

PREPARATION AND CHARACTERIZATION OF ELECTROSPUN FIBERS BASED ON POLY(L-LACTIC ACID)/CELLULOSE ACETATE*

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Abstract PLLA/CA mixtures of different compositions were successfully electrospun to obtain composite nanofibrous membranes. The microstructures of the membranes changed from homogeneous to heterogeneous with the addition of CA, which was observed by FE-ESEM. The PLLA/CA fabric membranes were characterized by mechanical testing, DSC and contact angle measurements. The tensile stress of the composite fibrous membranes increased obviously with the increase of CA content. DSC results indicated that the CA component was the main factor for the changes of enthalpies in the composite fibers. Contact angle measurements showed the hydrophilicity of the electrospun nanofiber membranes was improved with the addition of CA.

Keywords: Electrospinning; Poly(L-lactic acid); Cellulose acetate; Fiber; Tensile stress.

INTRODUCTION

Electrospinning is used to produce microfibers or nanofibers from a polymeric solution or melt under the high electrostatic field^[1]. The diameter of the electrospun fibers achieved ranges from 10 μm to 10 nm, which is much finer than that achieved from conventional polymer melt or solution spinning processes^[2–4]. Recently, increasing interests have been drawn in electrospinning porous nanofiber membranes from natural or synthetic biodegradable polymers for tissue engineering in regenerative medicine. Non-woven structures of nanofibers provide a highly accessible three-dimensional structure characterized by a high surface area-to-volume ratio and three-dimensional interconnected pore network, both of which can enhance cell attachment and proliferation^[5].

Good biocompatibility, high permeability, excellent mechanical properties and degradation ability are the basic requirements for tissue engineering scaffolds materials. Among all kinds of materials used for tissue engineering scaffolds, poly(L-lactic acid) (PLLA) is one of the most extensively used biopolymers. PLLA has good biocompatibility and degradation ability, which have been approved by the U.S. Food and Drug Administration for *in vivo* applications^[6–8]. But PLLA fibrous membrane is brittle. Several attempts have been made to improve the mechanical properties^[9, 10]. PLLA is hydrophobic and hard to adhere cells or certain drugs with poor hydrophilicity. Zhang *et al.* have successfully prepared PLLA/silk fibroin composite fiber membranes

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with improved mechanical performance and solubility in water to help the proliferation of cells on fiber membranes^[11].

Cellulose acetate (CA) is a typical hydrophilic polymer. Electrospinning of cellulose and its derivatives has been widely studied due to their biocompatibility, biodegradability and high affinity with other substances^[12]. CA is often used as substitute material of cellulose because cellulose is hard to dissolve in common solvent^[13]. Electrospun CA fiber membranes as carries for drug delivery and prodrugs loading are widely reported^[14, 15].

In this work, in order to further develop the mechanical properties and hydrophilicity of PLLA fibers^[16] and exploit its potential biological applications, the ultrafine PLLA/CA fibers^[17] as the substrate materials were prepared *via* electrospinning. The effect of CA content in the composite fibers on mechanical and hydrophilic properties was systematically investigated. To the best of our knowledge, this is the first time PLLA correlates with a CA component.

EXPERIMENTAL

Materials

Poly(L-lactic acid) (PLLA) with $M_n = 7.2 \times 10^4$ characterized by GPC was supplied by Hisun Company. Gel permeation chromatography (GPC) measurements were conducted with a Waters 515 GPC instrument with CHCl_3 as the eluent (flow rate: 1 mL min^{-1} at 35°C). The molecular weights were calibrated against polystyrene (PS) standards. Cellulose acetate (CA) ($M_n = 50000$, 39.7 wt% acetyl content) was purchased from Aldrich Chemical Company Inc. Acetone was obtained from Tianjin Xintong Chemical Agent Company, China. CHCl_3 was purchased from Beijing Chemical Works. All chemicals were used as provided without any purification.

Electrospinning Process

Homogenous solutions were obtained by dissolving PLLA and CA in CHCl_3 /acetone binary solvent mixture under vibration overnight at room temperature. The CHCl_3 /acetone ratio of 3/1 (*V/V*) was used. Several solutions with different weight percents at various ratios of PLLA/CA (9%/0.6%, 9%/1.5% and 9%/3%) were prepared.

