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Crystallization Behavior of Electrospun PB/PMP Blend Fibrous Membranes

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ABSTRACT: Although polyolefins are used extensively in the plastics industry, these polymers have found restricted use in electrospinning due to the limited number of solvents which provide reasonable solubility and dielectric constant. We have successfully prepared polyolefin fibrous membranes via electrospinning from multicomponent solvent systems. Fibers spun using a PB/PMP blend have a twisted-ribbon structure with irregular twisting points along the length of the fibers. The crystallization behavior was investigated by wide-angle X-ray diffraction, differential scanning calorimetry, and Fourier transform infrared spectroscopy. It was found that the crystallization of poly(1-butene) (PB) was strongly affected by the addition of poly(4-methyl-1-pentene) (PMP) to the blend. In pure PB fibrous membranes, a mixture of forms I and II were obtained, and the thermodynamically metastable form II gradually transformed into form I with aging at room temperature. However, this transformation did not occur in the PB/PMP blends, due to stabilization of the metastable form II of PB in the blend. Consequently, the rate of transformation (II → I) of PB in the blend was retarded, whereas pure PMP fibers and fibers made from the PB/PMP blend both show PMP present in crystal form I, indicating that the crystallization behavior of PMP is not affected by blending.

Introduction

Electrospinning is a simple method for the production of fibers with submicron diameters.[1,2] A patent was first applied for by Formhals in 1934.[3] This technique has recently attracted considerable attention and has been extensively studied by many researchers because of its potential and practical applications for filtration, protective clothes, fiber reinforcement in composite materials, sensors, optical and electrical devices and biomaterial applications (e.g., wound dressing, drug delivery system, scaffold in tissue engineering, etc.).[2,4–6]

Although polyolefins such as polyethylene, polypropylene, poly(1-butene), and poly(4-methyl-1-pentene), as well as their copolymers and blends, comprise a large portion of the industrially relevant polymers market, studies of electrospun olefin polymers, despite their excellent chemical resistance, have been limited due to their poor solubility in the polar solvents. Recently, however, electrospinning of olefin polymers from solution at slightly elevated temperature was reported.[7–9]

Phase separation in a mixture of chemically different polymers occurs by the reduction of the entropy of mixing[10] and can lead to novel materials, which have properties that could not be obtained from a single polymer. Moreover, blending has been used for the reduction of basic costs (e.g., carbon black in tire industry) and increased processability. The properties of the blends are strongly dependent on the compatibility of the components of the polymer blends as well as their inherent properties. In the case of structurally different, crystalline polymer blends, these polymers can either cocrystallize or form two distinct crystalline structures. The degree of compatibility plays a key role in determining the final properties of polymer blends. In this study, we focus on the crystallization behavior of electrospun fibrous membranes of poly(1-butene) (PB), poly(4-methyl-1-pentene) (PMP), and their blends. Careful manipulation of PB/PMP blends could lead to materials with greater flexibility than those found for either of the pure components of the blend while maintaining the robust physical characteristics and toughness of both PB and PMP, since forms II and III of PB[9] are more pliable than the remaining crystalline forms of PB and all forms of PMP.

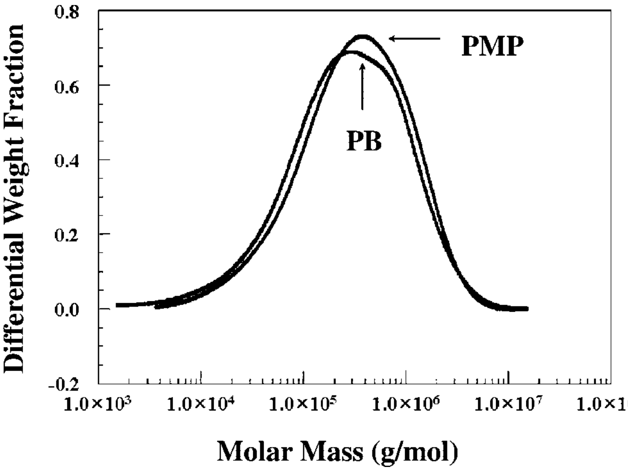

Figure 1. GPC profiles of PB and PMP.

