

Analysis of Porous Electrospun Fibers from Poly(L-lactic acid)/Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) Blends

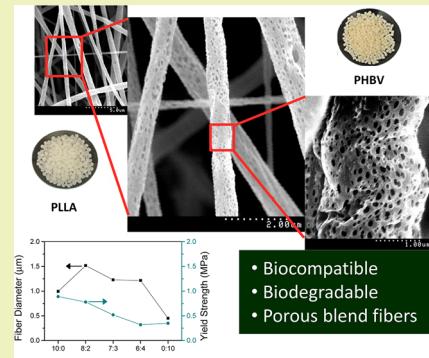
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ABSTRACT: Solution blends of poly(L-lactic acid) (PLLA) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) in chloroform/DMF were electrospun at room temperature on a stationary collection plate. Polymer blend ratio, PHBV hydroxyvalerate content, solvent ratio, polymer concentration, and electrospinning process parameters were varied to determine optimal electrospinning conditions. The success of each formulation at producing nonwoven mats of continuous submicron diameter fibers was evaluated by optical and scanning electron microscopy. The diameter of the blend fibers was larger than electrospun fibers of either neat electrospun polymer, with a higher PLLA ratio favoring a porous surface morphology and higher PHBV ratios favoring beaded fiber morphology. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used to analyze the thermal properties of the fibrous mats. The glass transition temperatures of the fibers from blends decreased as the PHBV weight ratio increased. The crystallinity of the PHBV fraction decreased as the ratio of the polymer in the blend decreased, whereas the crystallinity of PLLA was unaffected by the blend ratio. Dynamic mechanical analysis (DMA) indicated that the tensile strength of electrospun PHBV was improved by blending. Porous PLLA/PHBV electrospun fibers have potential for applications that need a high surface to volume ratio such as filtration, biomedical, energy storage devices, etc.

KEYWORDS: PLLA, PHBV, *Electrospinning, Composite fiber, Fiber characterization, Porosity*



INTRODUCTION

Production of ultrafine biopolymer fibers satisfies an increasing demand for petroleum-based polymer substitutes and a growing interest in micron-scale structures.^{1–5} Electrospun materials have been utilized in a variety of fields, including flexible electronics, filtration, sensors, and tissue engineering.^{6–8} High surface area and porosity, superior mechanical properties, and structural similarity to the natural extracellular matrix lead to a potential application of electrospun fibers in tissue engineering.^{9–12} Biobased polyesters, including poly(lactic acid) (PLA) and polyhydroxylalkanoates (PHAs), are sustainable alternatives to petroleum-based polyesters due to their biodegradability and renewability.

PLA, one of the most widely used biopolymers, is produced via fermentation of corn dextrose.¹³ PLA is a linear aliphatic thermoplastic characterized by a high tensile strength and modulus but low ductility.^{13–15} PLA is relatively inexpensive, resulting in its widespread application and use.¹⁶ Lactic acid is a chiral molecule, and poly(L-lactic acid) (PLLA) is synthesized from the polymerization of the L-form enantiomer of lactic acid.

PHAs are biological polyesters synthesized by the bacterial fermentation of sugars and lipids. In bacteria, the PHAs are used as carbon storage for energy inside cells.¹⁷ Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) is a PHA random copolymer of 3-hydroxybutyrate and 3-hydroxyvalerate

(HV) groups. By increasing HV content, melting point and brittleness of neat PHB is reduced.^{18,19} PHBV is more ductile than PLA, but its relative immaturity corresponds to an increased cost.²⁰

PLLA/PHBV blending via twin-screw microcompounding and other techniques has been studied.^{18,21} Results indicated an improvement in strength, modulus, and ductility of PHBV after blending with PLA.¹⁸ Feng et al. demonstrated that the utilization of PHBV alongside PLLA improves the biocompatibility and wettability of electrospun polymer scaffolds used for tissue engineering over neat electrospun PLLA.¹¹ The biocompatibility of PLLA and PHBV, combined with the inherent porosity of electrospun scaffolds, make the polymer blend well suited to electrospinning.