The CA solutions were electrospun by using syringe with metallic needle (inner diameter = 0.7 mm) which was fixed horizontally on the syringe pump (ALC-IP900, Shanghai Alcott Biotech Co., Ltd.). The needle was connected to a high voltage power supply (Tianjin Dongwen High Voltage Facility), which provided positive DC voltages of 15 kV. The cathode (a piece of grounded stationary aluminum foil) was placed about 10 cm away from the tip of the needle. The electrospinning process was carried out at room temperature at 30% relative humidity.

Measurements and Characterization

The morphology and the diameter of the electrospun fibers were determined by using a field-emission environmental scanning electron microscope (FE-ESEM, XL 30 Philips) at an accelerating voltage of 20 kV. Samples were coated with 5 nm gold prior to SEM imaging. The fiber diameter ranges were measured by Image J software. Differential scanning calorimetry (DSC) measurements were performed from 0°C to 200°C at a 10 K/min heating rate with a PE DSC-100 system in a 50 mL/min dynamic nitrogen atmosphere. Approximately 5 mg of each sample was loaded into DSC pans sealed using a crimping tool. All tests were carried out in duplicate. Static material mechanical performance testing was conducted using a mechanical analyzer Q800 (USA). The fiber membranes were carefully cut with dimensions of $20 \text{ mm} \times 4 \text{ mm}$. Samples were tested at a displacement rate of 50 mm/min at room temperature in nitrogen atmosphere in order to avoid humidity effects and fiber degradation. Reported results corresponded to the average values of three similar tests. The water contact angles of samples were measured with a sessile water drop using a KRÜSS DSA 10-MK2 contact angle measuring system at ambient temperature. A water droplet was placed on electrospun nanofibrous membranes coated slide glass and a water contact angle at certain time was recorded until the water droplet was absorbed totally. The timekeeping was about 25 min to 35 min in our experiments. Data corresponded to the average values of measurements were obtained from at least six droplets of 12 mg freshly distilled water.

RESULTS AND DISCUSSION

Microstructure of Fibrous Membranes

As shown in Fig. 1, when CA was added to the PLLA solution, morphologies of fibrous membranes varied from homogeneous to heterogeneous state. Some finer and uniform composite nanofibers were fabricated, linked with the primary nanofibers, the finer fibers had one tenth of diameters of the thicker fibers. These fibers were distributed as a bimodal size, similar to PEO/CNC composite fibers and other polymer systems^[18, 19]. The pure CA in CHCl_3 /acetone solvent with concentration lower than 3% could not electrospin to fibers. This behavior might be the unstable jet flow, which caused by the unbalanced force among the viscoelastic, surface tension and electrostatic forces. Because of the fact that the electrospinning solution at a high concentration level was highly viscoelastic, the primary jet and subsequently branched mini-jets underwent a long elongation flow and then splayed into thousands of mini-jets during the electrospinning process. This prolonged the splitting and splaying region and induced the unstable and repeated splaying of the jets. The multiple splaying could form various mini jets during its transit to the collector and contributed to the formation of bimodal diameter distribution for the deposition fibers^[18–20]. The average diameter of the pure PLLA fiber was 1.57 μm , while for the thicker fibers of

