Controlling numbers and sizes of beads in electrospun nanofibers

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Abstract

BACKGROUND: Electrospinning is a powerful and effective method to produce nanofibers. Beads have been observed widely in electrospun products, but effects of solvents, weight concentrations and salt additives on the number and morphology of beads in the electrospinning process have not been systematically studied.

RESULTS: Both theoretical analysis and experimental results show that beads strongly depend upon solvents, weight concentrations and salt additives. Either a suitable weight concentration or a suitable salt additive can completely prevent the occurrence of beads in the electrospinning process; solvents can affect the number of beads and the morphology of electrospun fibers.

CONCLUSION: Beads are mainly caused by lower surface tension. With a higher surface tension, the size and number of beads in electrospun products are smaller and fewer, respectively.
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Keywords: electrospinning; beads; weight concentration; solvent; additive

INTRODUCTION

Electrospinning, which produces continuous polymer nanofibers from polymer solutions or melts, has been a focus of wide discussion in academic and industry circles.[1–14] Now electrospinning can also produce nanoporous fibers or spheres,[15–18] which have many potential applications.[19] Many new electrospinning techniques have appeared, such as vibration electrospinning,[10,20] magneto-electrospinning,[21] Siro-electrospinning[18] and bubble electrospinning.[22]

Nanotechnology bridges the gap between deterministic laws (Newtonian mechanics) and probabilistic laws (quantum mechanics). The nano-effect has been demonstrated for unusual strength, high surface energy, surface reactivity and high thermal and electric conductivity. It is a challenge to develop technologies capable of preparing nanofibers with diameters under 100 nm without beads,[18] especially for smaller nanofibers. Recently Huang *et al*.[23] produced nanofibers as small as 1 nm. At such a small scale, it is very important to avoid the occurrence of beads. Beads were observed widely in the electrospinning process,[24,25] and were considered as the main demerit of the electrospun fibers. There are many factors affecting the occurrence of beads, such as applied voltage, viscoelasticity of the solution, charge density and surface tension of the solution. Much attention has been directed towards the formation and morphology of beads in electrospun products.[16,17,26,27] However, the mechanism for the formation of beads is still unknown and little research on this has been performed so far. In this paper we suggest three methods to reduce the numbers and sizes of beads, namely adjusting weight concentrations, adding salt additives and variation of the solvent.

EXPERIMENTAL

Materials

Poly(butylene succinate) (PBS) pellets were supplied by Shanghai Institute of Organic Chemistry, Chinese Academy of Science. The weight average molecular weight was about $2 \times 10^5\,\mathrm{g\,mol^{-1}}$. The solvents, chloroform (CF), dichloromethane (DCM), 2-chloroethanol (CE) and isopropanol (IPA), were purchased from Shanghai Chemical Reagent Co. Ltd. LiCl was purchased from Pinjiang Chemical Co. Ltd. All the chemicals were used directly without further purification. The polymer pellets were dissolved in a single solvent or a mixture of the solvents mentioned above. The weight concentrations were adjusted from 11 to 17 wt%. LiCl, as a salt additive, with a weight concentration of either 0.5 or 1.0 wt% was added into the polymer solution of 14 wt%.

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Electrospinning process

An electrospinning setup equipped with a variable DC high-voltage power generator (0–100 kV, F180-L, Shanghai Fudan High School) was used in this work. The polymer solution was placed into a 20 mL plastic syringe vertically and delivered to the orifice of the stainless steel needle by the syringe pump (AJ-5803, Shanghai Angel Electronic Equipment Co.) at a constant flow rate. An applied voltage was connected to the needle using the DC high-voltage power generator via an alligator clip. A flat aluminium foil, as a collector, was connected to ground below the needle. The distance between the orifice and the collector was 10 cm. The diameter of the orifice was 0.9 mm. The polymer pellets were dissolved in a single solvent or mixed solvents and stirred for *ca* 2 h at 40 °C. All electrospinning experiments were performed at room temperature.

Characterization

The morphologies of the electrospun products were examined using SEM (JSM-5610, JEOL, Japan) after the samples were coated with gold. The surface tensions of different polymer concentrations were measured with a surface dynamic contact angle analyzer (ThermoCahn DCA322).

