AN INVESTIGATION ON THE MOISTURE REGAIN AND MECHANICAL PROPERTIES OF ELECTROSPUN HYBRID YARNS INCLUDING POROUS POLY L LACTIC ACID AND POLY VINYL ALCOHOL NANOFIBERS

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Abstract

Producing the yarn from nanofibres is considered as one of the great potentials in electrospinning. These yarns can be used in various fields of medical applications such as surgery yarns and media for drug delivery. Among various polymers, biodegradable and biocompatible polymers such as poly (L-lactic acid) (PLLA) and poly(vinyl alcohol) (PVA) are of great interest due to useful biological properties. The goal of the study is to enhance the hydrophilicity of PLLA porous electrospun yarns. In this study, porous electrospun PLLA yarn, PVA electrospun nanofibers yarn and Hybrid yarns of PLLA/PVA (i.e. 0/100, 60/40, 80/20 and 100/0) were electrospun via two differently charged nozzles. Consequently, moisture absorbance and some mechanical properties such as strength, elongation and elastic modulus were assessed and compared with each other. The results showed that, increasing the hydrophilic PVA nanofibers content in various hybrid yarns could improve the moisture absorption of hybrid PLLA/PVA nanofiber yarns. Also some mechanical properties have not been influenced by different ratios of two parts in hybrid structure. Study on the surface morphology was carried out by SEM to determine the average fiber diameter existing in the hybrid PLLA/PVA yarns. SEM studies revealed the porous surface of PLLA nanofibers which was explaining the properties of hybrid PLLA/PVA nanofiber yarns.

Keywords: Hybrid yarns, electrospinning, nanofibers, regain, mechanical properties

INTRODUCTION

To blend some polymers together is an appropriate way to improve material properties, so scientists made effort to investigate the electrospinning possibility of polymer blends for medical applications [1]. Since, there is no common solvent for some polymers or it is difficult or impossible to electrospin of polymer mixture, another method has been used for electrospinning of polymer mixture, such as electrospinning of two polymer solutions simultaneously in a side-by-side style [2] and also using spinneret with two coaxial capillaries [3].

Some polymer solutions such as PVA in water and PLA in chloroform cannot form a stable bicomponent jet, because of different solvent evaporating rates [4]. Hence, multi jet electrospinning is another way to produce the nanofiber mixture. Herein, researchers modified the electrospinning system to produce the blend nonwoven mats including different types of nanofibers [1, 5-7].

Although PLLA is a safe biomaterial with properties appropriaing to use in tissue engineering and absorbable suture [8,9], it is a hydrophobic polymer [7]. Even though there are different methods to produce electrospun yarns [10-20], but no success has been reported about production of hybrid yarns including two types of electrospun nanofibers.

This study is based on increment hydrophilicity of PLLA porous electrospun yarn. For this purpose, hybrid yarns including of PLLA / PVA nanofibers with different blend ratio were electrospun, because PVA is hydrophilic polymer. The electrospinning apparatus used in this study was shown schematically in Figure 1. In addition, the effect of blend ratio of PLLA / PVA nanofibers on hygroscopic property and some mechanical properties has been investigated. Also, the surface morphological of these yarns was studied.
EXPERIMENTAL

Materials and polymer solution preparation

Poly(vinyl alcohol) (average molecular weight $\approx 72,000 \text{ g \cdot mol}^{-1}$; hydrolysis rate = 98%) was purchased from Merck and twice distilled water was used as its solvent. PLLA granules (average molecular weight $\approx 250,000 \text{ g \cdot mol}^{-1}$) were prepared from Boehringer Ingelheim company and Dichloromethane (DCM) was selected as its solvent. To prepare a PVA solution of 7.5 wt%, the PVA powder was added into doubled distilled water and was stirred vigorously at 90 °C for 2 hours, also to prepare PLLA/DCM solution with concentrations of 10wt%, the PLLA polymer granules were added into DCM and was gently stirred. After about one hour, PLLA dissolved in DCM.

Yarn production

As shown in figure 1, the twisted yarn is produced continuously. Each syringe can contain a type of solution. Two syringe pumps (STC-527; Terumo Corp., Tokyo, Japan) have been used to control the feeding rate of solutions. The electrospinning apparatus used in this study has been previously described in detail [17].