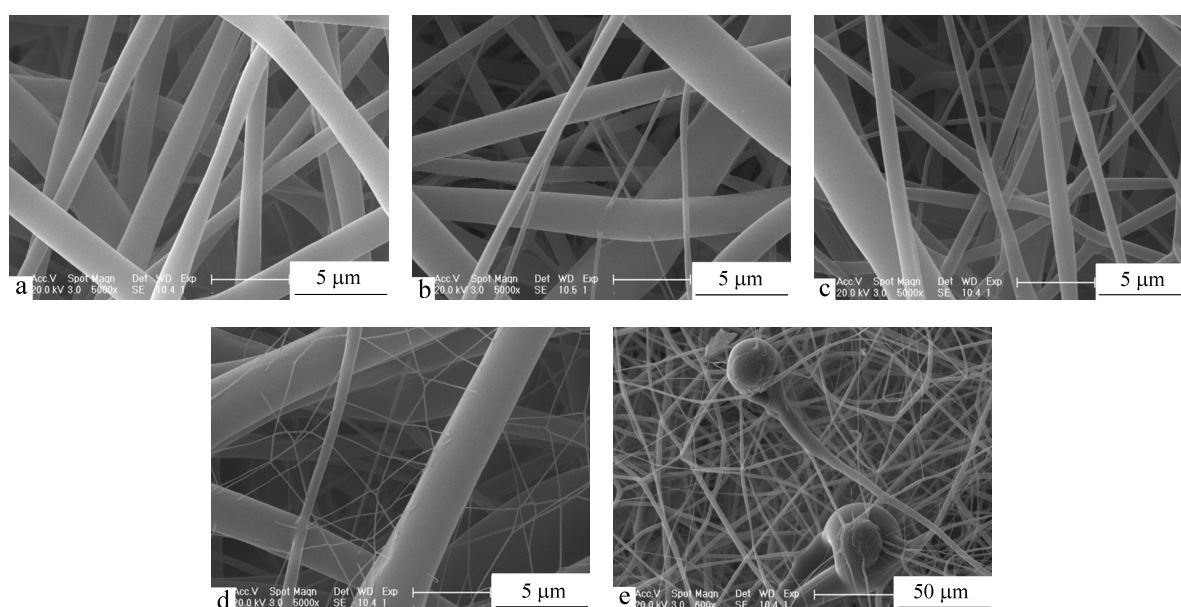


Fig. 1 SEM images of electrospun PLLA/CA fibers with different CA contents (a) 0%, (b) 0.6%, (c) 1.5%, (d) 3% and (e) 3% (enlarge image)

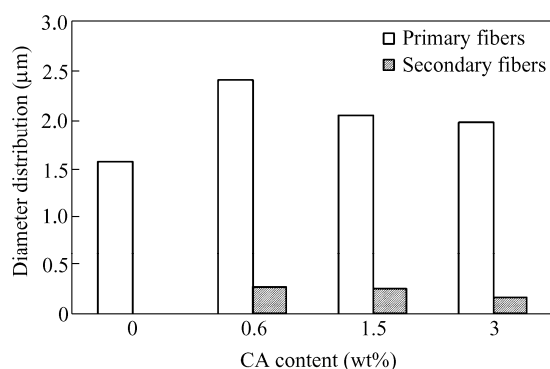


Fig. 2 Effects of CA content on the diameter distribution of PLLA/CA electrospun nanofibers

PLLA/CA (9%/0.6%) were 2.41 μm , 2.05 μm (9%/1.5%) and 1.98 μm (9%/3%) respectively. In the enlarge image of Fig. 1(e), the droplets were formed among PLLA/CA fibers while the CA content increased to 3%. It was because of the dense package of the fibers, the solvent at a high concentration was hard to volatilize during the electrospinning process. The average diameter of the primary fibers increased comparing with the pure PLLA fibers, which implied that CA in the primary nanofibers contributed to the increased diameter. For all the PLLA/CA fabrics, both modal nanofibers showed a slight decrease in average diameter and diameter variability with increased CA contents, the primary nanofibers were greatly strengthened compared with the secondary nanofibers (Fig. 2).

Thermal Behavior of Fibrous Membranes

DSC thermal behavior of electrospun fibers was evaluated in this work. In a normal DSC result of PLLA, a glass transition temperature (T_g) can be observed around 60–70°C. Frequently, the exothermic event is above T_g owing to the aging of PLLA. This was called cold crystallization peak. There were two melting peaks which were frequently observed^[10, 21]. For the DSC curves of pure CA, no peaks appeared from 20°C to 180°C. Compared with the DSC curves of second heating for the PLLA/CA electrospun fibers (Fig. 3), PLLA electrospun fibers showed a T_g at 50.01°C. The T_g for PLLA electrospun fiber was considerably lower than that of raw PLLA^[10]. This decrease in T_g of electrospun fibrous membranes was deemed to the very large surface to volume ratio of the fiber membranes, the inner stress and the orientation of the polymer chains caused by the electrospinning process^[22–24]. The shifts of the T_g from 50.01°C to 59.15°C implied the CA has mixed into the bicomponent fibers (Table 1). Meanwhile, a cold crystallization peak and melting peaks were observed in four samples. Electrospun fibrous membranes of PLLA showed a weak peak of cold crystallization (T_c) at 79.65°C and a small endothermic peak (T_m) at 171.71°C. Comparing with the electrospun fibrous membranes of PLLA, the crystallization peak was stronger due to the addition of CA. Meanwhile, there is no other emergence of crystallization peaks. It showed a good combination of CA and PLLA and there was no phase separation. T_m (174.15–175.31°C) and T_c (110.55–112.56°C) for the bicomponent fibers increased compared with pure PLLA electrospun fiber, which indicated that the presence of CA in PLLA matrix limited the mobility of PLLA chains *via* hydrogen bonds^[25].

