

## Effect of Fiber Structure on the Properties of the Electrospun Hybrid Membranes Composed of Poly( $\epsilon$ -caprolactone) and Gelatin

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**ABSTRACT:** To elucidate the effect of fiber structure on the properties of the electrospun gelatin/PCL hybrid membranes, three types of fibers with different structures, i.e., core-shell, blend, and mixed fibers were fabricated. The crystallinity, wettability, swelling degree, and mechanical properties of the hybrid membranes were compared. It was found that the crystalline characteristics of PCL in the core-shell fibers were different from the fibers fabricated by the other two methods. That is, the orientation degree of the PCL chains in the core-shell fibers was higher than that in both blend and mixed fibers. The wettability of the hybrid membrane was dependent on both the composition and structure of the electrospun fibers. Blended fibers exhibited the highest hydrophobicity because of the enrichment of PCL at the fiber surface. Contrarily, the mixed fibers possessed the highest mechanical strength of 3–5.18 MPa. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** electrospinning; fiber structure; hybrid membrane

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### INTRODUCTION

Within the last decade, electrospinning was widely utilized for fabricating fibrous membranes for various biomedical applications including tissue engineering, controlled release, wound dressing, etc.<sup>1</sup> The nanofibrous structure of the electrospun membranes essentially resembled the topography of extracellular matrix (ECM) and could promote the adhesion and proliferation of various cells.<sup>2</sup> Bioactive agents, such as small molecular drugs, growth factors, DNA, and even microorganisms, could be facilely integrated within the fibers.<sup>3–6</sup> This further broadened the bioapplication fields of the electrospun membranes. Up to now, there are numerous biopolymers successfully electrospun into fibers.<sup>7</sup> The electrospun membranes composed of biodegradable hydrophobic polymers, such as poly( $\epsilon$ -caprolactone) (PCL) and poly(L-lactide) (PLLA), always display robust mechanical property,<sup>8</sup> but lack of recognition cues for cell attachment.<sup>9</sup> In contrast, natural-occurring biomacromolecules, such as collagen and gelatin (Gt), could be electrospun into the fibrous membranes with inherent cell-binding domains. However, these membranes are mechanically fragile.<sup>10,11</sup> The combination of the two types of polymers to form hybrid fibrous

scaffolds is an effective strategy to circumvent the above limitations.<sup>12–14</sup> The hybrid membranes combine the advantages of biodegradable hydrophobic polymers and natural-occurring biomacromolecules, thereby having both high mechanical strength and excellent biospecific properties.

Hybrid fibrous membranes comprising of core-shell structured fibers (c-fibers), blended fibers (b-fibers), and unicomponent fiber mixtures (m-fibers) could be fabricated through various electrospinning techniques, namely coaxial electrospinning,<sup>15</sup> mixing electrospinning,<sup>16</sup> and blend electrospinning,<sup>17</sup> respectively. There were several biodegradable polymer pairs having been electrospun into hybrid fibrous membranes.<sup>12,14,18,19</sup> Among the evaluated polymer pairs, biodegradable polyester and Gt were the mostly studied,<sup>19–23</sup> possibly due to their cost-effectiveness, biodegradability, biocompatibility, and excellent electrospinnability. Polyester could enhance the mechanical strength of the hybrid membranes, while Gt could facilitate the cell adhesion.<sup>24</sup> The hybrid polyester/Gt membranes with various structures, such as core-shell fibrous structure and blend fibrous structure, have been prepared.<sup>21–23</sup> The effect of fiber composition on the membrane properties was reported.<sup>25</sup>

Although several electrospinning techniques are available for fabricating hybrid membranes, the electrospinning setups significantly varies from each other.<sup>25–28</sup> For example, mixing and blend electrospinning can be simply performed on uniaxial electrospinning apparatuses, while coaxial spinneret is essential for generating core-shell fibrous membranes. In addition, c-fibers could only be obtained by delicately optimizing processing parameters of coaxial electrospinning, while m-fibers and b-fibers could be generated over a relatively wide operation window. It is imperative that the two components used in blend electrospinning must be partially miscible in common solvents.

To elucidate the effect of fiber structure on the properties of the hybrid membranes, the crystalline characteristics, Gt swelling, wettability, and mechanical strength of the electrospun hybrid membranes prepared by different electrospinning methods were systematically compared in this study for the first time. The results revealed might also facilitate the selection of appropriate electrospinning setup for preparing hybrid membranes with desirable properties, especially the mechanical strength, to meet the needs of specific applications.

## MATERIALS AND METHODS

### Materials

PCL (Mn 150,000) was synthesized by ring opening polymerization of  $\epsilon$ -caprolactone at 140°C using stannous 2-ethyl hexanoate as a catalyst.<sup>29</sup> The molecular weight (Mn) of the product was determined by gel permeation chromatography (GPC) using tetrahydrofuran (THF) as a solvent. Gelatin (Gt, type A, 300 bloom) and bicinchoninic acid (BCA) were purchased from Sigma-Aldrich (Milwaukee, WI). Trifluoroethanol (TFE) was obtained from Xinyuan Chemical Corporation (Shandong, China) and used without further purification. Glutaraldehyde (GA, 25% aqueous solution) was supplied from Acros Organics (Geel, Belgium).