RESULTS AND DISCUSSION

Effects of different solvents

PBS was chosen because it is soluble in common organic solvents such as CF, DCM and CE. In order to investigate the morphology of beads in electrospun PBS nanofibers, the polymer was dissolved in a single solvent (CF or DCM), and a mixed solvent system with different weight ratios: CF/DCM (7/3 w/w), CF/IPA (8/2 w/w) and CF/CE (7/3 w/w). Such mixed solvents resulted in good electrospinnability and excellent efficiency. The electrospinning process was conducted under the following conditions: the applied voltage was 10 kV, the solution concentration was 11 wt%, the distance between the orifice and the collector was 10 cm and the diameter of the orifice was 0.9 mm. The solution concentration was adjusted to a fixed value, i.e. 11 wt%, because such a concentration led to a large number of beads and microspheres. Our experiment showed that the occurrence of beads did not depend upon the flow rate, which was set to 0.1 mL h^{-1} in the present experiment. The flow rate in the electrospinning process can be considered as an initial condition; due to the high voltage, the charged jet can be accelerated to a speed higher than the velocity of sound in an extremely short time. So a change of the initial condition will not affect much the accelerated jet.

SEM micrographs of electrospun PBS products in different solvents are illustrated in Fig. 1. When its solvent was chosen as 100% CF, the PBS electrospun products were ‘beads on a string’ (Fig. 1(a)); when 100% DCM solvent was used, many microspheres were observed. On the other hand, many bigger microporous beads appeared when the mixed solvent CF/DCM (7/3 w/w) or CF/IPA (8/2 w/w) (Fig. 1(b)) was applied; the fibers obtained were of higher quality with few beads and the spinning process was of the highest efficiency for the mixed solvent CF/CE (7/3 w/w) (Fig. 1(c)). For other solvent systems, such as CF/IPA (9/1 w/w), DCM/IPA (9/1 w/w) and CF/DCM/IPA (8/1/1 w/w/w), either beads or microspheres were observed in our experiment.

Table 1 summarizes the effects of different solvents and polymer concentrations on electrospun products.

