Electrospinning of Polymethyl Methacrylate Nanofibres in Different Solvents

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ABSTRACT

Electrospinning is one of the most popular techniques for generating fibres with the diameters ranged from tens of nanometers to several micrometers. The properties of as-spun nanofibres including crystallizability, mechanical performances, and biofunctioning are controlled and affected by several parameters, e.g., electrospinning solvent, temperature, humidity, and polymer characteristics. In order to re-verify the theory that the morphology of electrospun nanofibres is influenced by solvents used to dissolve polymer, the present study was carried out in which polymethyl methacrylate (PMMA) was chosen as the solute and processed into nanofibres by means of electrospinning. Seven solvents were separately used to dissolve PMMA at the concentration of 0.06 g/mL. As a result, ring-like, bead-like, ultrafine, and nano-porous nanofibres were generated from PMMA solutions by electrospinning. Because all solvents used in this study dissolved PMMA readily, the different morphologies were not due to their abilities to dissolve PMMA, but rather due to other properties such as boiling points, molecular weight, and molecular structure. Therefore, ring-like PMMA fibres was obtained due to the high boiling point (110°C) and stereo-hindrance effect of toluene. Bead-like nanofibres were generated from PMMA/chloroform and PMMA/dichloromethane solutions. Moreover, two kinds of ultrafine nanofibres were produced through electrospinning of PMMA/1,1,1,3,3,3-hexafluoro-2-propanol, and PMMA/2,2,2-trifluoroethanol solutions.

INTRODUCTION

Electrospinning is a technique that utilizes electric force alone to drive the spinning process and to produce polymer fibres from solutions or melts \cite{1-5}. Unlike conventional spinning techniques (e.g., solution- and melt-spinning) which are capable of producing fibres with diameters in micrometer scale, electrospinning is capable of producing fibres with diameters in nanometer range. Electrospun polymer nanofibres possess many extraordinary properties including small diameters and the concomitant large specific surface areas, a high degree of structural perfection, and the resultant superior mechanical properties. Additionally, the non-woven fabrics (mats) made of electrospun polymer nanofibres offer a unique capability to control the pore size among the nanofibres. Unlike nanorods, nanotubes, and nanowires that are produced mainly...
by synthetic bottom-up methods, electrospun nanofibres are produced through a top-down nano-manufacturing process which results in continuous and low-cost nanofibres that are also relatively easy to align, assemble, and process into final applications [3].

In the electrospinning process, a high electric field is applied to polymer solution which is held in plastic syringe with a capillary needle. An electric force caused by mutual charge repulsion acts opposite to surface tension [3,6]. When the electric field is high enough, the polymer solution in the tip of the capillary needle elongates and forms a cone, known as Taylor cone. A critical value of the electric field exists for which the repulsive electrical force overcomes the surface tension. The polymer solution could generate a charge jet from the tip of the Taylor cone when a critical value is reached. As the jet accelerates and thins in the electric field, radial charge repulsion results in splitting of the primary jet into multiple filaments [6].

The number of publications on electrospinning has increased dramatically during the past decade, focusing on the morphologies of nanofibres. The morphology of electrospun nanofibres is affected by many factors, such as needle diameter, polymer concentration, electrospinning voltage, etc. [6,7]. For example, low polymer concentration and thin needle diameter may produce bead structure fibres, whereas high concentration can lead to larger fibre diameter, and the latter tends to decrease with increasing electrospinning voltage, although its influence is not as great as that of the polymer concentration. Beside these criteria, the electrospun solvent is also a major determining factor which affects fibre morphology [8-12].

It is well known that the solution properties strongly depend on the components of polymers and solvents. In general, the original properties of solvents such as boiling point, viscosity, surface tension, conductivity, solubility parameter, dielectric constant, etc., affect the ultimate property of polymer solutions. Based on the theoretical analysis and experimental studies carried out by Liu et al. [13] it has been revealed that beads-like nanofibre structure strongly depends upon type of solvent, weight concentration, and presence of a salt as additive. It was also reported that either a suitable weight concentration or a proper salt additive can completely prevent the occurrence of beads in the electrospinning process and solvents may have effect on the number of beads and the morphology of electrospun fibres.

In order to re-verify the conclusions made by Liu et al. [13] some experiments were conducted for testing the solvents effect on the morphologies of electrospun polymers. PMMA was selected to dissolve separately in seven different solvents (acetone, chloroform (CH<sub>3</sub>Cl), dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), tetrahydrofuran (THF), toluene, 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), and 2,2,2-trifluoroethanol (TFE)) to make clear solutions, and then these solutions were processed by electrospinning. The morphologies of the produced nanofibres were observed by scanning electron microscopy (SEM) and explained by theoretical analysis.