**Preparation of the Hybrid Membranes Composed of PCL and Gt**  
Fiber mixtures (m-fibers) were produced by using the apparatus described by Kidoaki et al.<sup>27</sup> with some modifications, i.e., the

two spinnerets were located at the opposite sides of the collector. Briefly, PCL (14 wt % in TFE) and Gt (12 wt % in TFE) were separately electrospun from opposite sides of the mandrel-type collector. The distance between the needles and the mandrel was adjusted to make sure that the two types of fibers were collected in the same area. The feed rate of Gt dope was fixed at 1 mL/h. Detailed electrospinning conditions have been summarized in Table I.

The polymer solution with concentration of 10 wt % was prepared by codissolving PCL and Gt in TFE and stirred for 48 h at room temperature. The solution was electrospun using a man-made electrospinning setup to generate blend fibers (b-fibers).<sup>21,30</sup>

The core-shell structured fibers (c-fibers) were fabricated by the procedure described previously.<sup>21</sup> The two liquids were independently fed through concentrically configured needles with their bevels previously blunted to facilitate the formation of a stable jet. The inner diameters of the needles were 0.9 and 0.57 mm, respectively. The solution concentrations of PCL and Gt in TFE were 14 and 12 % w/v, respectively. Both PCL and Gt solutions were delivered with a programmable syringe pump. A collecting plate (aluminum foil) was placed on a grounded rotating drum that was manually controlled by a stepping motor. The feed rate of the outer dope was set at 1 mL/h. The electrospinning voltage was in the range of 9–13 kV (Table I).

### Characterization

Surface morphologies of the electrospun hybrid membranes were observed on a JEOL JSM-5300 scanning electron microscope (SEM). Samples for SEM were dried under vacuum, mounted on metal stubs, and sputter-coated with gold-palladium for 30–60 sec. The average diameters and distribution of the fibers were analyzed with the software Image-Pro Plus (Media Cybernetics, Bethesda, MD;  $n = 80$ ). Fibers were freeze-fractured in liquid nitrogen and their cross-sections were observed with SEM. Tensile tests of the electrospun membranes were carried out on a Zwicki Z2.5/TH1S Universal Mechanical Testing Machine (Zwick, Ulm, Germany) equipped with GTM load cell. The  $1 \times 7 \text{ cm}^2$  rectangular specimen of  $\sim 50\text{--}80 \mu\text{m}$  thickness was vertically mounted onto

**Table I.** Preparation Parameters and the Structural Characteristics of the Electrospun PCL/gelatin Hybrid Membranes

Sample <sup>a</sup>	$r_{\text{feed}}^b$	$C_{\text{PCL}}^c$ (mg/mL)	$C_{\text{gelatin}}^c$ (mg/mL)	Voltage (kV)	$D^d$ (cm)	$W_{\text{PCL}}^e$ (%)	$D_{\text{iam}}^f$ ( $\mu\text{m}$ )	$D_{\text{ist}}^g$ ( $\mu\text{m}$ )
B-1	70/30	30	70	4.81	25	26.2	$0.80 \pm 0.11$	2.42
B-2	50/50	50	50	5.32	22	46.7	$1.81 \pm 0.32$	3.32
B-3	30/70	70	30	5.28	22	67.8	$2.66 \pm 0.64$	4.05
C-1	70/30	140	120	10.16	19	32.0	$1.06 \pm 0.29$	3.7
C-2	50/50	140	120	11.32	19	47.2	$3.25 \pm 0.40$	4.67
C-3	30/70	140	120	11.67	19	71.2	$4.04 \pm 0.44$	5.14
M-1	70/30	140	120	10.1/8.9 <sup>h</sup>	22/21 <sup>i</sup>	24	$0.86 \pm 0.22$	2.74
M-2	50/50	140	120	10.3/9.6	22/22	44.5	$1.03 \pm 0.30$	2.62
M-3	30/70	140	120	10.2/11.2	22/23	66.2	$1.17 \pm 0.43$	2.77

<sup>a</sup>B1–B3 were prepared by blend electrospinning, C1–C3 by coaxial electrospinning, and M1–M3 by mixing electrospinning.

<sup>b</sup>Gt/PCL feed ratio in weight.

<sup>c</sup>The concentration of PCL solution used for electrospinning.

<sup>d</sup>The distance between the spinneret and the collector.

<sup>e</sup>PCL weight percentage in the electrospun hybrid membranes.

<sup>f</sup>The average diameter of the fibers after crosslinking ( $n = 80$ ).

<sup>g</sup>The average fiber distance calculated according to eq. ( $\text{Dist} = 0.5/\sqrt{N_o/A}$ ).

<sup>h</sup>The left number means the voltage for gelatin solution, the right PCL solution.