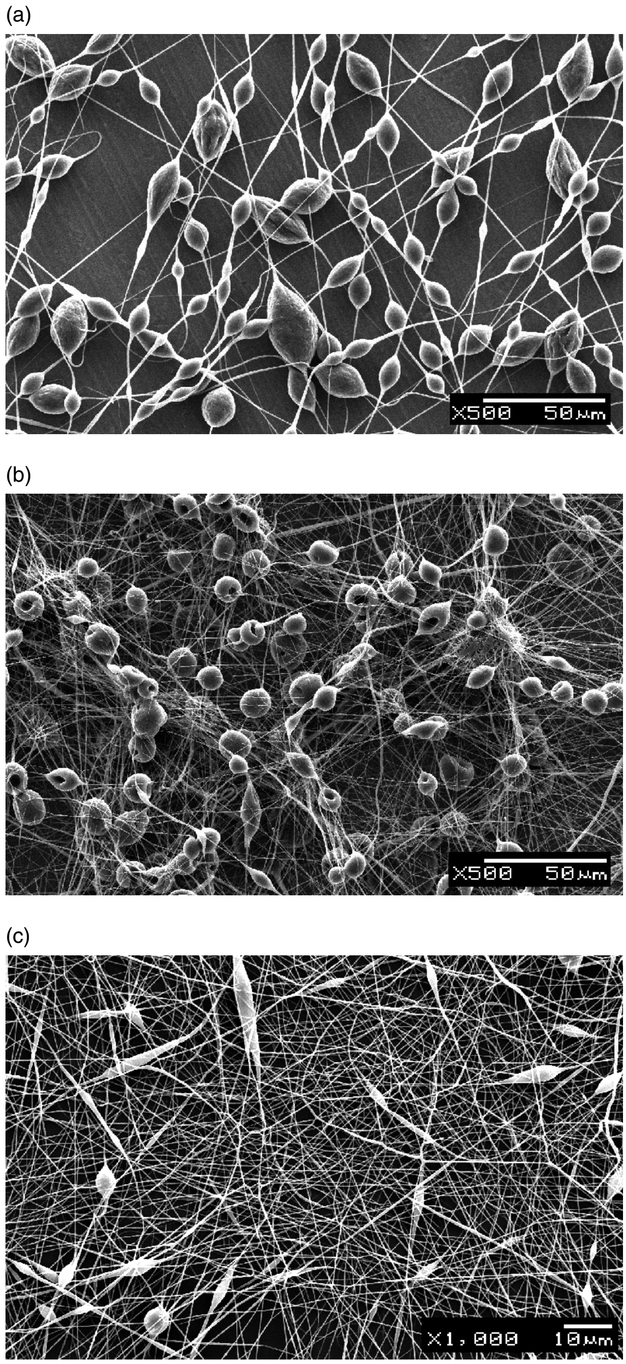

Figure 1. SEM micrographs of PBS electrospun products. The solvent was (a) CF, (b) CF/IPA (8/2 w/w), (c) CF/CE (7/3 w/w), with all other conditions being equal.

Table 1. Electrospun products in different solvents

Solvent (w/w)	Polymer concentration (wt%)	Electrospun products
CF	11	Beads + few fibers
CF/DCM (7/3)	11	Microspheres + few fibers
CF/IPA (8/2)	11	Spoon-shaped beads + fibers
CF/CE (7/3)	11	Few beads + fibers
DCM/CE (5/5)[a]	15	Beaded fibers
CF/1-CP (9/1)[a]	15	Beaded fibers
DCM/3-CP (9/1)[a]	15	Beaded fibers
DCM/1-CP (9/1)[a]	15	Beaded fibers
CF/3-CP (9/1)[a]	15	Fibers
DCM/CE (7/3)[a]	15	Fibers
DCM/CE (6/4)[a]	15	Fibers

[a] Experimental results of Jeong *et al.*[28] for PBS ($M_n = 75\,000\ \mathrm{g\,mol^{-1}}$) in different solvents.

From Table 1, we found that an appropriate choice of solvents in the electrospinning process resulted in fewer beads in the case of 11 wt% polymer concentration.

Our experiment revealed that there was an optimal solvent system which could almost eliminate beads in electrospun products, and the efficiency of the electrospinning process depended strongly upon the chosen solvent system.

Recently Jeong *et al*. conducted a similar experiment using three mixed solvent systems, CF/3-CP (9/1), DCM/CE (7/3), DCM/CE (6/4) under 15 wt% polymer concentration,[28] and different morphologies were reported (Table 1).

Additionally, there are also some other possible factors affecting the morphologies of the electrospun nanofibers, such as the volatilization rate, solvent polarity, solution conductivity, surface tension, solution viscoelasticity, chain entanglement and ambient temperature.[26,27,29,30]

Effect of polymer concentration

It is well known that polymer concentration is one of the most important parameters in the electrospinning process because it is strongly related to the viscosity of the solution. Fabrication and morphology of nanofibers are dependent on solution viscosity.[31] When the polymer concentration was low, either many beads or many microspheres appeared in electrospun products, and the process became electrospraying when the concentration became low enough.[31,32] Increase of the polymer concentration, therefore, might decrease the numbers and sizes of beads, and eliminate beads completely in some cases.

In order to confirm the above results, seven polymer concentrations from 11 to17 wt% were used in our experiments. SEM micrographs of the obtained nanofibers are shown in Figs 1(c) and 2. The number of beads gradually decreased with an increase of the polymer concentration from 11 wt% (Fig. 1(c)) to 14 wt% (Fig. 2(a)). Furthermore, there were no beads and microspheres in the electrospun products when the polymer concentration exceeded 16 wt% and the fibers produced were more uniform (Fig. 2(b)). The reason for this might be that beads are mainly caused by the surface tension which minimizes the surface area. In the case of no surface tension, the jet would be broken down into drops. Lower surface tension tends to form more beads in the electrospun products. With an increase of polymer concentration, the surface tension becomes increasingly large, resulting in fewer beads. The surface tensions of different polymer solutions and their electrospun products are listed in Table 2, and the relationship between the solution concentration and surface tension is shown in Fig. 3.

