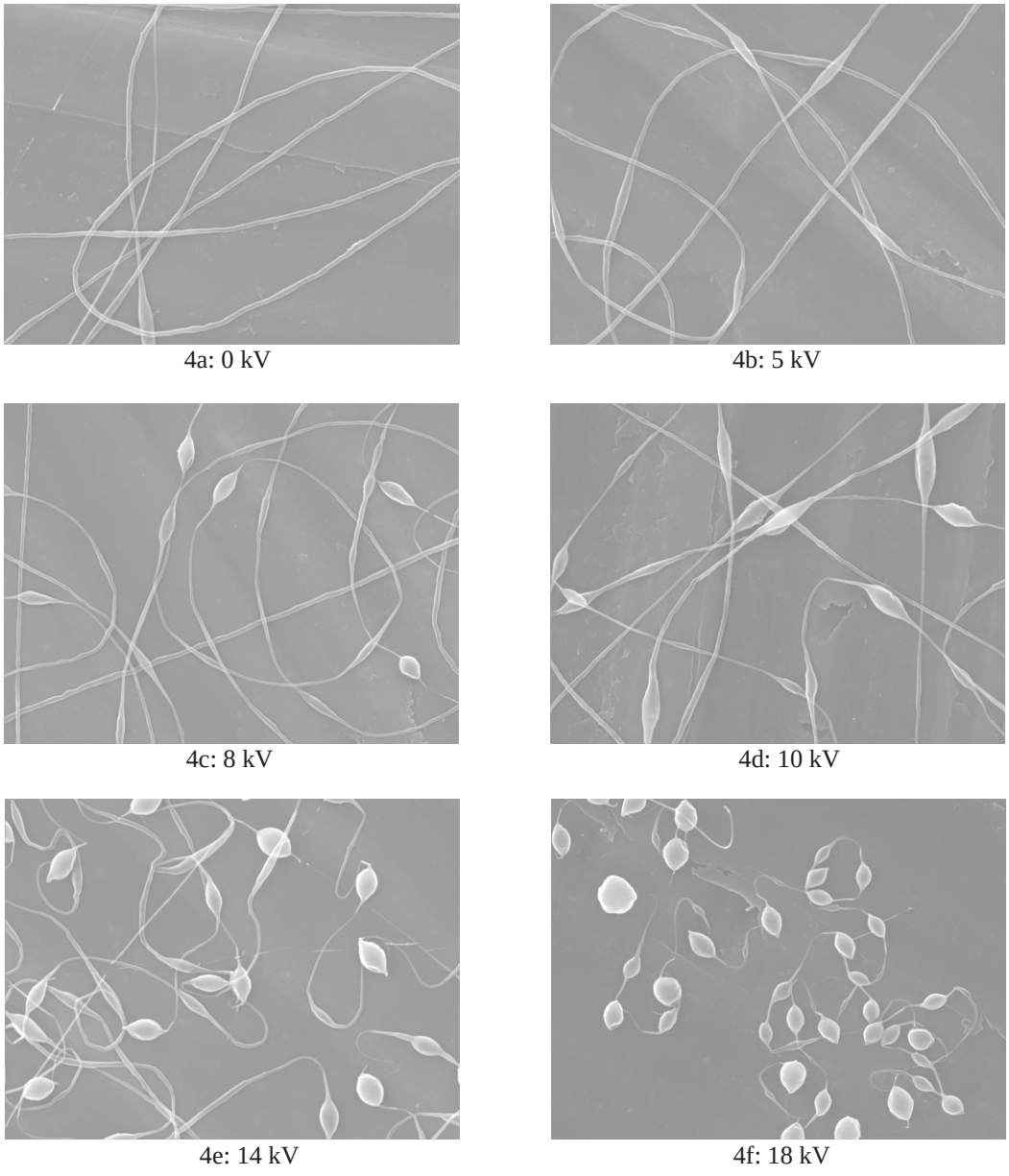
Fig. 3. Variation of beaded fibers as the mass ratio of water/ethanol is changed. Electric field is 0.5 kV/cm, weight fraction of PEO is 3.0%. The horizontal edge of each of the figures is 20 microns long.

not large enough for simple ionic conductivity through the jet to account for the increase in transported charge. The observed decrease in resistivity on addition of salt is due to the increased net charge that flows into the jet as it passes through the orifice of the metal spoon. This higher net charge then increases the force exerted on the jet and the mechanism that forms the beads. Details of the ionic currents, as the solution potential changes during passage through the orifice, appear to be important.

3.3. Surface tension

The formation of beads and beaded fibers is driven by the surface tension [13]. Surface tension tries to make the surface area per unit mass smaller, by changing the jets into spheres; the forces from the excess charge try to increase the surface area, which opposes the formation of beads and favors thinner jets; viscoelastic force resists rapid changes in shape. In Fig. 1, the major competition is between the surface tension and viscoelastic force. Increasing the viscosity favors the formation of smooth fibers. In Fig. 2, the major competition is between the electrical force and viscoelastic force. The increase of net charge density and the associated electrical forces favors the formation of smooth fibers.