<sup>i</sup>The left number means the distance for gelatin solution, the right for PCL solution.

the two mechanically gripping units of the machine at their ends, leaving a 5-cm gauge length for mechanical loading. The load was 2.5 kN and the tensile rate was set at 1 mm/min. X-ray photoelectron spectroscopy (XPS) spectra of the fibers were taken on the ESCALAB MK II (VG Scientific, UK). Dynamic water contact angle measurements were conducted using a Rame' Hart contact angle goniometer. Water was dispensed from a needle attached to a Gilmont microliter syringe filled with ultrapure water. Water droplets, 1  $\mu\text{L}$  in size, were placed on the surface of the electrospun membranes and images of the drop silhouette were taken with a video camera and stored for analysis on a computer. Wide-angle X-ray diffractograms were obtained on a Rigaku Geiger Flex D-Max III using nickel-filtrated  $\text{Cu K}_\alpha$  radiation.

#### Determination of Gt Content in the Hybrid Membranes

To determine the Gt content in the three types of membranes, 10 mg of the hybrid membranes were immersed in 10 mL of water at 37°C in a thermostatical shaking incubator (HZ-9610K, Taicang instrument, Taicang, China) at 100 rotation/min (rpm) for 90 min to extract Gt. The Gt content in the supernatant was quantified by a BCA protein microassay according to the protocol described by the supplier. Each sample was assayed in triplicate.

#### Crosslinking of Gt

The procedure for crosslinking Gt was similar to that previously described.<sup>31</sup> About 40 mg of the electrospun membranes was exposed to the GA vapor at room temperature for 72 h in a sealed vial containing 1 mL of aqueous GA solution (concentration 25%). Thereafter, the membranes were put in a vacuum oven for 3 days and stored in refrigerator before use.

#### Swelling Degree of the Hybrid Membranes

The swelling degree of the hybrid membranes was determined as described by Bigi et al.<sup>32</sup> In brief,  $1 \times 1 \text{ cm}^2$  rectangular specimens cut from the crosslinked membranes were weighed and then submerged in distilled water for 24 h at 37°C. The degree of swelling of these specimens was determined according to eq. (1), where  $W_{\text{wet}}$  is the weight of each specimen after submerged in distilled water for 24 h and wiped with filter paper to remove liquid till the samples were constant weight, and  $W_{\text{dry}}$  is the weight of the air-dried specimens after immersion in distilled water.

$$\text{Swelling degree} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \quad (1)$$

#### Estimation of Surface Compositions of the Blend Fibers

The surface composition of the blend fibers was expressed as relative molar percent of carbon atoms from Gt molecules to all the carbon atoms at the surface of the blend fibers, and calculated according to the eq. (2):

$$C_{\text{gelatin}}\% = \frac{(N_s/N_g) \times C_g}{C_s} \times 100\% \quad (2)$$

where  $C_{\text{Gt}}\%$  is the relative molar percent of carbon atoms from Gt molecules to all the carbon atoms at the surface of the blend fibers;  $N_s$  and  $N_g$  are the molar fraction of nitrogen atoms at the surface of the blend fibers and the electrospun Gt fibers, respectively;  $C_s$  and  $C_g$  are the molar fraction of carbon atoms at the surface of the blend fibers and the electrospun Gt fibers, respectively.  $N_s$ ,  $N_g$ ,  $C_s$ , and  $C_g$  are estimated by XPS.