**EXPERIMENTAL**

**Materials**

PMMA (M<sub>w</sub> =350000) was purchased from Sigma-Aldrich (USA). Seven solvents of acetone, CH<sub>3</sub>Cl, CH<sub>2</sub>Cl<sub>2</sub>, THF, toluene, HFIP, and TFE of analytical research grades were obtained from Darui Finechem Co. Ltd. (China). Each solution was used without further purification to dissolve PMMA at room temperature with sufficient stirring where the concentration of PMMA in electrospinning solution was 0.06 g/mL.

**Electrospinning**

The experimental set-up used for conducting electrospinning is schematically shown in Figure 1. The setup included a high voltage power supply (BGG DC high-voltage generator) purchased from the BMEI Co. Ltd. (Beijing, China) and a digitally controlled and extremely accurate syringe pump (789100C, Cole-Palmer, USA). During electrospinning, a positive high voltage of 20 kV was applied at the tip of a syringe needle of 0.9 mm inner diameter. The electrospun nanofibres were collected on a piece of aluminium foil placed at a distance of 15 cm below the tip of the syringe needle. The mass flow rate was...
RESULTS AND DISCUSSION

To examine the quality of solvents for dissolving PMMA, we cited a general rule which had been mentioned in Pattamaprom et al. study [14]. The calculation of chi parameter ($\chi$) for polystyrene solution produced from each solvent was carried out according to eqn (1):

$$\chi = \left(\delta_s - \delta_p\right)^2 \frac{M_s}{RT\rho_s} + 0.34$$  \hspace{1cm} (1)

The chi parameter ($\chi$) shows the degree of solvent/polymer compatibility for which $\chi$ of less than 0.5 represents favourable solvents and above 0.5 shows unfavourable polymer-solvent interactions and therefore the solvent is not able to dissolve the polymer. It is also a classical theory that, the lower value of $\chi$ in a polymer solution system indicates the better solvent for the dissolved polymer. The solvents used in this study can be evaluated by eqn (2):

$$\chi = \left(\delta_s - \delta_p\right)^2 \frac{M_s}{RT\rho_s}$$  \hspace{1cm} (2)

where the subscripts s and p denote solvent and polymer, respectively. The solubility parameter ($\delta$) and the density ($\rho$) were determined at an absolute temperature $T$. $M_s$ is the solvent molecular weight and R is the universal gas constant. Also in the study by Pattamaprom et al. [14], it is found that the general rule has some exceptions as it does not compare each

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Chemical formula</th>
<th>$T_b$ (°C)</th>
<th>$\eta$ (g cm$^{-3}$)</th>
<th>$\delta$ (MPa$^{1/2}$)</th>
<th>$\chi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>C$_6$H$_5$CH$_3$</td>
<td>111.0</td>
<td>0.82</td>
<td>18.2</td>
<td>0.03</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>CH$_2$Cl$_2$</td>
<td>40.0</td>
<td>1.33</td>
<td>19.7</td>
<td>0.02</td>
</tr>
<tr>
<td>Tetrahydrofuran (THF)</td>
<td>C$_4$H$_8$O</td>
<td>66.0</td>
<td>0.87</td>
<td>19.5</td>
<td>0.01</td>
</tr>
<tr>
<td>1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP)</td>
<td>C$_3$H$_2$OF$_6$</td>
<td>59.0</td>
<td>1.60</td>
<td>20.0</td>
<td>0.04</td>
</tr>
<tr>
<td>Acetone</td>
<td>C$_3$H$_6$O</td>
<td>56.0</td>
<td>0.78</td>
<td>20.0</td>
<td>0.03</td>
</tr>
<tr>
<td>Chloroform</td>
<td>CHCl$_3$</td>
<td>62.0</td>
<td>1.47</td>
<td>19.0</td>
<td>0.00</td>
</tr>
<tr>
<td>2,2,2-Trifluoroethanol (TFE)</td>
<td>C$_2$H$_3$OF$_3$</td>
<td>73.6</td>
<td>1.38</td>
<td>22.5</td>
<td>0.32</td>
</tr>
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</table>
type of secondary forces individually. For example, DMF and nitrobenzene could dissolve polystyrene at all concentrations even though the $\chi$ parameter is much higher than 0.5. Therefore, the general rule is only a relative estimated standard for polymer solutions. Some basic properties of these solutions (boiling point, density, viscosity, and solubility parameter) are summarized in Table 1. The solubility parameter of PMMA was set as 19.0.

**Effect of Solvent Properties and Functionality**

In order to explain the effect of solvents on the morphology of the as-spun fibres, analysis of all forces acting on a small segment of a charged jet is necessary. As it is described in the study by Jarusuwannapoom et al. [15], six types of acting forces may be considered; (1) body or gravitational force, (2) electrostatic force which carries the charged jet from the spinneret to the target, (3) Coulombic force which tries to push apart adjacent charged carriers being present within the jet segment and is responsible for the stretching of the charged jet during its flight to the target, (4) viscoelastic force which tries to prevent the charged jet from stretching, (5) surface tension which also acts against the stretching of the surface of the charged jet, and (6) drag force from the friction between the charged jet and the surrounding air. Among these forces, because gravitational force, electrostatic force, and drag force between charged jet and air are generally the same for each solvent used in electrospinning, only forces due to the Coulombic, the viscoelastic, and the surface tension are responsible for the formation of nanofibres morphology during the electrospinning processes from needle end to the target.

