Effects of Polymer Concentration and Cationic Surfactant on the Morphology of Electrospun Polyacrylonitrile Nanofibres

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PAN nanofibres were prepared via an electrospinning process. The effect of polymer concentration on the fibre morphology was studied. At a very dilute solution, no fibres were obtained in the electrospinning process. As the concentration increased, the fibre morphology evolved from a beads-on-string structure to a uniform fibre structure with increasing fibre diameters. However, when the same electrospinning process was conducted with the addition of a cationic surfactant, the formation of disconnected beads was prevented, and the number of beads-on-string structures reduced significantly. In addition, the presence of cationic surfactant reduced the average diameter of the electrospun PAN nanofibres.

KEY WORDS: PAN nanofibre; Electrospinning; Fibre morphology; Cationic surfactant

1. Introduction

Electrospun polyacrylonitrile (PAN) nanofibres have received much attention recently because of their potential applications as precursors for making ultrafine carbon nanofibres[11-4], Tubes-by-fiber templates (TUFT) for preparing metal nanotubes[5], matrices for carbon nanotube reinforced fibres[6,7] and nanocomposite materials[8,9], as well as catalyst carriers for chemical reactions[10], etc. These applications require the fibres are as fine as possible, so that the fabrics have high surface to volume ratio and small pore size. In addition, reducing the fibre diameter could improve the fibre mechanical properties. For example, the strength of a carbon filament increases as the diameter decreases[11].

Methods for reducing fibre diameter in the electrospinning process include adjusting the operating parameters[12] and lowering the polymer concentration[13-18]. Although electrospinning lower concentrations of polymer solution usually produces finer fibres, beads or beads-on-string structures often occur if the concentration is too dilute[14,10]. The formation of beads in the dilute solution is attributed to the low solution viscosity[16,17]. However, there has not been a well established theory to predict the concentration level at which the fibre beads would appear[18].

In our previous research[19], we have proved that the formation of beads-on-string structure in the electrospun polystyrene comes from a low charge density of jet that stops the filament from being stretched fully into homogeneous fibres, and that the addition of cationic surfactants can effectively prevent the formation of beaded fibres in the electrospinning process. However, it is not clear if this method applies to the PAN system, especially for dilute polymer solutions.

In this paper, the effect of polymer concentration on the morphology of electrospun nanofibres and the effectiveness of a cationic surfactant to stop the formation of beads in the electrospinning process have been investigated.

2. Material and Experimental

The PAN, DMF and dodecyltrimethylammonium bromide (DTAB) were obtained from Aldrich, and were used as received. The viscosity and conductivity were measured with a digital rotational viscometer (D443 Rheology International) and a conductivity meter (LF330 Merck), respectively. The morphology of the electrospun fibres was observed under a scanning electron microscope (SEM, LE01530 microscope). The average fibre diameter and bead size were calculated from the SEM photos, with the aid of an image processing software (ImagePro plus 4.5).

The electrospinning unit used for this work is shown in Fig. 1. A high voltage was applied to the polymer solution via a metal syringe needle. A ground aluminum sheet was placed about 15 centimetres away from the tip of the needle. The electrospinning experiments were conducted under ambient temperature, with 1.5 kV/cm of applied electric field and 1.0 ml/h of polymer flow rate.

3. Results and Analysis

The effect of PAN concentration on the fibre mor-
SEM images of fibres electrospun from different concentrations of PAN solution (a) 2%, (b) 3%, (c) 4%, (d) 5%, (e) 6%, (f) 7% (w/v)

Average diameter of nanofibre electrospun from the PAN/DMF solution

SEM images of PAN fibres electrospun with the presence of DTAB (5 mg/ml). PAN concentrations are (a) 2% (w/v) and (b) 3%

Fig.3 Average diameter of nanofibre electrospun from the PAN/DMF solution

Fig.4 SEM images of PAN fibres electrospun with the presence of DTAB (5 mg/ml). PAN concentrations are (a) 2% (w/v) and (b) 3%

Phenology is illustrated in the SEM images as shown in Fig.2. At a dilute solution (2%, w/v), no continuous fibres except for beads and bead assemblage structures were obtained. The average bead size was measured to be about 1.18 μm with a narrow size distribution (standard deviation, 0.035). As the polymer concentration increased, the beads turned into a beads-on-string structure. Compared to the disconnected beads, these beads had smaller size. The bead number reduced with the increase in polymer concentration, but bead size increased slightly. Such beads-on-string structures remained until the concentration reached 5% (w/v). Further increasing the polymer concentration resulted in the formation of homogeneous fibres of larger diameters. Similar morphology changes were also observed for other polymer systems[16,20–22].

As shown in Fig.3, the as-spun PAN fibres have relatively narrow diameter distributions (i.e. small error bars) when the polymer concentration is less than 8%. However, higher concentrations increased the spread of fibre diameters. It is also worth noting that the fibre diameter was slightly decreased when the concentration was in the range of 6–8%.