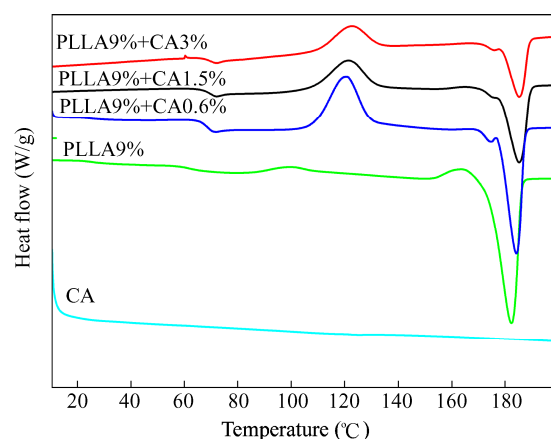


Fig. 3 DSC curves of PLLA and PLLA/CA (9%/0.6%, 9%/1.5%, 9%/3%) electrospun nanofibrous membranes

Table 1. Thermal behaviors of PLLA/CA bicomponent fibers

	T_g (°C)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)
PLLA9%	50.01	79.65	20.59	171.71	37.33
PLLA9% + CA0.6%	58.72	110.55	27.72	174.15	32.47
PLLA9% + CA1.5%	58.18	111.36	26.31	175.24	33.57
PLLA9% + CA3%	59.15	112.56	26.08	175.31	33.52

Mechanical Properties of Fibrous Membranes

The mechanical performance, especially tensile properties of the electrospun fibers could be affected by some factors, such as the solution concentration, components and individual properties of each component, fiber alignments and testing direction^[25–29]. In this study, the component and fiber alignments on the electrospun PLLA/CA nanofibrous membranes were discussed.

The typical stress-strain curves of PLLA and PLLA/CA fibers are shown in Fig. 4. Table 2 summarized the maximum tensile stress (σ_m), tensile fracture stress (σ_b), tensile fracture strain (ε_b) and Young's modulus (E_t) of fibers with different CA %. From this plot, the ultimate strength and strain of PLLA fibers were about 0.402 MPa and 26%, respectively. The values of ultimate strength and strain of all the bicomponent fibers were higher than those of PLLA fibers, and increased with the increase of CA content. As seen in Table 2, the PLLA nanofibrous membranes had σ_m of 0.402 MPa, σ_b of 0.402 MPa, ε_b of 26%, and E_t of 9.59 MPa. After the incorporation of CA, the tensile strength of nanofibrous membranes increased slightly. When the CA content increased from 0.6% to 3%, E_t of the nanofibrous membranes increased from 16.5 MPa to 29.0 MPa, ε_b increased from 26% to 51%. Therefore, the addition of CA has a positive effect to the tensile properties of the composite fibers. The enhanced mechanical properties might be attributed to the interactions between the PLLA matrix and CA through hydrogen bonding. From the microstructure of PLLA/CA, the formation of ordered organization improved the mechanical properties of composite materials effectively^[30]. The increase of T_c in DSC curves supported the results. Zhou *et al.* has reported that the bimodal microstructure of electrospun composite nanofibrous membranes was directly correlated with their mechanical properties^[18, 31]. The improved Young's modulus of heterogeneous fiber mats could be explained that finer nanofibers interacted with primary nanofibers through the adhesion points and entanglement (Figs. 1b, 1c and 1d). In contrast, there were no finer fibers in the homogeneous fiber membranes and no entanglement among fibers was formed. As a result, relatively weak interactions existed among them. With increasing tensile stress, a few of the primary fibers were necked and fractured. Meanwhile finer fibers were pulled to break off from the primary fibers, which delayed the