(a)

(b)

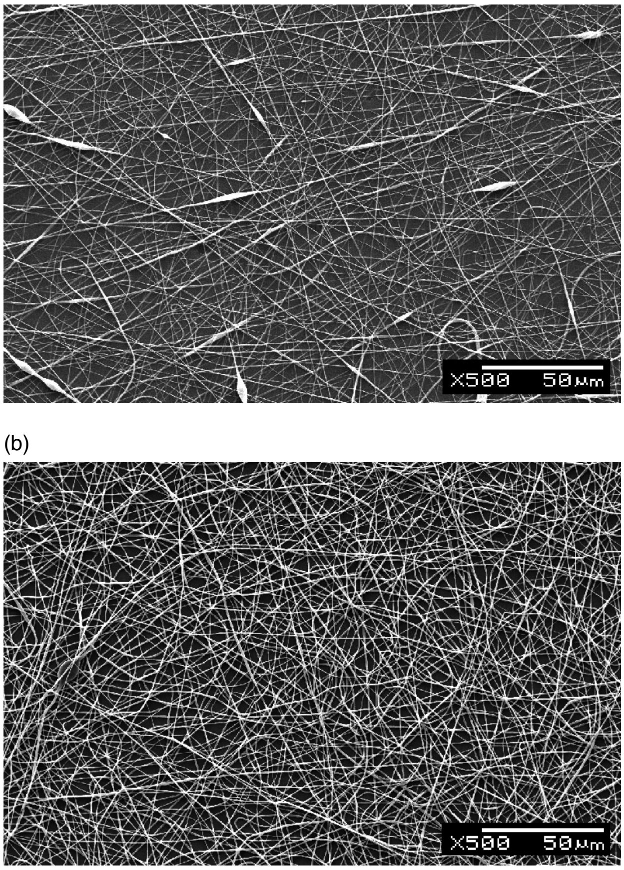

Figure 2. SEM micrographs of PBS electrospun products. The concentration was (a) 14 wt%, (b) 17 wt% in the mixed solvent CF/CE (7/3 w/w) with all other conditions being equal.

Table 2. The surface tensions of different polymer solutions and their products

Polymer concentration (wt%)	Surface tension ($\mathrm{mN\,m^{-1}}$)	Electrospun products
13	32.5	Many beads + fibers
14	32.9	Beads + fibers
15	33.2	Few beads + fibers
16	34.0	Fibers

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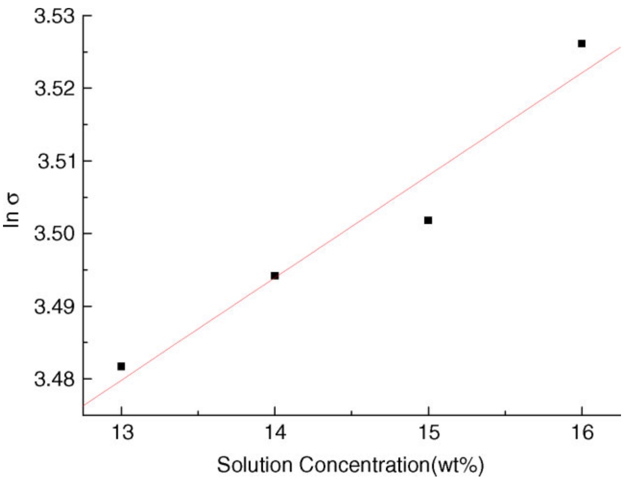

Figure 3. Relation between the solution concentration and surface tension.

Effect of different salt additives

Fong and co-workers[29] concluded that the net charge density carried by the electrospinning jet is another important factor which largely influences the morphology of electrospun products besides the viscosity and the surface tension of the solution. Their experiments showed that beads became smaller and spindle-like with an increase of the net charge density. Using their results as a guide, an experiment was designed with the following conditions: the solvent was CF/CE (7/3 w/w), the applied voltage was 20 kV, the diameter of the needle orifice was 0.7 mm, the distance between the orifice and the collector was 14 cm and the flow rate was 0.1 mL h^{-1}. Furthermore a small amount of a salt, LiCl, was added into the 14 wt% PBS/(CF/CE) solution in order to determine the effect of the salt on the occurrence of beads.