When a small amount of DTAB (5 mg/ml) was added to the dilute PAN solutions, the same electrospinning process produced fibres with a different morphology. No individual beads, but the beads-on-string structure was produced even for a very dilute PAN solution (1% w/v). Although the beads-on-string structure appeared in the same concentration range as in the normal PAN solution (2–5%), the bead size was reduced considerably, from 500–900 nm to 150–300 nm. In addition, the fibre diameter was decreased as well, as shown in Figs.3 and 4.

The effect of PAN concentration on the solution viscosity was shown in Fig.5. For dilute solutions, the viscosity value increased slowly with the increase in polymer concentration. When the PAN concentration reached 4%, the rate of increase began to increase
The conductivity value increased by 42 \( \mu \)S/cm when PAN concentration was increased from 1% to 11%. This can be explained by the existence of a strong polar group, nitrile group, in every repeat unit of PAN. When the surfactant was added into the polymer solution, the conductivity was improved significantly. However, increasing the PAN concentration caused a reduction in the conductivity, as shown in Fig.6. This decrease in the conductivity could be attributed to that the polymer linkages restricted the movement of surfactant ions in the solution.

4. Discussion

The formation of disconnected beads in electrospinning of an extremely dilute polymer solution is often called electrospaying\[^{23,24}\]. This has been explained by that the viscoelastic force in the jet is too small to hold the fibrous structure. The jet gets dissociated into individual charged sections, and these sections turn into droplets due to the action of surface tension. With the evaporation of solvent, the droplet reduces its size and the charge density increases on the surface of droplet. The droplet could further split into smaller droplets due to higher electrostatic repulsion.

As the polymer concentration increases, the solution viscosity is increased. The jet under the higher viscoelastic force is more difficult to be broken into individual sections of beads during electrospinning. Instead, the electrostatic repulsion amongst the like-charged sections elongates the thin 'links' between the sections to even thinner filaments. As a result of the orientation of the macromolecular polymer, these filaments become hyper-stabilized as the elongation continues. Meanwhile, the relatively thick sections get stretched thinner as well, but to a less extent than the 'links'. Under the action of surface tension, they tend to take the shape of a droplet or bead. With the evaporation of the solvent, an apparent beads-on-string structure is thus formed. Further increasing the solution viscosity provides larger viscoelastic force to resist rapid changes in shape. This allows more uniform stretching, resulting in a continuous and homogeneous fibre structure.

It has been well established that the solution viscosity is highly dependent on the intermolecular interaction of polymer. Generally, in a dilute polymer solution, the intermolecular distance is so large that the intermolecular interactions are very weak. The intermolecular interactions become predominant gradually with the increase in polymer concentration. At a certain concentration, \( c^* \), the domains of the polymer molecules begin to overlap and eventually an entanglement may develop. Thus, \( c^* \) is a critical concentration to distinguish whether an obvious intermolecular interaction happens in the polymer solution. The higher concentration regime, which was named as semi-dilute, is characterized by the intermolecular interaction and eventual entanglements\[^{25}\].

The \( c^* \) value for the studied PAN/DMF system was estimated, based on the change of viscosity, to be about 5%. It is reasonable to assume that the formation of smooth and homogeneous fibres could come from the concentration range within which intermolecular interaction or certain entanglement appears. This suggests that the homogeneous fibre could be electrospun mainly in the semi-dilute solution, which is in accordance with the experiment observation. Gel particles could appear in a higher concentration of polymer solution, which could cause unevenness in fibre diameters.

In the electrospinning process, charges on the surface of jet interact with the external electrical field, besides repulsion within the jet. The jet thus becomes instable and experiences a whipping process, stretching itself thinner. The increase in solution conductivity suggests that the net charge density of the jet is increased\[^{26}\]. With a higher conductivity, the jet gets stretched under stronger forces. The fact that the fibre diameters decreased for the 7-8% PAN solution could be explained by that the jet was stretched under larger forces due to the improvement in conductivity.

When the cationic surfactant was added to the PAN solution, the net charge density was improved largely. For the dilute PAN solutions, only a small amount of DTAB (5 mg/ml) could improve the solution conductivity by more than three times. The improvement in the conductivity did stop the formation of disconnected beads, but it could not eliminate the beads-on-string structure from the electro-
spun fibres. However, the addition of DTAB reduced both the bead size and fibre diameter, which suggests that the elimination of beaded fibres may be possible through a more effective ionic additive in the polymer solution.

5. Conclusion

(1) The beads or beads-on-string structures are formed when electrospinning dilute PAN solutions. Homogeneous electrospun fibres can be produced from a semi-dilute polymer solution.

(2) The addition of a small amount of cationic surfactant not only reduces the number of beads and beads-on-string structures in electrospinning PAN solutions, it effectively reduces the average diameter of the electrospun fibres as well. A more effective surfactant may be able to eliminate the beads completely.

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