Experimental Section

Materials. Isotactic poly(1-butene) (PB) and isotactic poly(4-methyl-1-pentene) (PMP) were purchased from Aldrich and used as received. Figure 1 shows the GPC traces for both PB and PMP with the relevant molecular weight information summarized in Table 1. Both the pure polymers and their blends

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Table 1. Molecular Weight Information for PB and PMP

	Molar Mass Moments (g/mol)		
polymer	M_n	M_w	polydispersity (M_w/M_n)
PB	93 000	560 000	6.0
PMP	125 000	590 000	4.7

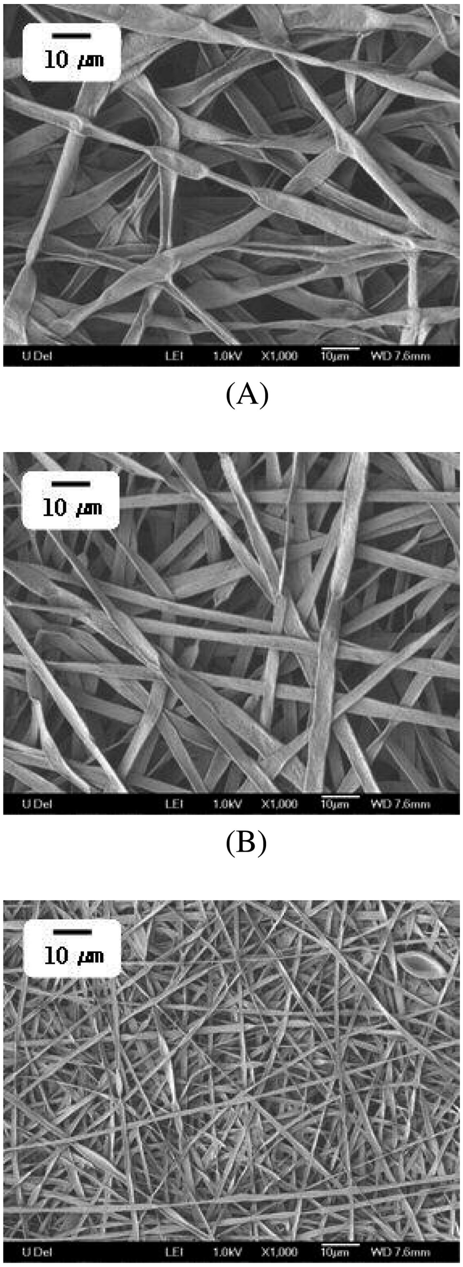
were dissolved in a mixture of cyclohexane, acetone, and dimethylformamide (DMF) (80/10/10 by weight ratio) at a temperature above 60 °C and then slowly cooled to a temperature slightly higher than room temperature (25−30 °C) for electrospinning. All solutions contained 2.5% w/w polymer and were processed under identical conditions with a solution flow rate of 0.25 mL/hr, a syringe tip to collector distance (working distance) of 15 cm, and an applied voltage of 11 kV. After electrospinning, the fibers were dried in a vacuum oven at room temperature for 2 weeks to remove the residual solvents. The details of the electrospinning apparatus used in this study have been described previously.[8,9]

Characterization. The morphology of the electrospun fibers was characterized using a field emission scanning electron microscope (FE-SEM, JSM-7400F, JEOL) operating at 1 kV and 10 μA. Wide angle X-ray diffraction (WAXD) measurements were carried out with a fixed anode X-ray generator (Rigaku, Geigerflex, 40 kV and 30 mA) with Cu Kα radiation ($\lambda = 1.5402$ Å). All viscosity measurements were carried out in triplicate at 25 °C on a Brookfield Engineering (Middleboro, MA) CAP 2000+ viscometer using a number 4 spindle at 100 s^{-1} shear, and are reported in poise (P). Thermal properties were evaluated under a N_2 atmosphere using a differential scanning calorimeter (DSC, Q100, TA Instrument) using 20 °C/min heating and cooling rates. FTIR spectra were acquired with a Nexus 670 interferometer (Thermo Nicolet) and were recorded in the range from 750−4000 cm^{-1} using an average coaddition of 128 scans. Except where noted all samples were measured after 2 months of aging.

Results and discussion

All blends (PB/PMP = 100/0, 75/25, 50/50, 25/75, and 0/100, w/w) were successfully prepared in the form of fibers without beads at 2.5% w/w concentration. As detailed in previous investigations,[8,9] solvent cast films of PB are predominantly forms I and III, with the metastable form II being present only in electrospun PB fibers. Solvent cast PMP films were form I only. Figure 2 shows FE-SEM images of fibrous membranes electrospun from pure PB, 50/50 blend, and pure PMP. Solution viscosities indicate that pure PB solutions were the most viscous with a value of 1.11 ± 0.03 P while PMP, with its larger side chain, had a viscosity of 0.88 ± 0.03 P. The 50/50 w/w PB/PMP blend solution had a viscosity of 0.99 ± 0.05 P. Although not shown, all blends studied exhibit a twisted-ribbon fiber morphology with irregular twist points. This structure is a result of the different evaporation times of the different solvents used and the phase separation formed by adding nonsolvents and a collapse of the fibers as the solvent "core" evaporates.[8] Furthermore, the fiber diameter decreases with increasing PMP composition, which can be attributed to the lower viscosity of PMP (0.88 ± 0.03 P for pure PMP vs 1.11 ± 0.03 P for pure PB) in solution. As a general trend, increasing the molecular side group size results in a lower solution viscosity although the molecular weight of PMP is slightly higher than that of PB.

