Preparation and Characterization of Electrospun Poly(butylene succinate-co-butylene adipate) Nanofibrous Nonwoven Mats

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Abstract - Nanofibrous mats of poly(butylene succinate-co-butylene adipate) (PBSA) were prepared by electrospinning PBSA solutions in methylene chloride (MC) and MC / (N,N-dimethylformamide) (DMF) mixtures. The morphology and the thermal properties of the electrospun mats were investigated by scanning electron microscopy (SEM), wide angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC). Results showed that the addition of 20-30 %v/v DMF led to denser, more uniform and without beads PBSA mats, with nanofibres average diameter ranging between 450 to 550 nm. The fibres morphology was also improved with increasing concentration and voltage. WAXD and DSC analysis showed a reduction in crystallinity and the thermal properties of the electrospun nanofibres, as compared to the raw material.

I. INTRODUCTION

Electrospinning has gained much attention in the last decade not only due to its versatility in spinning a wide variety of polymeric fibres but also due to its consistency in producing fibres in the submicron range [1]. This technique has been developed since patented by Formhals in 1934 [2]. In electrospinning, the spinning of fibres is achieved primarily by the tensile forces created in the axial direction of the flow of the polymer by the induced charges in the presence of an electric field, as has been quite well described by other studies [1,3-5].

The manufacturing of fibrous polymeric mats, with diameters in the range from several to hundreds of nanometers, is of considerable interest for various applications, such as filtration, nanocomposites and tissue engineering [1,6,7]. The morphology of electrospun fibres depends on many factors such as (a) solution properties including solvent volatility, concentration, viscosity, surface tension and conductivity, (b) process parameters including applied voltage, flow rate, nozzle-collector distance, and (c) electrospinning environment including relative humidity and temperature [1].

To date, electrospinning has been applied for nanofibre production of numerous polymer solutions, such as poly(ethylene oxide) in water [8], polyacrylonitrile in DMF [9], poly(vinyl alcohol) in water [10], poly(vinylidene fluoride) in DMF/acetone [11], poly(trimethylene terephthalate) in MC/trifluoroacetic acid [12], polyurethane in DMF [13], and so on. In addition, aliphatic polyesters such as poly(ε-caprolactone) (PCL) [14,15], poly(lactic acid) (PLA) [16,17], poly(glycolic acid) (PGA) [18] and their copolymers [18,19] have also been processed by electrospinning to generate nanofibres. However, there is no study regarding the use electrospinning for the development of biodegradable nanofibrous mats of aliphatic polyesters made from dicarboxylic acids and diols, such as poly(butylene succinate) (PBS), poly(butylene adipate) (PBA) and their copolymers (PBSA).

Hence, the aim of the present work was the development of biodegradable poly(butylene succinate-co-butylene adipate) (PBSA) electrospun mats with potential applications both as filters, and fiber mats serving as reinforcing component in composite systems. In particular, the effect of parameters, including polymer concentration, solvent and applied voltage on the morphology, crystallinity and thermal properties of the electrospun nanofibres was evaluated.

II. EXPERIMENTAL

The commercial polyester Bionolle 3001 with an inherent viscosity of 1.15 dlv/g was purchased by Showa Highpolymer Co., Ltd (Tokyo, Japan). Bionolle 3001 is a copolyester of succinic acid (S), adipic acid (A), and 1,4 butanediol (B) with a composition ratio 40/10/50, respectively. The number average molecular weight (Mn) of Bionolle 3001 was 101300, as determined by gel permeation chromatography (GPC). Methylene chloride (MC) and N,N-dimethylformamide (DMF) were obtained from Fluka.

The concentration of the polymer solutions used for electrospinning was 5, 10 and 15 wt% in four mixing solvent systems with MC/DMF ratios of 100/0, 90/10, 80/20 and 70/30 (v/v). The schematic diagram of the electrospinning device that was used for nanofibres manufacturing is shown in Fig.1.

![Fig. 1 Schematic diagram of the electrospinning apparatus.](image-url)
The polyester solution was placed in a 10 ml glass syringe equipped with a 0.8 mm (21 G) needle. The flow rate of polyester solution was controlled by a syringe pump at 1 ml/h. The fibres were collected on an aluminum-covered rotating drum (Fig. 2), which was grounded and controlled by a motor. The distance between the capillary tip and the collector was 9 cm and the applied voltage was ranged between 5-20 kV.

![Image](318x647 to 409x714)

**Fig. 2** Example of PBSA electrospun sheet on the drum.

The morphology of the electrospun fibres was examined using a SEM microscope (JEOL, model JSM-840A). Prior to the analysis, the samples were coated with graphite to avoid charging under the electron beam. The average diameter and the diameter distribution were obtained by using a custom image analysis program to analyze the SEM micrographs. WAXD measurements were carried out with a four-circle diffractometer (Siemens Karlsruhe; 40 kV and 30mA) with CuKα radiation (λ = 1.5402 Å). Glass transition temperature (Tg), melting point (Tm) and heat of fusion (∆Hf) were measured using a Shimadzu DSC-50Q analyzer equipped with a liquid nitrogen-cooling accessory. Indium was used as the calibration standard. A heating rate of 10 °C/min was applied and polymer samples of 6-8 mg were heated under a nitrogen flow of 20 ml/min.