Electrospinning involves the application of an electric potential to a polymeric solution, fed through a metallic needle, toward a grounded collection plate. Once the applied voltage exceeds a critical level, a conical droplet of solution, called the Taylor cone, forms at the tip of the needle and a charged jet is ejected from the cone.²² The solvent evaporates as the continuous jet of polymeric solution travels in whip-like

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motion toward the collector. Electrospinning is a promising production technique for the fabrication of nanofibers due to its simplicity, scalability, and continuous production using a variety of polymers and blends.^{7,20,23,24}

Electrospinning involves a number of parameters that affect the resultant fiber morphology and diameter including characteristics of the polymer, concentration of the polymer, and resultant solution viscosity, solvent, needle gauge, applied voltage, feed rate, and distance from needle to collector.^{22,25,26} Ambient temperature and humidity also play a large role on the resultant fibers.²⁷ When utilizing a blend of polymers and solvents, the ratio of the blend and selected components in the blend also affect the fiber morphology.

In this study, electrospinning was used to fabricate nonwoven fiber mats of PLLA, PHBV, and their blends. Polymer blend ratio, PHBV hydroxyvalerate content, solvent ratio, polymer concentration, and electrospinning process parameters were varied to determine optimal conditions. Solution blends of PLLA and PHBV in chloroform/DMF were electrospun at room temperature on a stationary collection plate. In other studies on electrospinning of solutions containing PHBV, dissolution was aided by heating the solution during preparation and electrospinning.^{20,28,29} Fiber morphology and thermal and mechanical characteristics absent from previous studies were tested using optical and scanning electron microscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and dynamic mechanical analysis (DMA) to enable further tailoring of the nonwoven mat for highly specialized applications. The study demonstrates that PLLA/PHBV electrospun fibers have porous structures and improved mechanical strength over neat electrospun PHBV. Therefore, they have the potential for many applications such as biomedical applications, filtration, energy storage devices, etc.

EXPERIMENTAL SECTION

Materials. Poly(L-lactic acid) (PLLA, Biomer L9000, $M_w = 200\,000$ g/mol, 2% D-lactide) was purchased from Biomer, Krailling, Germany. Three grades of poly(3-hydroxybutyrate-co-hydroxyvalerate) (PHBV) were tested for blending: (1) PHBV Enmat Y1000P, hydroxyvalerate (HV) content = 2.9 mol %, $M_w = 520\,000$ g/mol from Tianan Biological Material, Ltd., China, (2) PHBV Biopol D411GN, HV content = 11 mol %, $M_w = 690\,000$ g/mol from Monsanto, U.K., and (3) PHBV Biopol D600GN, HV content = 14 mol %, $M_w = 450\,000$ g/mol from Monsanto, U.K. Analytical grade chloroform and N,N-dimethylformamide (DMF) were procured from Sigma-Aldrich and were used as received.

Methods. Preparation of Electrospinning Solutions. A preliminary investigation was first conducted to determine the optimal ratio of the solvents for the electrospinning solutions. Solutions of chloroform/DMF with ratios of 7:3, 8:2, 9:1, and 1:0 v/v were tested as solvents for the dissolution and electrospinning of 10 w/v PLLA. Formation of smooth fibers and continuous spinning was compared between the different solvent ratios to find the suitable solution composition for the main experiments of interest.

The solubility of PHBV based on its HV content was tested. One pellet of each grade of the PHBV copolymers was placed in test tubes containing 10 mL of chloroform/DMF, 9:1 v/v. The test tubes were sealed and left undisturbed for 2 days prior to centrifugation to determine the amount of suspended undissolved polymer in each solvent.

To determine the optimal polymer concentration and blend ratio, solutions with 6, 8, and 10 w/v of total polymer content (PLLA/PHBV, 8:2 w/w) and solutions with 8, 10, and 14 w/v total polymer content (PLLA/PHBV, 7:3 w/w) were prepared. All the solutions were prepared in the solvent mixture (chloroform/DMF, 9:1 v/v).