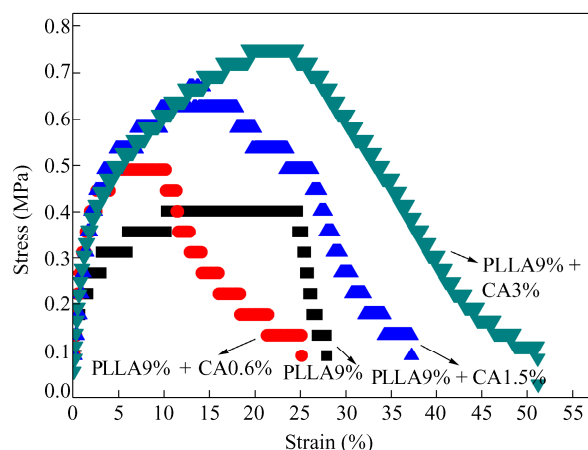


Fig. 4 Stress-strain curves of PLLA and PLLA/CA (9%/0.6%, 9%/1.5%, 9%/3%) electrospun nanofibrous membranes

Table 2. Tensile properties of PLLA/CA electrospun nanofibrous membranes

	σ_m (MPa)	σ_b (MPa)	ε_b (%)	E_t (MPa)
PLLA9%	0.402	0.402	26	9.59
PLLA9% + CA0.6%	0.491	0.134	26	16.50
PLLA9% + CA1.5%	0.670	0.134	38	16.50
PLLA9% + CA3%	0.750	0.083	51	29.00

fracture of primary nanofibers and increased the elongation at break for heterogeneous membranes. So the heterogeneous fibrous membranes could bear higher stress, leading to higher tensile strength in comparison with the homogeneous fibrous membranes. Data obtained from our measurements supported this view.

Hydrophilic Performance of Nanofibrous Membranes

Contact Angle measurement was considered to be effective way to test the surface hydrophilicity or hydrophobicity of the fibrous membranes^[32]. For pure CA nanofibrous membranes, the contact angle was 47° initially and the contact angle decreased rapidly from 47° to 30°^[33–36]. Figure 5 shows the water contact angles of different compositions electrospun membranes. The contact angle of the bicomponent nanofibrous membranes decreased with the increase of CA content. It was found that the PLLA electrospun membrane was hydrophobic with a water contact angle of 134.69°, and the contact angle decreased to 125° after 15 min. While for the other PLA/CA fabric membranes, the contact angle was about 120° after 15 min. The contact angle decreased faster at 25 min for all fabric samples. The value of the contact angle of PLLA, PLLA/CA(0.6%), PLLA/CA(1.5%) and PLLA/CA(3%) membranes were 102°, 94°, 76° and 69°, respectively. The electrospun nanofibrous membranes absorbed the water completely^[33]. It took almost 35 min for the water droplet to be absorbed completely for PLLA fabric membrane. The addition of CA shortened the time by nearly 5–10 min, and the contact angles reduced a lot. The hydrophilicity of the nanofibrous membranes was improved with increased CA content.

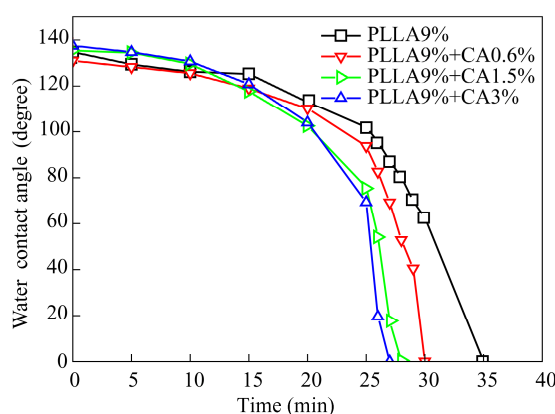


Fig. 5 Variation of water contact angles with time for electrospun membranes of different compositions

CONCLUSIONS

In this study, PLLA/CA bicomponent electrospun fibrous membranes with different CA contents were successfully prepared. Morphology investigation of nanofibrous membranes demonstrated that the addition of CA could obtain heterogeneous fibers with bimodal diameter distributions. The mechanical performance was reinforced with the increase of CA content. DSC results demonstrated that PLLA was compatible with CA. The CA content in the composite fibers was the main factor for the changes of enthalpies of the fibers. PLLA was a typical hydrophobic material, with a contact angle of more than 90°. Compared with the pure PLLA electrospun nanofibrous membranes, PLLA/CA component membranes showed better hydrophilicity, and the water droplet was completely absorbed in shorter time, especially for the membranes with the content of CA increased to 3%. CA component was used to improve the hydrophilicity of electrospun fiber membranes, a very important character for scaffold materials.

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