By changing the solvent from pure water to a water/



4a: 0 kV 4b: 5 kV

4c: 8 kV 4d: 10 kV

4e: 14 kV 4f: 18 kV

Fig. 4. The effect of neutralizing ions transported to the jet through the air. Sample is 3.85 wt.% PEO in water. Electric field is 0.4 kV/cm. The horizontal edge of each of the figures is 20 microns long.

ethanol mixture while holding the PEO concentration constant, smooth fibers with larger diameters were produced. (Fig. 3.).

As shown in Table 1, increasing ethanol concentration makes the solution viscosity higher, and the surface tension lower. Both these effects favor the formation of smooth filaments. The increase of the diameter of the filaments is associated with the decrease in net charge density, which makes the charge repulsion force smaller. The net charge density carried by the jet was decreased from about 1 C/l to about 0.2 C/l by the addition of ethanol. At the same time, the addition of ethanol makes the solvent easier to evaporate, which increases the viscosity and slows the rate of bead formation. The results shown in Fig. 3 can be considered as the combination of all these effects.

3.4. Neutralization of charge on the jet

The formation of the beaded fibers is also greatly affected by neutralizing the charges on the jet with ions of opposite polarity which are generated by a corona discharge and carried to the jet by flowing air, using the apparatus described in the experimental section. The electrical forces on the jet are reduced by the neutralizing charge, so that the jet behavior gradually becomes that of an uncharged jet, and the beads are formed. Higher voltages on the corona

Table 2
The characterization of electrospun beads and fibers

Figures	Sample number	Electric field (kV/cm)	BL (10^{-9} m)	BW (10^{-9} m)	FD (10^{-9} m)	FL (10^{-6} m)	AR (in %)
1a	1	0.7	460	400	<80	1.5	>90
1b	2	0.7	550	450	80	2	75
1c	3	0.7	700	480	100	4	60
1d	4	0.7	750	500	150	6	35
1e	5	0.7	850	450	180	7	25
1f	6	0.7	1000	450	200	10	5
1g	7	0.7			250		<2
1h	8	0.7			250		<0.5
2a	A	0.7	900	550	200	6	30
2b	B	0.7	900	400	200	10	10
2c	C	0.7	1000	350	150	>15	5
2d	D	0.7	800	250	180	>15	2
2e	E	0.7			180		<1
2f	F	0.7			<80		<1
3a	I	0.5	850	500	180	7	30
3b	II	0.5	900	500	180	8	25
3c	III	0.5	900	500	200	8	20
3d	IV	0.5	1500	700	250	>15	10
3e	V	0.5			300		<5
3f	VI	0.5			350		<1
4a	7	0.4	1000	450	200	>20	<5
4b	7	0.4	1000	400	200	10	10
4c	7	0.4	550	400	180	8	15
4d	7	0.4	650	400	160	5	35
4e	7	0.4	620	550	<150	2.5	60
4f	7	0.4	600	500	<50	1	>80

discharge apparatus produced more neutralizing ions and caused more beads to form. This process is shown in Fig. 4.

The effects of the neutralizing ions are consistent with the results produced by the addition of NaCl. Both show that the net charge density carried by the moving jet tends to resist the formation of beads. The higher the net charge density carried by the jet, the more likely that a smooth fiber will be formed.

3.5. Stability of polymer fibers

Surface tension acts on a solid rod in the same way as it does on a jet, tending to convert segments of the rods to spheres. The ability of a solid to resist deformation is high enough that the surface tension forces do not usually produce significant deformation. As the axial force caused by the surface tension is πDT, where D is the diameter and T, the surface tension coefficient, and the area is $\pi D^2/4$, the pressure on a circular cross section is $4T/D$. As D approaches the diameter of a single molecule, the effects of surface tension will make the extended conformation unstable. The compressive strength of polymer fibers is not a very well defined parameter, but the available information, which was summarized by Macturk, Eby, and Adams [17], suggest that a value in the range of 200–400 MPa is representative. The surface tension coefficient of solid polymers is also not well known, but probably can be approximated satisfactorily for the purposes of this argument, as being equal to the surface tension coefficient of a polymer liquid, which is around 40 mN/m [18]. These values can be used to solve for the diameter of a polymer fiber that is unstable because of its surface tension. If D is less than about 2 nm, a nanofiber that is produced by stretching is likely to twist, bend, fold or distort in some other way when the tension is removed, in order to minimize its surface energy. The nanofibers produced by electrospinning may provide fibers that are small enough to be deformed by surface tension if the tensile force along the axes is zero.

4. Summary

The formation of the beaded nanofibers can be considered as the capillary breakup of the electrospinning jets by surface tension, altered by the presence of electrical forces. The surface tension and viscoelastic properties of the polymer solution are the key parameters in the process. Increasing net charge density favors formation of small diameter fibers. Decreasing the surface tension coefficient of the solvent favors the formation of larger diameter fibers. Details of ionic currents, where the jet moves through

regions of different electrical potential near the orifice are also important.

Acknowledgements

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