To produce the single component yarns of PVA and PLLA, each syringe must have the same solution and for production of hybrid yarns, one syringe contains PVA/distilled water and the other one contains PLLA/DCM solution. Hybrid yarns with different polymer ratio can be obtained by altering the feeding rate of solutions. The electrospinning conditions of these yarns have been shown in Table 1. The distance between the centers of two nozzles and take up unit as well as neutral plate are 22 cm and 5 cm, respectively. The optimal rate of production was 1.52 m/h and twist (rotation) per meter of yarn is 50 TPM. Also, the production has been carried out at the relative humidity of 55%±5 and room temperature.
Fig. 1 schematic illustration of yarn formation manner using two nozzles with opposite charges

Table 1. The optimum electrospinning conditions of single component yarns and hybrid yarns

<table>
<thead>
<tr>
<th>Sample</th>
<th>Voltage(kV)</th>
<th>PLLA Flow Rate (ml/h)</th>
<th>PVA Flow Rate (ml/h)</th>
<th>DN **(cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA</td>
<td>9.7</td>
<td>---</td>
<td>0.195</td>
<td>18</td>
</tr>
<tr>
<td>PLLA</td>
<td>9.5</td>
<td>0.34</td>
<td>---</td>
<td>24</td>
</tr>
<tr>
<td>PLPVI</td>
<td>10.7</td>
<td>0.29</td>
<td>0.2</td>
<td>20</td>
</tr>
<tr>
<td>PLPVII</td>
<td>10.4</td>
<td>0.37</td>
<td>0.15</td>
<td>18</td>
</tr>
<tr>
<td>PLPVIII</td>
<td>10.4</td>
<td>0.37</td>
<td>0.1</td>
<td>18</td>
</tr>
</tbody>
</table>

** Distance between nozzles

CHARACTERIZATION

PVA and PLLA ratio assessment in electrospun hybrid yarns

The dried weighed hybrid yarns containing PVA and PLLA were settled in dichloromethane in order to dissolve the PLLA part. Each sample was immersed two times with the time of 2 hours for each cycle. Afterwards the
remained yarn was dried for 10 hours in an oven at 50 °C. The percentage of each part can be calculated by the loss weight of yarn.

**Structural investigation**

The morphological properties of yarns are investigated with a Philips scanning electron microscope (XL-30). The measurement software is used to determine the fiber diameter in the yarn.

**Moisture regain assessment of electrospun yarns**

The yarns was dried in an oven at 45 °C for 10 hours, then weighed and conditioned for 24 hours in relative humidity of 65% and temperature of 20 °C. The samples were weighed and the regain moisture obtained using the following formula.

\[
\text{Moisture regain \%} = \frac{W - D}{D} \times 100
\]

Where, \(W\): weight (g) of the specimen after conditioning under standard conditions, and \(D\): weight (g) of dried specimen

**Mechanical properties of electrospun yarns**

After determining the yarn fineness, the samples were placed on a rectangular paper frame and assessed by the Zwick equipment (1446-60). The sample length between two gages was 2.5 cm with cross head speed of 60 mm/min.

**RESULTS AND DISCUSSION**

**PVA and PLLA ratio in hybrid yarns**

The mass percentage of each part of hybrid yarn could be theoretically calculated based on volumetric flow rate and concentration of polymeric solutions as well as the real ratio of each component measuring by immersing test. The results have been shown in table 2 indicating that although there is similar trend between real ratios and calculated ratios, there is difference between their values. One of the reasons for this difference is the using of same voltage for both solutions which implements inappropriate electrical forces on one of the solutions. Altering the voltage causes feeding rate changes. Another reasons for this dissimilarity is drop of PVA solution from tip of nozzle and fast drying of PLLA droplet (the boiling point of DCM is 40 °C).

<table>
<thead>
<tr>
<th>sample</th>
<th>Arithmetical weight ratio(PLLA/PVA)</th>
<th>Real weight ratio(PLLA/PVA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA</td>
<td>0:100</td>
<td>0:100</td>
</tr>
<tr>
<td>PLPVI</td>
<td>66:34</td>
<td>78:22</td>
</tr>
<tr>
<td>PLPVII</td>
<td>76:24</td>
<td>83:17</td>
</tr>
<tr>
<td>PLPVIII</td>
<td>82:18</td>
<td>88:12</td>
</tr>
<tr>
<td>PLLA</td>
<td>100:0</td>
<td>100:0</td>
</tr>
</tbody>
</table>
**Morphological study of single component and hybrid yarns**

Figures, 2a to 2d, show the SEM pictures of PVA and PLLA single component yarns as well as hybrid yarns, respectively. It must be noted that the average diameter of PVA nanofibers is 392±14 nm, whereas that of PLLA nanofibers is 1400±180 nm.