Comparison of the SEM micrographs of these products with the samples without adding salt under same conditions showed a sharp decrease in the number of beads with an increase of salt content (Fig. 4). The reason for this phenomenon might be that the addition of a salt leads to better electric conductivity of the jet, and, as a result, higher electrostatic force is imposed on the jet in the electrospinning process.[33] The size of beads, therefore, became smaller and their morphology became spindle-like with an increase of the charge density.

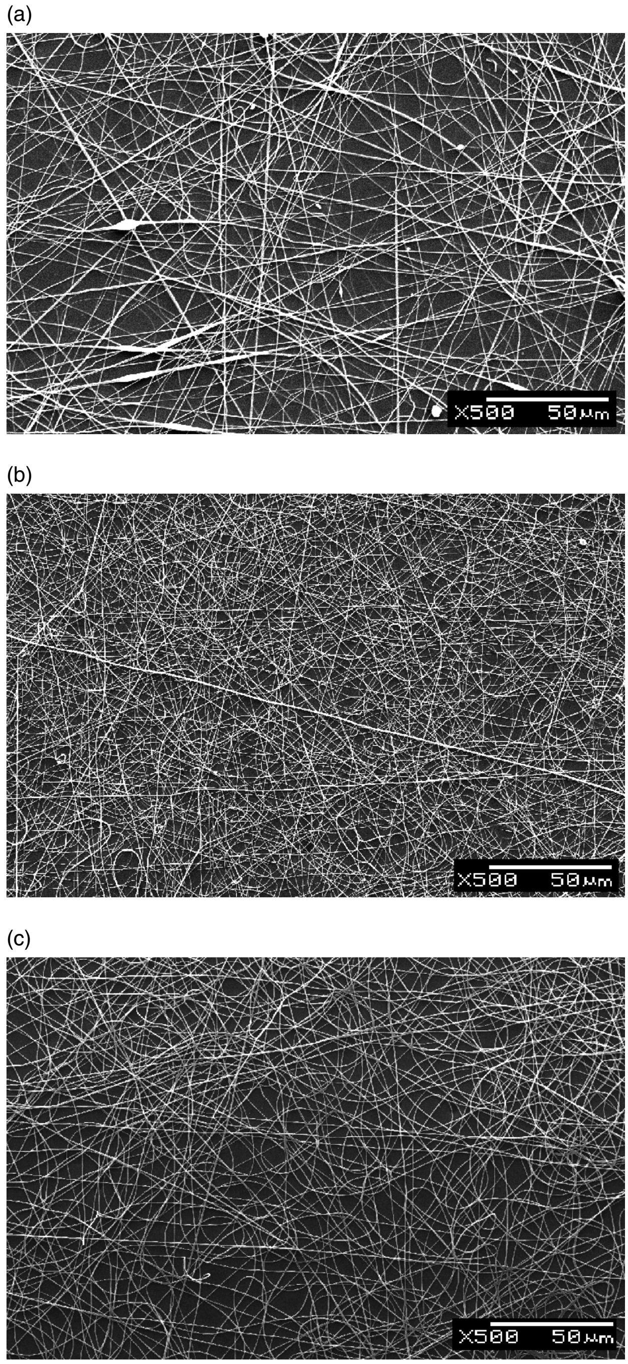

Figure 4. SEM micrographs of PBS electrospun products. The concentration was 14 wt% with (a) solution with no LiCl, (b) solution with 0.5wt% LiCl, (c) solution with 1 wt% LiCl, in the mixed solvent CF/CE (7/3 w/w) with all other conditions being equal.

CONCLUSIONS

The effects of solvents, weight concentrations and salt additives on the number and morphology of beads in electrospun products were studied in this work. The results showed that the three parameters could affect the number of beads and the efficiency of the electrospinning process. Controlling the concentrations of polymer solutions and salt additives could prevent beads from occurring in the electrospinning process, and solvents could also affect the number and morphology of beads and also the size of the electrospun fibers.

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