#### Statistical Analyses

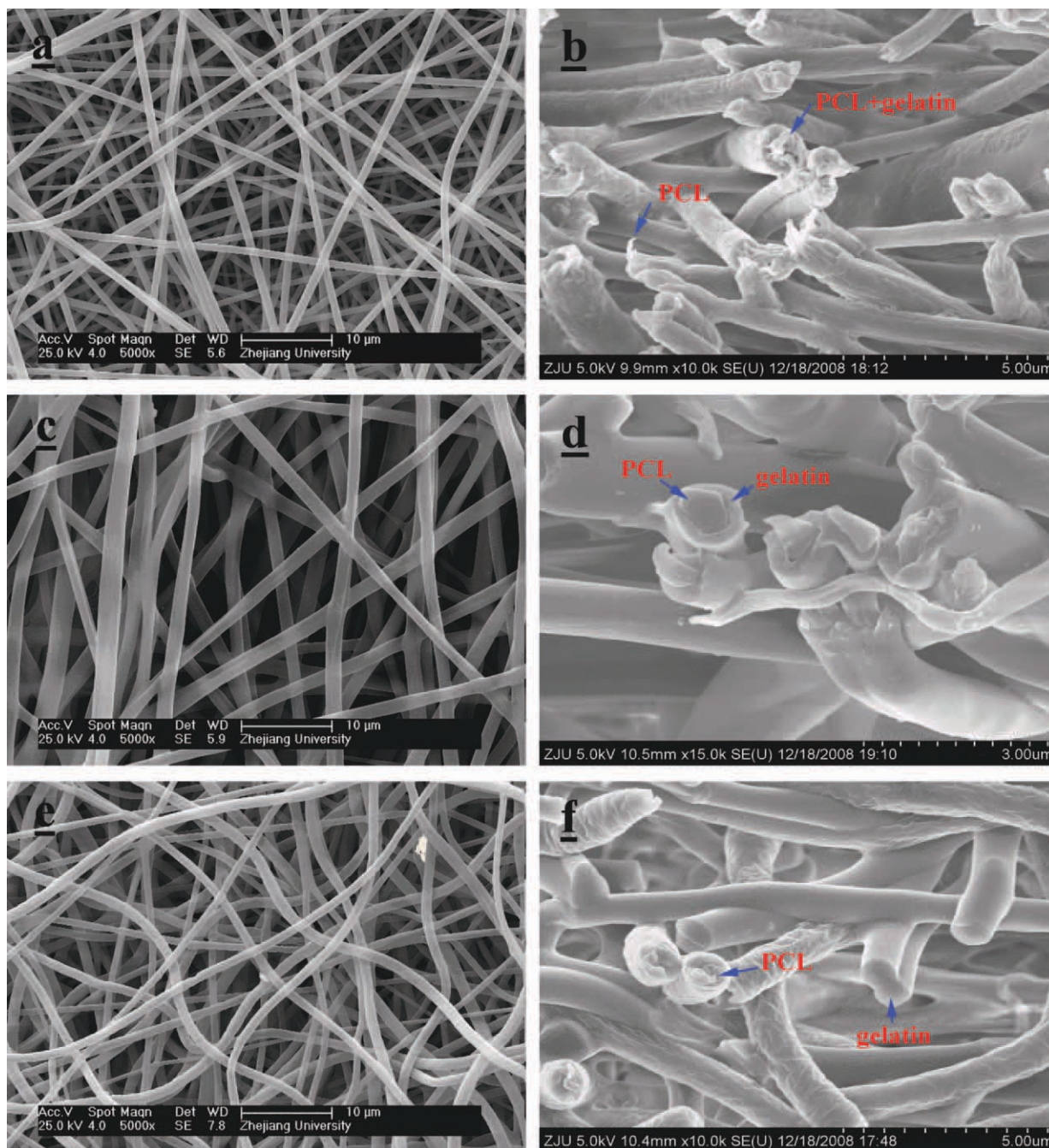
The data of mechanical properties were evaluated by one-way ANOVA in SPSS (17.0).  $P < 0.05$  was considered statistically significant throughout the study.

## RESULTS AND DISCUSSION

#### Preparation of the Electrospun Hybrid Membranes

The morphologies of surface and cross-section of the fibers prepared by different electrospinning methods are shown in Figure 1. Bead-free fibers with smooth surface morphology could be obtained through all the three electrospinning processes. Two components could be distinguished from the cross-section of the b-fibers [Figure 1(b)]. The subfibers extended from the cross-section of the b-fibers were supposed to be generated during the freeze-fracturing process and should be composed of the elastic PCL components. It was reported that PCL and Gt were immiscible even in their mixed solution. In addition, serious phase separation was observed within the electrospun fibers.<sup>33</sup> We also observed that the mixed solution of PCL and Gt looked opaque. c-Fibers displayed a typical core-shell structure [Figure 1(d)].<sup>3,21,30</sup> In contrast to the above two electrospinning techniques, mixing electrospinning produced the fibers displaying two distinct surface and cross-section morphologies. In our previous study (unpublished results), it was found that the electrospun PCL fibers had rough surface according to SEM observation, while the Gt fibers were smooth. As a result, the rough fibers shown in Figure 1(f) were composed of PCL, while the smooth counterpart consisted of Gt. This indicated that separated, individual fibers were produced through mixing electrospinning.

The effect of Gt/PCL feed ratio on the average fiber diameter is shown in Figure 2. The average diameters of pure Gt and PCL fibers were  $1.23 \pm 0.32 \mu\text{m}$  and  $0.73 \pm 0.24 \mu\text{m}$ , respectively. With the increase of PCL/Gt feed ratio, there was an increase in the average diameter of b-fibers and c-fibers. For example, the average diameter of the b-fibers increased from 0.80 to 2.66  $\mu\text{m}$  when the PCL/Gt feed ratio was raised from 30/70 to 70/30. However, the effect of the feed ratio on the average diameter of m-fibers was insignificant. In general, the average diameter of the electrospun fibers is affected by several electrospinning parameters, such as concentration of polymer solution, flow rate, and applied voltage, etc.<sup>21,30,34,35</sup> For c-fibers, the increase of PCL/Gt ratio in the fibers was achieved by raising the flow rate of the inner PCL dope while keeping the flow rate of the outer Gt dope constant. In other words, an increase in PCL/Gt ratio led to the increase of the flow rate of the compound jet. This would result in the enlargement of the c-fibers although there was a slight increase in the applied voltage. On the contrary, the increase of PCL/Gt ratio in m-membrane only led to an increase in the flow rate of the PCL jet. The diameter of Gt fibers was not affected by the feed ratio. In addition, the effect of the flow rate of PCL solution on the diameter of PCL fibers might also be counteracted by the applied voltage (Table I). That is why there was only a slight increase in the average diameter of the m-fibers with PCL/Gt ratio. The crosslinking process has little effect on the average diameter of all the three types of fibers. In contrast to the electrospun Gt membrane that was found to be subject to serious fiber fusion and shrinkage