PLLA/PHBV electrospinning solutions were prepared by dissolving the polymer pellets in the solvent (chloroform/DMF, 9:1 v/v), with vigorous stirring for 16 h at room temperature. In order to achieve complete dissolution, PHBV was first dissolved in the chloroform. Then PLLA was added after 2–3 h of stirring. The DMF was added 1 h before electrospinning. The weight ratios of PLLA/PHBV were 10:0, 8:2, 7:3, 6:4, and 0:10 w/w. The total polymer concentration of each solution was fixed at 10 w/v. Prior to electrospinning, the surface tension of each solution was measured using the Wilhelmy plate method.^{30,31}

Electrospinning. Electrospinning was performed in a NANON-01A electrospinning setup (MECC Co., Ltd. Japan). It has a vertical setup as shown in Figure 1. For the principle electrospinning trials, a

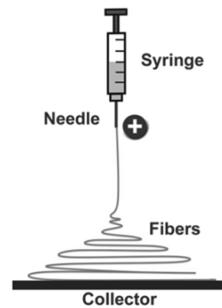


Figure 1. Schematic diagram of vertical electrospinning setup employed.

total polymer content of 10 w/v, needle gauge of 24, collector distance of 15 cm, and solvent (chloroform/DMF, 9:1 v/v) were held constant while the blend ratio was varied. For each blend ratio, the applied voltage and solution feed rate were optimized to achieve continuous spinning and smooth fibers, with the latter checked by optical microscope. A total of 6 mL of each solution was electrospun onto the collector (collection time varied based on cleaning frequency of the needle and feed rate). To evaporate any residual solvent, electrospun fibers were kept under a fume hood for 24 h prior to characterization and storage. The electrospinning experiments were performed at temperatures in the range of 18–22 °C.

Characterization of Electrospun Fiber Mats. Optical microscopy (Nikon UDM Eclipse LV100D-U) was used for immediate study of the fiber integrity and mat formation for optimization of the electrospinning voltage and feed rate for each polymer blend ratio. A glass microscope slide was placed on the aluminum collection plate and allowed to collect fibers for 1–2 min. The microscope slide was then viewed under the optical microscope at 10X, 100X, and 1000X magnification to check for the formation of fibers and the presence of beads. Feed rate and voltage were adjusted for each solution until continuous fibers with the least amount of beading were formed.

Morphology and diameter of the fibers were analyzed using a Hitachi S-570 scanning electron microscope (SEM) (Hitachi High Technologies, Tokyo, Japan) at an accelerating voltage of 15 kV. SEM samples were prepared by affixing a rectangular piece of the aluminum collection sheet to the sample stand with carbon tape. Each specimen was gold/palladium-coated using an Emitech K550 sputtering device (Ashford-Kent) up to a thickness of 15 nm at a rate of 7 nm min⁻¹ prior to imaging.

Diameters of the fibers were measured directly from the images using ImageJ software, with the average value being calculated from at least 100 measurements. The presence or absence of beads was determined at 5000X magnification, and the presence or absence of pores was determined at 15000X magnification.

Differential Scanning Calorimetry (DSC). The glass transition, melting and crystallization temperatures, and degree of crystallinity of the fibers from neat polymers and their blends were obtained using a differential scanning calorimeter (TA Instruments DSC Q 200) in a nitrogen atmosphere. Approximately 8 mg of each fiber mat was encased in an aluminum sample pan and heated from –50 to 180 °C

at 10 °C/min followed by cooling to –50 °C at 5 °C/min, followed by a second heating ramp to 180 °C at 10 °C/min.

The degree of crystallinity, X_c , is estimated from the area under the endotherm by the equation:

$$X_c (\%) = \frac{\Delta H_f - \Delta H_c}{\Delta H_f^\circ} \times 100\% \quad (1)$$

where ΔH_f and ΔH_c are the measured enthalpy of fusion and enthalpy of crystallization, respectively, and ΔH_f° is the enthalpy of fusion for 100% crystalline PLLA (93.6 J/g) or 100% crystalline PHBV (109 J/g).^{32–34} Figure 5 displays the exothermic peaks of cold crystallization during the first heating cycle. Recrystallization of the amorphous PLLA fraction only occurs above the T_g when the mobility of the PLLA chains is sufficient enough to favor reorganization into crystalline conformations.³⁵ The newly formed crystallites are also melted during continuous heating, and thus the percentage crystallinity is calculated by subtracting the heat of cold crystallization on the exotherm from the heat of fusion on the endotherm.