**III. RESULTS AND DISCUSSION**

**A. Electrospinning processing parameters**

SEM micrographs of electrospun nanofibres from 10 wt% PBSA solutions in mixed solvents with MC/DMF ratios ranging between 100/0-70/30 (v/v) at 15 kV are given in Fig. 3. As seen from Fig. 3 (a), big spherical and spindle-like beads, 1-8 μm, as well as thin fibres with average diameters ~215 nm are formed when MC was used as solvent. When 10 %v/v DMF was added (Fig. 3 (b)), fewer, smaller (<5 μm) and more spindle-like beads, in combination with thicker fibres with average diameter ~410 nm are seen. As the amount of DMF increased to 20-30 %v/v, the bead morphology was totally disappeared, while a denser web of fibres was generated. The fact that the solution in pure MC led to bead morphology is probably attributed to its low concentration, and thus, its low viscosity [20]. As it is already known, below a critical concentration, chain entanglements are insufficient to stabilize the jet, leading rather to electrospraying of droplets than electrospinning of fibres [17,21,22]. Thus, with the addition of a nonsolvent for PBSA, as DMF, everyone would expect an increase in the solution viscosity, which leads to less beads and more uniform fibres. Indeed, as the amount of DMF increased, the bead morphology gradually weakened, leading to a pure electrospun mat. Another factor, which contributed to the improvement of electrospinning procedure with DMF addition, is its electrical properties.

![Image](435x647 to 526x633)

**Fig. 3** SEM micrographs of electrospun fibres from 10 wt% PBSA solution in a) MC, b) MC/DMF (90/10), c) MC/DMF (80/20), and d) MC/DMF (70/30). Applied voltage 15kV.

According to Table 1, DMF shows higher dielectric constant and dipole moment than MC, and this could facilitate the formation of ultrafine fibres [11]. In the literature, many researchers use ionic salts in order to increase the solution conductivity, obtaining beadless and uniform fibres [1,10]. Therefore, it can be regarded that both, electric properties of DMF and the fact that it is a nonsolvent for PBSA, enhanced significantly the quality of the nanofibres.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dielectric constant&lt;sup&gt;1&lt;/sup&gt;</th>
<th>Electric dipole moment&lt;sup&gt;1&lt;/sup&gt; (D)</th>
<th>Viscosity&lt;sup&gt;1&lt;/sup&gt; (mPas)</th>
<th>Boiling point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MC</td>
<td>8.93</td>
<td>1.60</td>
<td>0.413</td>
<td>40</td>
</tr>
<tr>
<td>DMF</td>
<td>38.25</td>
<td>3.82</td>
<td>0.794</td>
<td>153</td>
</tr>
</tbody>
</table>

<sup>1</sup> [23]

Polymer concentration seems to be one of the most effective parameters, which determines the morphology of the electrospun fibres. The SEM micrographs of electrospun mats from different PBSA solutions ranging from 5-15 wt% in MC and MC/DMF (80/20) are given in Fig. 4. As seen in Fig. 4 (a-c), in case of MC solvent and for concentrations between 5-10 wt%, a mixture of large beads and nanofibres was generated, while for PBSA concentration 15 wt% well-defined fibres are observed. In particular, at 5 wt% concentration, big spherical-like beads 2-10 μm, in combination with very thin fibres (~140 nm) are seen. With increasing concentration from 5 to 10 wt%, the shape of the beads changed from big spherical to smaller, more spindle-like, while the diameter of the fibres became higher (~215 nm). Above the concentration of 10...
wt%, no beads were seen, while the average diameter of the fibres became thicker (~450 nm). In case of the mixture of MC/DMF (80/20) as solvent, beads were observed only at 5 wt%, while above this concentration, uniform nanofibres with average diameter ranging from 450-500 nm were seen.

Fig. 4 SEM micrographs of electrospun fibres from a) 5 wt%, b) 10 wt%, c) 15 wt% PBSA in MC, and d) 5 wt%, e) 10 wt%, f) 15 wt% PBSA in MC/DMF (80/20). Applied voltage 15kV.

SEM micrographs of PBSA electrospun fibres from 10 wt% solution in MC/DMF (80/20) at 5, 10, 15 and 20 kV are shown in Fig. 5. Results suggested that the average fibre diameter increased with increasing applied voltage. Electrospinning at low voltage of 5 and 10 kV resulted in fibre formation with beads, as seen in Fig. 5 (a,b).

Fig. 5 SEM micrographs of electrospun fibres from a 10 wt% PBSA solution in MC/DMF (80/20) a) 5 kV, b) 10 kV, c) 15 kV and d) 20kV.