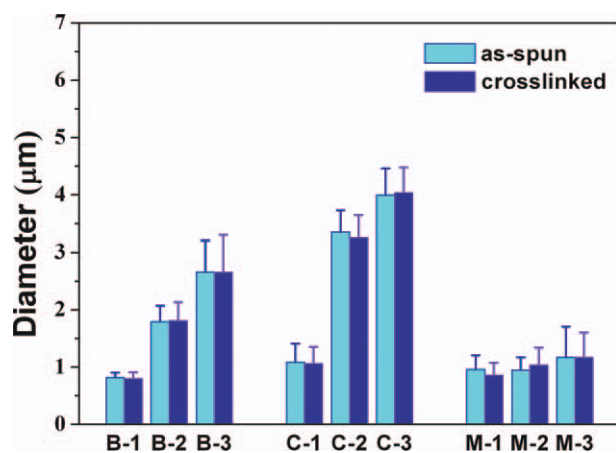
**Figure 1.** SEM micrographs of the electrospun fibers prepared by blend electrospinning (a, b), coaxial electrospinning (c, d), and mixing electrospinning (e, f). (a, c, e) displays the surface morphology of the fibers and (b, d, f) shows the cross-section of the fibers. Gt/PCL feed ratio was 50/50. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

upon crosslinking,<sup>34</sup> all of the three types of hybrid membranes displayed stable morphology which could be attributed to the presence of robust PCL. Detailed information of the hybrid membranes is summarized in Table I.

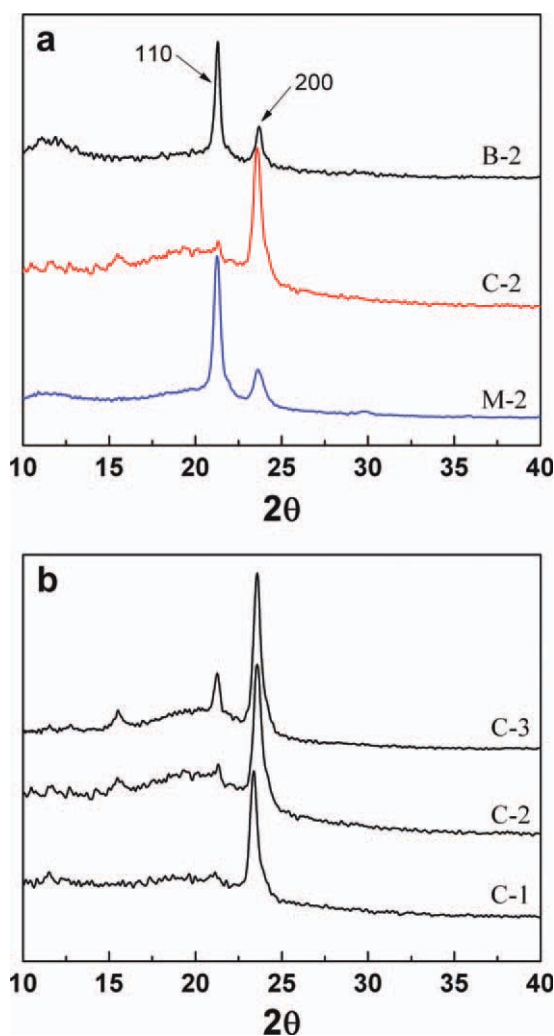
#### Effect of Fiber Structure on the Properties of the Hybrid Membranes

The effect of fiber structure on the membrane properties, including the crystallization of PCL, swelling degree, wettability, and mechanical properties, was investigated.

Wide-angle X-ray diffractograms of the electrospun hybrid membranes are shown in Figure 3. The diffraction profiles of the membranes prepared by blend electrospinning (designated as b-membranes) and mixing electrospinning (designated as m-membranes) were similar to that of the electrospun PCL membranes. However, there was a significant decrease in intensity ratio of two main peaks ( $I_{110}/I_{200}$ ) when comparing the core-shell fibrous membranes (designated as c-membranes) with the other two types of hybrid membranes. Similar trends have been



**Figure 2.** The effect of Gt/PCL feed ratio on the average fiber diameters. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