Thermogravimetric Analysis (TGA). The thermal degradation characteristics of the fibers, from neat polymers and their blends, were obtained using thermogravimetric analysis (TA Instruments TGA Q500) in a nitrogen atmosphere. Approximately 8 mg of each fiber mat was heated from 20 to 600 °C at 20 °C/min.

Dynamic Mechanical Analysis (DMA). The yield strength and Young's modulus of the electrospun fiber mats were determined using dynamic mechanical analysis (TA Instruments DMA Q800). Fiber mats approximately 0.15 mm thick were cut into rectangular samples 5 mm wide. An isothermal stress-strain test was conducted with 18 mm of the sample between the tension film clamps of the DMA at 40 °C with a 0.001 N preload force, 5 min soak time, and 0.1 N/min ramp rate.

RESULTS AND DISCUSSION

Electrospinning involves a number of parameters that affect the resultant fiber morphology and diameter including characteristics of the polymer, concentration of the polymer, and resultant solution viscosity, solvent, needle gauge, applied voltage, feed rate, and distance from needle to collector.^{22,25,26} Ambient temperature and humidity also affect the resultant fibers.²⁷ When utilizing a blend of polymers and solvents, the ratio of the blend and selected components in the blend also affect the fiber morphology.

Effects of Solution Parameters. The solvent ratio and processing parameters for electrospinning of varying PLLA/PHBV blends were optimized to obtain a visible Taylor cone at the tip of the needle and one continuous stream of fluid emerging from the Taylor Cone. The ideal electrospinning parameters for each solution displayed continuous fibers collecting on the plate and the lowest occurrence of needle blockage.

The optimal ratio of the cosolvents in the solvent system was determined by electrospinning solutions of 10 w/v PLLA in solvents with varying ratios of chloroform and DMF. Many groups have used chloroform as a solvent for PHBV.^{20,31,36,37} However, the fast evaporation of chloroform causes needle blockage due to drying the solution at the needle tip. Addition of a second solvent with low vapor pressure such as DMF lowers the drying rate, facilitates the spinning process, and reduces the needle blockage. The mixed solvent (chloroform/DMF, 9:1 v/v) produced thin continuous fibers, and the quantity of DMF was high enough to prevent rapid needle blockage. Increasing the concentration of DMF (chloroform/DMF, 8:2 v/v) resulted in fibers that appeared wet on the collection plate with large diameters. The mixed solvent (chloroform/DMF, 7:3 v/v) could not completely dissolve

the PLLA pellets, even after 48 h of stirring. From these observations, the solvent ratio of (chloroform/DMF, 9:1 v/v) was selected for testing the solubility of PHBV with different HV contents.

Pellets of the three grades of PHBV were added separately to the solvent mixture (chloroform/DMF, 9:1 v/v) to prepare solutions of 10 w/v polymer if completely dissolved. After 48 h, the pellets with 11 mol % and 14 mol % HV content were fully soluble in (chloroform/DMF, 9:1 v/v). Solutions prepared with 2.9 mol % HV content PHBV pellets exhibited marginal dissolution, despite additional trials with varying solution concentrations and the application of heat. Even though the undissolved particles did not block the needle during electrospinning, SEM images of electrospun fibers of these suspensions revealed dense collections of fibers around an undissolved clump of polymer (Figure 2). With increasing HV

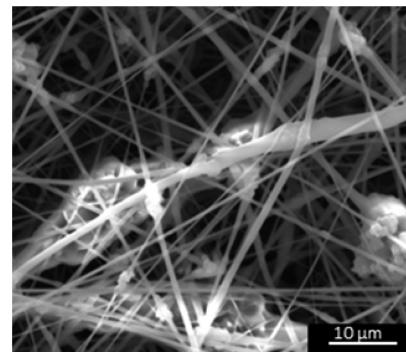


Figure 2. Undissolved particles on the electrospun fibers from solution of (PLLA/PHBV, 7:3 w/w) in a mixture of chloroform/DMF, 8/2 v/v; HV content of PHBV was 2.9 mol %. PHBV was not completely soluble in the solvent mixture and made a suspension.

content, solubility of the PHBV in the solution mixture increased. The PHBV with the highest HV content (Biopol PHBV, HV content 14 mol %) was thus used henceforth in all blends. In other studies on electrospinning of solutions containing PHBV, dissolution was aided by heating or required electrospinning at an elevated temperature.^{20,28,29,38} However, in this study, solutions were prepared at room temperature using the two-step dissolution method explained in the Experimental section. Centrifugation of the solutions resulted in limited polymer stratification, indicating dissolution of the polymers.