**Fig. 2** SEM images of nanofibers yarns (a) PVA (b) PLLA (c) PLPVI (d) PLPVII (e) PLPVIII

**Surface morphology of PLLA nano/ micro fibers**

Though the attempts were made to maintain stable conditions of electrospinning, e.g., using DCM as a solvent with boiling point of 40 °C and relative humidity of 55%±5, but the phase separation was occurred during electrospinning causing porosity on the PLLA surface [21] as shown in figure 3. This surface porosity leads to better wetting properties [7].
Moisture regain

One of the disadvantages of PLLA is the hydrophobicity, so the efforts have been done in order to produce hybrid yarns including different percentages of PVA fibers, so the moisture absorbance of yarn would be improved. Figure 4 shows the moisture regain results of single component and hybrid yarns. The number and power of hydrophilic groups in a macromolecule cause significant effect on yarns wettability. The powerful hydrophilic groups are hydroxyl (-OH), carboxyl (-COOH) and Amino cyanogen (-NH2) which links to the water molecules and improves the wettability of materials [7].

As can be seen in figure 4, increasing the PVA nanofiber ratio enhance the moisture regain of the yarns. Moisture regain of PLLA yarn is the minimum though it is the maximum for the PVA yarn, due to the hydrophilicity of PVA containing hydroxyl groups. Besides the low percentage of PVA nanofibers in hybrid yarn, moisture regain of hybrid yarn is significantly more than PLLA yarn.

![Fig. 3 SEM images (a) PLLA yarn (b) hybrid yarn](image)

![Fig. 4 Moisture regain of single component yarns and hybrid yarns](image)

The tensile properties of electrospun yarns

Table 3 shows the results of tensile properties of single component and hybrid yarns and figure 5 illustrates the stress-strength curve of these yarns.

The consequences specify the high elongation of PLLA yarns. One reason is the high rate of solvent evaporation in PLLA system, due to its low boiling point (DCM) causing fast drying of fluid jet, so it has no chance to be drawn by the bending instability, and makes the inner structure of fiber to be amorphous. An amorphous structure has high elongation.

One another reason could be related to the electrical conductivity of solvent. Therefore, Lower electrical conductivity decreased the charge density of the polymer solution or the jet and reduced the effect of drawing...
forces. As a result, lower conductivity increased the PLLA nanofiber diameter. The strength of such yarns due to the pores that are defects and serve as stress concentration points, decrease.

The statistical results (P-value < 0.05) clarify no significant difference among maximum strengths of hybrid yarns. Tensile properties of hybrid yarns with different ratios of PLLA/PVA show no major dissimilarity. By the other words, no changes in tensile properties can be seen with altering the PVA ratio in hybrid yarn. Except the elastic modulus, other properties of hybrid and PLLA yarns are varied. It should be noted that modulus and strength of hybrid yarns is in the range of those of PLLA yarns because of the lower ratio of PVA nanofibers in hybrid yarn.

<table>
<thead>
<tr>
<th>property</th>
<th>Number of tests</th>
<th>Specific Stress at F_max</th>
<th>Extension at F_max</th>
<th>E-Modulus</th>
</tr>
</thead>
<tbody>
<tr>
<td>sample</td>
<td></td>
<td>cN/tex</td>
<td>CV%</td>
<td>%</td>
</tr>
<tr>
<td>PVA</td>
<td>30</td>
<td>5.78</td>
<td>10.27</td>
<td>70.19</td>
</tr>
<tr>
<td>PLLA</td>
<td>30</td>
<td>2.23</td>
<td>9.74</td>
<td>172.9</td>
</tr>
<tr>
<td>PLPVI</td>
<td>30</td>
<td>1.81</td>
<td>8.41</td>
<td>42.07</td>
</tr>
<tr>
<td>PLPVII</td>
<td>30</td>
<td>1.79</td>
<td>24.47</td>
<td>67.8</td>
</tr>
<tr>
<td>PLPVIII</td>
<td>30</td>
<td>1.78</td>
<td>31.02</td>
<td>47.2</td>
</tr>
</tbody>
</table>

Fig. 5 Stress–strain behavior of nanofibers yarn (a) PVA (b) PLLA (c) PLPVI (d) PLPVII (e) PLPVIII

**CONCLUSION**

In this research hybrid yarns with different ratios of PLLA/PVA were electrospun using two opposed nozzles with different charges. The morphological study shows the porosity on PLLA nanofibers. The moisture regain of PVA, PLLA and hybrid yarns has been assessed to investigate the effect of PVA fibers on the hydrophilicity of hybrid yarn. The results show the increase in moisture regain with enhancing the PVA fibers in hybrid yarns due to the existence of OH groups in PVA macromolecules.

The modulus and strength of hybrid yarns is in the range of modulus and strength of PLLA yarns, because of the lower ratio of PVA nanofiber in hybrid yarn.

All the yarns produced in this study with biodegradable and biocompatible properties, has the potential to be used in medical applications; specially hybrid nanofibers, besides the low percentage of PVA nanofibers, show proper hydrophilicity. These yarns can be applied to weave the fabrics for tissue engineering, cell culture and absorbable stitches.
REFERENCES