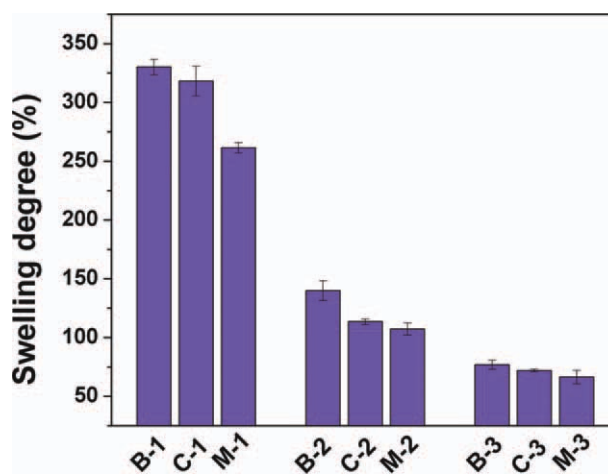


**Figure 3.** Wide-angle X-ray diffraction profiles of (a) the electrospun hybrid membranes prepared by different electrospinning techniques; (b) the electrospun hybrid membranes prepared by coaxial electrospinning. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

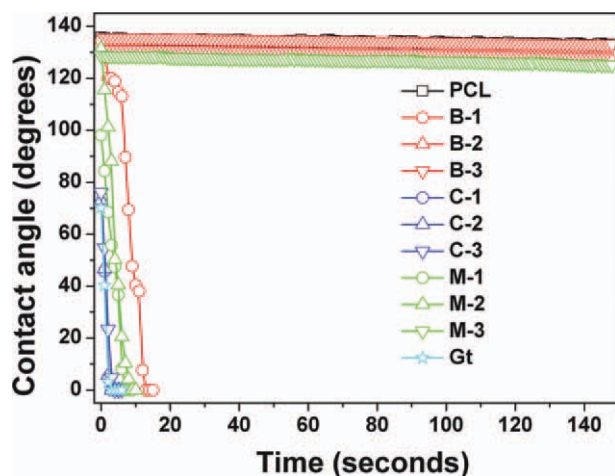
frequently reported during uniaxial tensile deformation process of orthorhombic semicrystalline polymers, and this is attributable to the increase in the orientation of the polymer chains and crystallinity with the elongation of the polymers.<sup>8</sup> During coaxial electrospinning, the electrostatic repulsions between the surface charges of the outer Gt dope rapidly elongated the shell component, exerting high shear force on the inner PCL dopes and leading to alignment of the PCL polymer chains. Although orientation of polymer chains in electrospun fibers had been reported previously,<sup>8,36–38</sup> the results shown in Figure 3 strongly suggested that the orientation degree of the PCL chains in the core section of the core-shell fibers was higher than that of PCL fibers prepared by uniaxial electrospinning. In addition, it could also be observed that  $I_{110}/I_{200}$  increased with PCL content in the core-shell fibers [Figure 3(b)], suggesting that the alignment of the PCL chains in the fibers decreased with an increase in the feed rate of the inner PCL dope.

Figure 4 shows the swelling degree of the electrospun hybrid membranes in distilled water at 37°C. The swelling degree of all the three types of membranes decreased with the increase of PCL content. This could be attributed to the high hydrophobicity of PCL. In addition, it could also be distinguished that the b-membranes displayed highest swelling degree and m-membranes the lowest, especially when PCL content in the fibers was low. This might be explained by the fact that the fiber structure could have an effect on the crosslinking extent of Gt. The presence of hydrophobic PCL within the b-fibers could prevent the swelling of the fibers in the vapor of aqueous glutaraldehyde solution, leading to the inadequate crosslinking of Gt. On the contrary, Gt in m-membranes could be adequately crosslinked by glutaraldehyde due to both the single-component nature and small diameter of the Gt fibers.

The wettability of the electrospun hybrid membranes was evaluated by measuring their contact angles (Figure 5). The contact angle of the c-membranes was reasonably independent of the fiber composition. On the contrary, the wettability of m-



**Figure 4.** Swelling degree of the electrospun hybrid membranes in distilled water at 37°C. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