After the (chloroform/DMF, 9:1 v/v) solvent system and the PHBV with 14 mol % HV content were selected, electrospinning of solutions with different ratios of the overall concentrations of PLLA and PHBV were tested. Solution concentration influences the amount of chain entanglement, which resultantly determines whether electrospinning or electrospraying occurs.³⁹ PLLA increased the viscosity of the solution more than PHBV, and thus a higher PLLA content was required to lower total polymer concentrations to produce a viable solution for electrospinning of continuous fibers.⁴⁰ Total polymer content of 10 w/v and needle gauge of 24 were selected for continuation in electrospinning trials.

Morphology of the nonwoven fiber mats from solutions with 10 w/v of varying PLLA/PHBV polymer ratios indicated the effects of the polymer content on the morphology of the fibers (Figure 3). The electrospun fibers of PLLA/PHBV blends had mean fiber diameters between 1.2–1.5 μm. Parameters such as

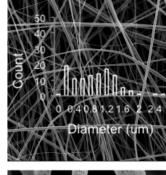
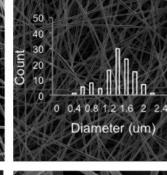
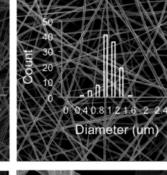
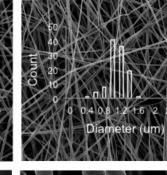
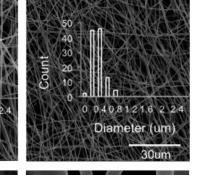
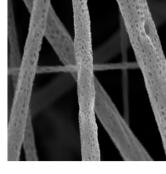
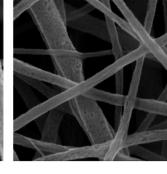
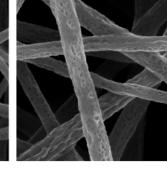
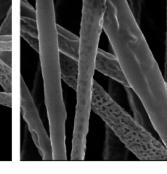
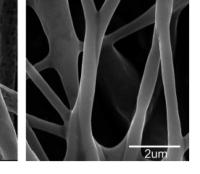
Mag.	PLLA/PHBV Blend Ratio (w/w)				
	10:0	8:2	7:3	6:4	0:10
1000X					
15000X					
Surface Tension (mN/m)	29.57	29.34	28.16	28.41	28.97
Voltage (kV)	17.0	15.0	15.5	14.5	12.5
Mean Fibre Diameter (μm)	0.995±0.321	1.517±0.368	1.228±0.177	1.216±0.419	0.451±0.154
Beads	N	N	N	Y	Y

Figure 3. Scanning electron micrographs for electrospun PLLA/PHBV blend fibers, their diameter distributions, solution, and electrospraying parameters and resulting fiber morphology.

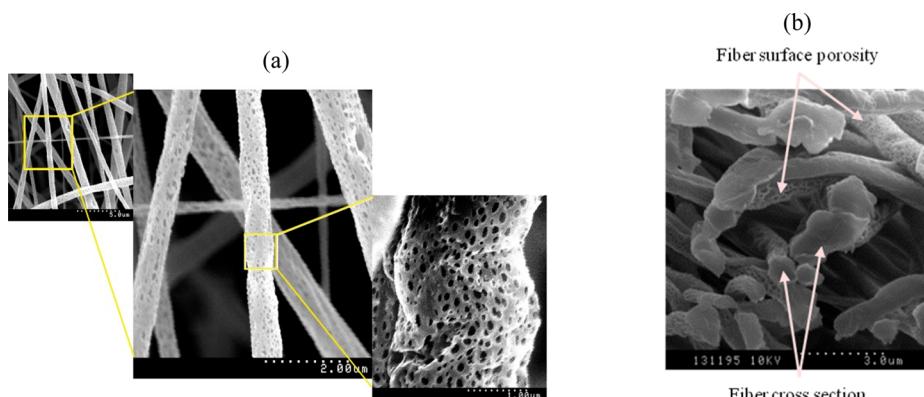


Figure 4. (a) Porous surface of (PLLA/PHBV, 10:0 w/w) fiber. SEM images at 6000X, 15000X, and 30000X magnification. (b) Cross-section of the porous fibers.