Fine fibre morphology without beads was achieved at higher voltage of 15 and 20 kV. As seen in Fig. 5 (a), a narrow distribution of the majority of fibre diameters between 200-300 nm was observed at low voltage of 5 kV. At higher voltage the range of distributions became broader and ranging between 200-600 nm at 10-15 kV and 300-700 nm at 20 kV respectively.

B. WAXD and DSC analysis of electrospun fibres

The degree of crystallinity values, calculated by WAXD data of raw and electrospun PBSA nanofibres prepared from various solutions in MC/DMF, are shown in Table 2.

Table 2 Crystallinity and thermal properties of raw and electrospun nanofibres PBSA of 10 wt% solutions in various solvents mixtures.

<table>
<thead>
<tr>
<th>Solvent Mixtures</th>
<th>Crystallinity (XRD) (%)</th>
<th>Tg (°C)</th>
<th>Tm (°C)</th>
<th>ΔHf (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RAW</td>
<td>52.2</td>
<td>-38.8</td>
<td>96.9</td>
<td>41.2</td>
</tr>
<tr>
<td>MC</td>
<td>50.2</td>
<td>-39.0</td>
<td>94.4</td>
<td>39.0</td>
</tr>
<tr>
<td>MC/DMF (90/10)</td>
<td>46.2</td>
<td>-39.0</td>
<td>94.1</td>
<td>36.9</td>
</tr>
<tr>
<td>MC/DMF (80/20)</td>
<td>45.7</td>
<td>-39.5</td>
<td>93.1</td>
<td>35.5</td>
</tr>
<tr>
<td>MC/DMF (70/30)</td>
<td>43.4</td>
<td>-41.7</td>
<td>92.8</td>
<td>35.1</td>
</tr>
</tbody>
</table>

Suggestively, in Fig. 6 are given the WAXD pattern of raw and electrospun PBSA nanofibres prepared from 10 wt% solution in MC/DMF (70/30) mixture at applied voltage of 15 kV, as well as the method used for calculating the degree of crystallinity.

Fig. 6 WAXD patterns of raw and electrospun PBSA.

The degree of crystallinity was estimated by the area ratio of crystalline and amorphous peaks. According to these patterns, the molecules of both raw and electrospun PBSA crystallize in a monoclinic crystal lattice and the diffraction peaks from (111), (002), (012), (110), (121) and (111) crystallographic planes are observed at 19.3, 21.5, 22.3, 25.6 and 28.5° 2θ angle, respectively [24]. As seen from Fig. 6, even though the patterns presented the same reflections, the intensities of the peaks of the electrospun sample seem to be a slight weaker as compared
to those of the raw PBSA. This fact in combination with the lack of higher order reflections indicates that there is no drawing process in electrospinning, confirming the results of other studies [4,8,15]. Quite interesting is the observation that as the amount of DMF increased, the degree of crystallinity decreased as seen in Table 2. This reduction could be probably attributed to the viscosity increase with DMF addition, which means that electrospun nanofibres from viscous solutions present a less ordered structure. However another factor that should be examined is the nature of the added solvent by means of its volatility and electrical properties. Zong et al. [4] attributed the decrease of crystallinity to the high evaporation rate of the solvent, as the chains do not have enough time to form crystalline registration. According to our first results, the use of a less volatile nonsolvent does not seem to change this trend. The reduction of crystallinity with DMF addition is further confirmed by DSC examination. Electrospinning procedure seems to reduce the thermal properties of PBSA. As seen from Table 2, $\Delta H_m$ values for raw PBSA are -38.8$^o$/C, 96.9$^o$/C and 41.2 J/g respectively. The electrospun fibres from 10 wt% in MC presented lower values, while a more significant reduction is noticed for electrospun fibres produced from MC/DMF solutions. The decrease in $T_m$ and $\Delta H_m$ values of electrospun fibres is in good agreement with the WAXD examination and is attributed to the fact that the crystalline microstructure of the electrospun fibres is not well-developed [8]. As far as concern $T_g$, Zong et al. [4] attributed its decrease after electrospinning procedure, to the air which acts as plasticizer due to the large surface to volume ratio in nanofibres.

It seems that the results of both WAXD and DSC measurements are quite interesting; however, it is clear that a more thorough study in order to result in safe conclusions is required.

IV. CONCLUSIONS

The scope of our study was the development of biodegradable PBSA electrospun mats with potential applications in filtration and as reinforcing component in composite systems. Fiber morphology was strongly dependent on the solvent, concentration and applied voltage. It was shown that the addition of 20-30 %v/v DMF in MC solutions suppressed the beads and favored the formation of uniform nanofibres. In addition, high concentration and voltage led to denser web with increased nanofibres diameters. Typically, the results from this work indicate that uniform mats of nanofibres with an average diameter between 450-500 nm are prepared with the addition of 20-30 %v/v DMF in a solution of 10 wt. % PBSA at 15 kV voltage. Moreover, analysis of WAXD and DSC showed that the crystallization of PBSA was weakened by electrospinning, and the thermal properties decreased. This observation was more intense as the DMF amount in the solution increased.

Acknowledgements

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IV. REFERENCES