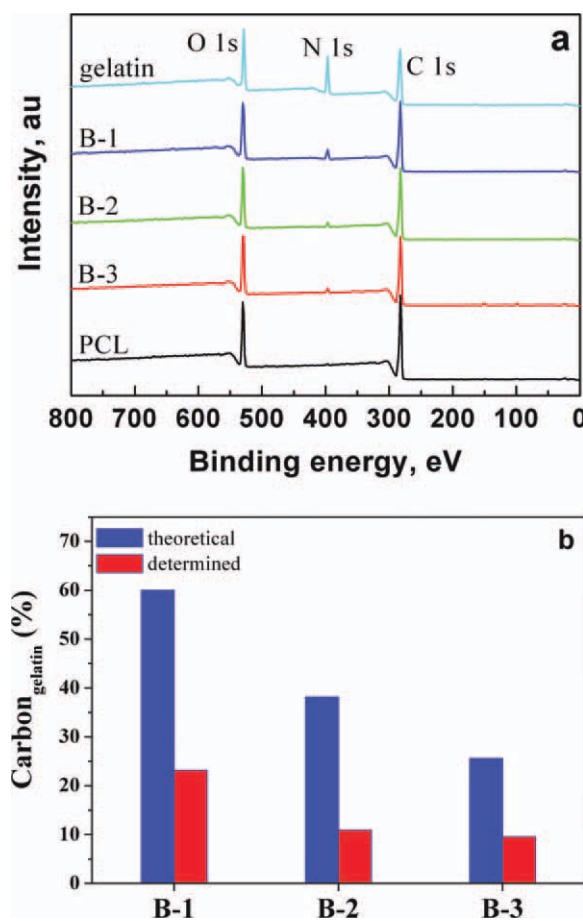


**Figure 5.** Contact angles of the electrospun hybrid membranes. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

membranes was affected by PCL content. When PCL content was raised to 66.2%, the hybrid membrane had similar wettability to the electrospun PCL nonwoven mats. Among the three types of electrospun hybrid membranes, the b-membranes displayed the highest hydrophobicity. For example, the contact angle of the b-membranes was comparable to that of the electrospun PCL mats even when PCL content was as low as 46.7%. The surface composition of the b-fibers was estimated by XPS characterization (Figure 6). Peaks signifying C 1s, N 1s, and O 1s all appeared in the spectra of b-fibers, indicating the presence of Gt at the surface of the fibers. Since the C 1s and O 1s peaks of Gt overlap with those of PCL, the surface composition of the blend fibers was estimated by the molar fractions of N 1s and C 1s peaks [eq. (2)]. A decrease in Gt/PCL feed ratio decreased Gt content at the fiber surface. It could also be observed that surface content of Gt was apparently lower than that in the bulk, indicating the preferential localization of PCL at the surface of the blend fibers. This might be due to the hydrophobic nature of PCL which tended to migrate to the jet surface in apolar ambient air. Similar results have been reported by Zhang et al.<sup>33</sup> The enrichment of PCL at the b-fiber surface prevented the water ingress, thereby decreased the wettability of the whole membrane.

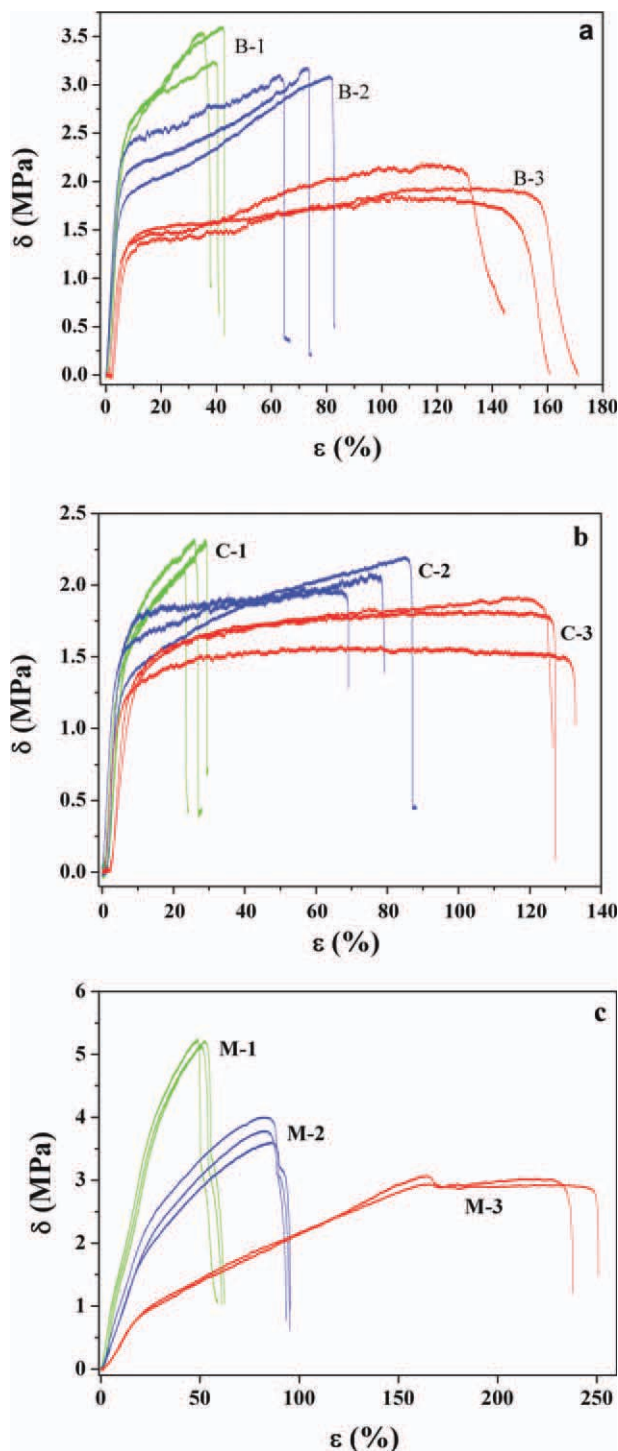
Although mechanical properties of the electrospun membranes have been investigated by several research groups, there were very few studies focusing on the effect of fiber structure.<sup>37–42</sup> The stress–strain curves of the electrospun hybrid membranes are shown in Figure 7. For all the three types of membranes, the increase of PCL content resulted in a decrease in the tensile strength and an increase in the elongation. This could be attributed to the fact that PCL exhibits elastic characteristics, while the crosslinked Gt is a tough, brittle material. The effect of fiber structure on the mechanical properties of the electrospun hybrid membranes is summarized in Figure 8. Among the three types of electrospun hybrid membranes, the m-membranes displayed the highest mechanical properties in both tensile strength and elongation, while the mechanical properties of the c-membranes