solution composition and applied voltage affect the fiber diameter and morphology. With an increasing fraction of PLLA in the blend, the fibril porosity increased and bead formation decreased. Blended solutions produced fibers with greater diameters than those produced from either neat polymer. Fiber diameters of different blend ratios were compared by ANOVA analysis, and the results showed that only PLLA fibers have significantly different diameters. Solutions containing a higher percentage of PHBV required a lower applied voltage, but resulted in beaded fibers. Continuous nonwoven mats of uniform nonbeaded fibers were produced by electrospinning of PLLA/PHBV with 10:0, 8:2 and 7:3 w/w blends.

Effects of Electrospinning Parameters. Formation of the solution jet from the Taylor cone in the electrospinning setup requires the electrostatic force applied to the charged solution to exceed the surface tension of the solution.⁴¹ Surface tension and viscosity are theorized to be codeterminants in bead formation on fibers.⁴² In a solution with low viscosity, the solvent molecules bead together due to surface tension.²³

Therefore, a higher viscosity (greater concentration of polymer, greater amount of PLLA in blend ratio) and lower surface tension favor nonbeaded fibers.

The electrospinning parameters (feed rate, voltage, distance from collector, diameter of needle, and temperature) influence the fiber morphology to a lesser degree than the solution parameters.²³ Voltage was the key experimental parameter in this study. Increased voltage was required to overcome a higher surface tension and also provided a quickened processing time for the given solution volume. The higher the voltage the more likely that secondary sites of fiber formation occurred on the Taylor cone, indicating instability and high variability in fiber diameter. The fiber diameter distribution becomes broader as the voltage increases, which limits usability for applications requiring uniform fiber diameters. As is consistent with similar studies on PHBV blends, increasing the applied voltage caused an increase in mean fiber diameter and a decrease in the tendency for bead formation.³¹

Porosity. Porosity of the electrospun fibers increased with increasing PLLA fraction of the total polymer content in the electrospinning solution (Figure 4). The high molecular weight of the PLLA results in a viscous electrospinning solution. It is hypothesized that the higher molecular weight PLLA molecules limit the ability of the solution to fill the pores during evaporation of the condensed moisture on the fibers, resulting in a porous fiber.

Ambient parameters, especially humidity of the electrospinning apparatus, greatly influence the resultant porosity of the fibers. An increase in humidity can cause pores to form on the surface of the fibers, with the pore size increasing with humidity.²⁷ In humid conditions, moisture condenses on the cold surface of the fibers as the solvent evaporates. When both the water and solvent evaporate, a pore is formed as a pocket where no polymer was present.

Thermal Analysis. The DSC thermograms of the electrospun PLLA/PHBV blend fibers are depicted in Figure 5. The

two distinct T_g appear, corresponding to PHBV and PLLA. In the peer-reviewed study on the miscibility of similar electrospun polymer blends, Cheng et al. concluded that PDLLA and PHBHHx do not cocrystallize, but the second cycle T_g of PHBHHx was difficult to identify, which was not the case in our results.⁴⁴ The results indicate some degree of engagement between PHBV and PLLA chains in the fibers or partial miscibility that may be caused by high shear and elongation during the spinning process.

A bimodal endothermic melting peak for PHBV was observed. Formation of heterogeneous crystals and their melting, recrystallization, and remelting causes the multiple melting peaks. The melting peaks of the neat electrospun PLLA and PHBV were observed at 170.1, 135.1, and 153.3 °C, respectively. In the electrospun blends, the melting peak of PLLA stays the same, but the two melting peaks of PHBV merge and appear as a broad peak with a center point between the two melting points of neat PHBV. This indicates that the elongational flow during spinning favors the more stable crystal formation. However, the fast drying does not provide enough time for crystallization. In the second heating cycle, two peaks of PHBV appear.