As shown in Table 1, the values of $\chi$ for each solvent was lower than 0.05, therefore, it is reasonable to understand that all the solvents used in this research showed favourable interactions with PMMA. However, as depicted in Figures 2-8, the morphologies of PMMA electrospun materials are different. There are four kinds of morphologies present as: ring-like particles, bead-like nanofibres, ultrafine nanofibres, and nanofibres with surface porosities.

**Ring-like Particles**

Toluene was able to dissolve PMMA of 0.06 g/mL concentration within 1 day. For the solubility parameters of both PMMA and toluene being close to each other, toluene easily dissolves PMMA and form a uniform solution. However, it is noted that toluene has a relatively high boiling point of 111°C, which could force some solvents out of the system at the time of electrospinning of PMMA. But, toluene molecule has a phenyl group, which might inhibit PMMA chains to elongate during the electrospinning process because of the stereohindrance effect of the phenyl groups and instead, PMMA is easily coagulated. Therefore, as shown in Figure 2, a ring-like shape of PMMA has been obtained on the collecting plate. Also, the PMMA electrospun filaments from this solution system have declined to bind with each other and have produced a honeycomb structure.

**Bead-like Nanofibres**

PMMA was dissolved in CH$_2$Cl$_2$ and CHCl$_3$ within a day. The two non-polar solvents have similar properties of solubility parameters and relative density. As universal polymer solvents, they were used for both research and industrial production. In this work, we have focused on the ability to dissolve PMMA to generate nanofibres by electrospinning. As shown in Figures 3-5, bead-like nanofibres are fabricated. Several researchers have investigated this kind of nanofibres, and given some reasonable explanations. Lee et al. [7] reported that the bead-like nanofibres would be electrospayed at low
concentration, whereas the process of ultrafine nanofibre formation, known as electrospinning, is favoured at high concentration. Furthermore, the low boiling point solvents such as of CH$_2$Cl$_2$ (40°C) and CHCl$_3$ (62°C) undergo rapid evaporation after the splaying and splitting of an unstable jet. The results of rapid evaporation have led to a porous appearance as shown in the inset images of Figures 3 and 4.

As evident in Figure 6, electrospun PMMA from TFE solution shows a porous surface. However, there is no bead-like nanofibre shown in the image. Moreover, the pore structure is different from the nanofibres observed in Figures 3 and 4. It is clear to see that both the pores in bead-like nanofibres are rounded, while the pores on the TFE solvent electrospun nanofibres are dimple-shapes.

**Ultrafine Nanofibres**

In this work, ultrafine nanofibres were defined as nanofibres with smooth surface and fine fibre structure without other types of blemishes. In Figures 7 and 8, there are two kinds of ultrafine PMMA nanofibres; nanofibres electrospun from PMMA/HFIP solution blend and nanofibres produced from THF which are generally uniform and similarly straight lines.

In electrospinning, the traveling jet solidifies through solvent evaporation and the solidified jet turns into a nanofibre. The solvent evaporation during...
Electrospinning occurs under special conditions including (1) the jet of micron- or submicron-scaled diameter, (2) the jet carrying excess charges, and (3) the solvent(s) evaporate under the influence of a strong electric field. This would result in abnormally fast evaporation of solvents during electrospinning. Nonetheless, the volatilities of solvents still significantly affect the solidification process, and further influence the morphologies of the electrospun nanofibres. The bent PMMA nanofibres might be the result of low volatility of solvent. As HFIP has a relatively high molecular weight it results in incomplete evaporation of HFIP molecules from the needle point to the collecting plate of the electrospun processing site.

CONCLUSION

The aim of this study was to investigate the potential fabrication of different nanofibre morphologies from PMMA solutions by electrospinning. Three kinds of nanofibres including bead-like, ring-like and ultrafine nanofibres were successfully made from seven different PMMA solutions. Moreover, the present study also re-verified Liu et al. [13] theory, which is said that beads-like nanofibres strongly depend upon the properties of solvents. There are several usages for the nanofibres with porous surfaces. For example, these nanofibres may serve as an invisible coating device (e.g., stealth plane, which is black to radar waves). As He et al. [16] have shown that in case of \(0.1 < \frac{d}{k} < 10\), where \(d\) is the diameter of the nanofibres, \(k\) is the wavelength of a radiation which is absorbed. In addition, nanofibres with porous surfaces also could be used as tissue engineering scaffold, because nanopores provide relatively large surface areas for cells to adhere and benefit nutrition to penetrate.

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