were the weakest. Duan et al.<sup>39</sup> and Lee et al.<sup>40</sup> considered that the increase in mechanical properties could be attributed to the increase of physical interactions of fibers making up the hybrid membranes. Wu et al.<sup>42</sup> also reported that the core/shell structured poly(lactide-co-glycolide) (PLGA)/chitosan possessed higher tensile strength than those of hybrid PLGA/chitosan membranes, but the component proportion in both core/shell structured PLGA/chitosan and hybrid PLGA/chitosan was extremely different (8.6 wt % and 40.8 wt % of PLGA in core/shell structured PLGA/chitosan and core/shell structured PLGA/chitosan, respectively). The mechanical properties of the hybrid membranes depend on the structure of the membranes, the mechanical properties of single fibers, and the interactions of the fibers in the hybrid membranes. We speculated that the more interactions of PCL and Gt fibers in the m-membranes than those in the c-membranes or b-membranes could attribute to the observed mechanical properties of the m-membranes. The difference in mechanical properties of c-membranes and b-membranes could be ascribed to the different interactions degree of PCL and Gt chains. The interactions of PCL and Gt chains lie

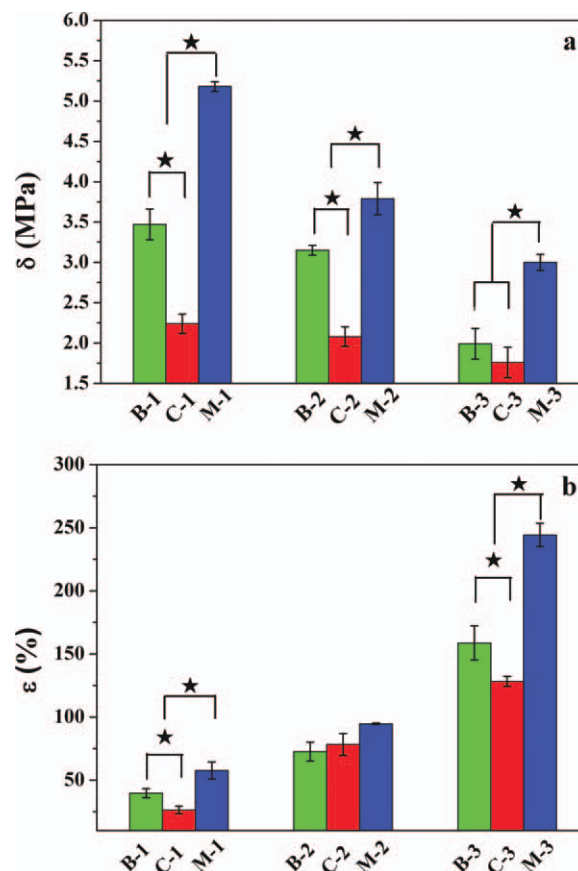


**Figure 6.** (a) XPS spectra of the electrospun hybrid membranes prepared by blend electrospinning; (b) the surface carbon content from gelatin versus that from PCL and Gt in hybrid membranes prepared by blend electrospinning. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

in the contact boundary of both components. For c-membranes, it is definite of core-shell structure, the contact boundary is between outside surface of core and internal surface of shell. For b-membranes, preferential localization of PCL at the surface of the blend fibers infers that there is more contact boundary



**Figure 7.** Stress-strain curves of the electrospun hybrid membranes prepared by: (a) blend electrospinning; (b) coaxial electrospinning; (c) mixing electrospinning. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 8.** Effect of fiber structure on (a) the tensile stress at break, (b) the tensile strain at break of the electrospun hybrid membranes ( $\star$  denotes statistical significance with  $P < 0.05$ ). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

between PCL and Gt components than the c-membranes. Hence, in the macro level, the mechanical properties of the c-membranes were the weakest. Although the underlying exact mechanism was not clear, the above results implicated that the mixing electrospinning seemed to be superior to the two other types of electrospinning methods for producing hybrid membranes with high mechanical strength due to the simpleness of the electrospinning setup and the wide operation window.

## CONCLUSIONS

The fiber structures could be controlled by electrospinning methods and had a substantial effect on the membrane properties. The crystallization characteristics of PCL in core-shell fibers were different from blend and mixed fibers. It is the higher orientation degree of PCL chains. The hybrid membranes composed of blend fibers displayed lowest wettability while that of mixed fibers showed highest mechanical strength. This study shows that by electrospinning two different polymer solutions in various ways, the physical properties of the membranes can be altered. As such, the appropriate method of electrospinning with desired properties can be selected for the various medical applications.

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