PLLA is a semi-crystalline polymer with both regular repeating crystalline and randomly arranged amorphous phases.⁴⁵ During electrospinning, as the fiber solidifies, the polymer chains are stretched in the direction of the electrostatic field. Rapid evaporation of the volatile solvent and solidification of the stretched polymer chains reduces chain mobility and does not allow sufficient time for crystal growth. The degree of crystallinity of the electrospun materials is lower than that of the neat PLLA and PHBV. In DSC experiments, a peak of cold crystallization in the first heating cycle is due to the movement of the chains into a more organized crystalline structure.

The enthalpies of fusion and crystallization are interrelated. Percent crystallinity of the blends is lower than each neat polymer alone. The presence of two materials together and the quick solidification of the jet during electrospinning reduce the ability of the chains to organize into the crystalline structure. As the ratio of PHBV decreased, the crystallinity of the PHBV fraction decreased. The crystallinity of the PLLA fraction in all blends was relatively consistent, as was the T_m for PLLA.

The results from TGA analysis indicate the characteristic thermal degradation of the polymeric electrospun samples (Figure 6). The decomposition temperature indicates the highest processing temperature that the electrospun mats can withstand, although the fiber structure is lost at temperatures above the melting point.

The onset temperature, T_{onset} , is calculated as the temperature at which the sample exhibits 1% mass loss. For the blends

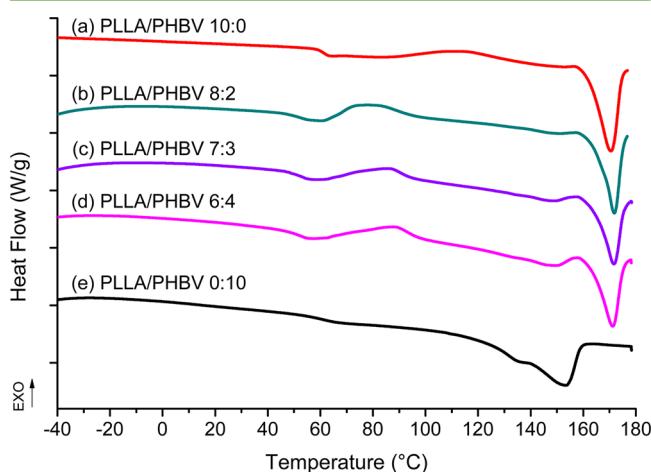


Figure 5. First heating cycle of DSC thermograms of PLLA/PHBV fibers.

cold crystallization temperature, T_c , melting temperature, T_m , heats of fusion and crystallization, H_f and H_c , and the percentage crystallinity, X_c , of the fibers are summarized in Table 1. The first heating cycle was analyzed to observe the as-spun properties of each sample.

Miscibility of the pure polymers in a blend can be determined by observation of the glass transition temperature of the blend. A single composition-dependent glass transition temperature for a polymer blend, located between the glass transition temperatures of the neat polymers, is an indication of polymer miscibility.^{18,43} However, in the second heating cycle,

Table 1. DSC Thermal Characteristics and Crystallinity of As-Spun PLLA/PHBV Fibers^a

fiber composition (PLLA/PHBV w/w)	T_m (°C)		T_c (°C)	H_f (J/g)		H_c (J/g)	X_c (%)	
	PLLA	PHBV		PLLA	PHBV		PLLA	PHBV
10:0	170.3	—	83.5	40	—	17	24.6	—
8:2	170.3	149.7	83.6	30.8	1.2	14.7	17.2	1.1
7:3	170.2	148.8	89.7	27.15	4.4	12.6	15.5	4
6:4	170	148	89.6	24	7.2	9.6	15.4	6.5
0:10	—	135.0	—	—	47.5	—	—	43.5
			153.3					

^aResults are obtained from the analysis of the first heating cycle. T_m , melting temperature; T_c , cold crystallization temperature; H_f and H_c , heat of fusion and heat of cold crystallization, respectively; and X_c , percentage of crystallinity.

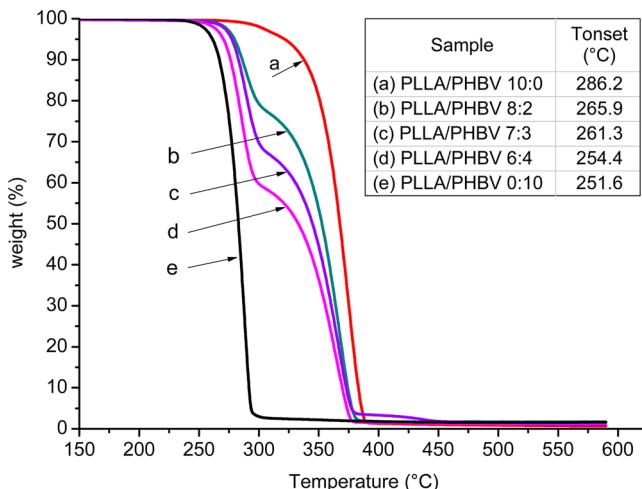


Figure 6. Thermal degradation of PLLA/PHBV blend fibers as measured through TGA. The table shows the temperature of onset of degradation, which is temperature at 1% weight loss.

with increasing PHBV content, the thermal degradation happens in two steps, indicating the degradation of the PHBV phase followed by the PLLA phase. The blend fibers are more stable than the pure PHBV fibers.

Mechanical Testing. Measuring tensile properties of the electrospun mats demonstrated that the yield strength increased as the fraction of PLLA in the blend was increased (Figure 7). PLLA electrospun fibers have higher yield strength

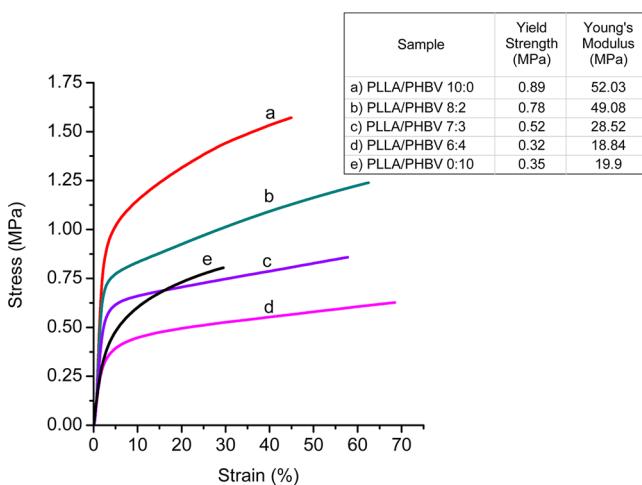


Figure 7. Stress-strain curve from DMA of PLLA/PHBV blend electrospun fiber mats, $100 \pm 10 \mu\text{m}$ thick.

compared to PHBV fibers. Blending PLLA with PHBV reduces the strength of the blend fibers. Fiber blends with 40% w/w PHBV have lower strength compared to the neat PHBV fibers. Immiscibility of the blend polymers or a weak interfacial adhesion at 30–40% PHBV content may cause the early failure of the blend fiber. In tensile tests of electrospun PLLA, the Young's modulus decreases linearly with increasing fiber diameter due to improved chain orientation in smaller fibers.⁴⁵ The values obtained for the Young's moduli are on the same order of magnitude as electrospun mats of similar polymers.³⁷ Sombatmankhong et al. obtained Young's modulus values 1 order of magnitude larger for PHBV fiber mats of comparable thickness using a universal testing machine.²⁰ The procedural

differences between the two tensile tests include increased sample size and decreased strain rate.

The optimization of processing parameters with PLLA/PHBV ratios of 8:2 w/w and 7:3 w/w could be used to fabricate bead-free nonwoven membranes with increased mechanical and thermal properties, as compared to neat electrospun PHBV.

CONCLUSIONS

Microfibers of PLLA, PHBV, and their blends were successfully obtained by electrospinning in (chloroform/DMF, 9:1 v/v) at room temperature. SEM showed that the PLLA/PHBV blend electrospun fibers had mean fiber diameters between 1.22–1.52 μm . With increasing fraction of PLLA in the blend, the fibril porosity increased and bead formation decreased. SEM images demonstrate that the fiber diameter and morphology were dependent on processing parameters such as solution composition and applied voltage. The optimization of processing parameters with PLLA/PHBV ratios of 8:2 w/w and 7:3 w/w could be used to fabricate bead-free nonwoven membranes with increased mechanical and thermal properties, as compared to neat electrospun PHBV.

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Notes

The authors declare no competing financial interest.

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■ NOTE ADDED AFTER ASAP PUBLICATION

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