Depending on the preparation methods, PB and PMP can be crystallized in several different crystalline structures,[11,12] which are summarized in Table 2.[11–24] Figure 3 shows WAXD profiles of electrospun fibrous membranes for both the pure PB and PMP as well as several PB/PMP blends. In the case of the pure PB membrane, crystalline forms I and II coexisted immediately after the fibers were spun. The metastable form II then transformed into the stable form I after aging one month at room temperature.[9] As shown in Figure 3A, pure PB fibers show three reflections at $2\theta = 9.9°$ (110), 17.3° (300), and 20.4° (220), indicative of a hexagonal structure with a 3/1 helix conformation.[11,25] Further evidence that the fibers adopted form I can be seen in the melting temperature of 120.2 °C (Figure 4A and Table 2). Also, a very weak peak at $2\theta = 11.8°$ (200) corresponding to tetragonal crystal of PB[25] still exists after aging, indicating that a small amounts of form II remains in the pure PB fibers.



(A)

(B)

(C)

Figure 2. FE-SEM images of fibers electrospun from a 2.5 wt % solution of (A) pure PB (100/0), (B) 50/50 blend, and (C) pure PMP (0/100).

The WAXD profiles of the blend membranes are more complicated. In the blend samples, there are two peaks (indicated by the arrows in Figures 3 and 5) at $2\theta = 11.8°$ (200) and 18.3° (213),[25] indicative of a tetragonal crystal (form II) of PB. Also, the reflection at $2\theta = 18.3°$ can indicate a tetragonal crystal of

Table 2. Crystallographic Data for PB and PMP

				unit cell dimension (Å)			
polymer	form	crystal lattice	helix	*a*	*b*	*c*	T_m (°C)
PB	I	hexagonal (twined)	3/1	17.70	17.70	6.50	120−135
	I′	hexagonal (untwined)	3/1	17.70	17.70	6.50	90−100
	II	tetragonal	11/3	14.60	14.60	21.20	110−120
	III	orthorhombic	4/1	12.50	8.90	7.60	90−100
PMP	I	tetragonal	7/2	18.66	18.66	13.80	Generally not dependent on crystalline form[b]
	II	tetragonal	4/1	19.16	19.16	7.12	Generally not dependent on crystalline form[b]
	III	tetragonal	4/1	19.46	19.46	7.02	Generally not dependent on crystalline form[b]
	IV	hexagonal	4/1	22.17	22.17	6.69	Generally not dependent on crystalline form[b]
	V[a]						

[a] No reported structure. [b] Generally not dependent on crystalline form (220−245).

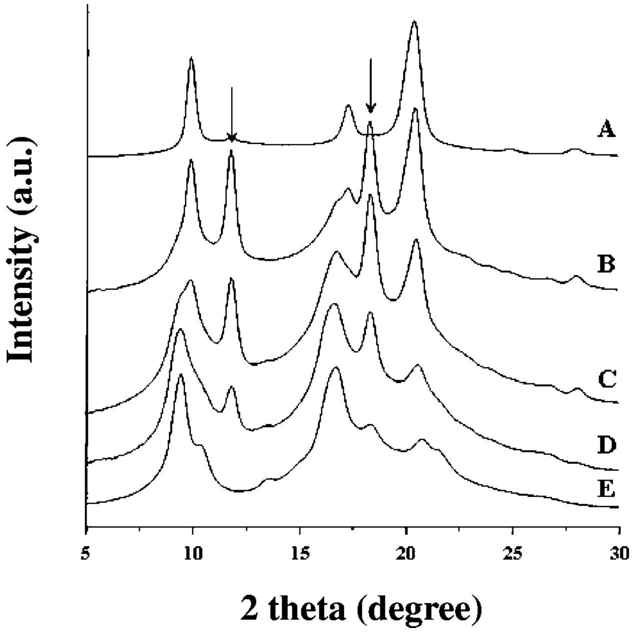


Figure 3. WAXD profiles of the electrospun (A) pure PB (100/0), (B) PB/PMP = 75/25, (C) PB/PMP = 50/50, (D) PB/PMP = 25/75, and (E) pure PMP (0/100) fibrous membranes after 60 days aging.

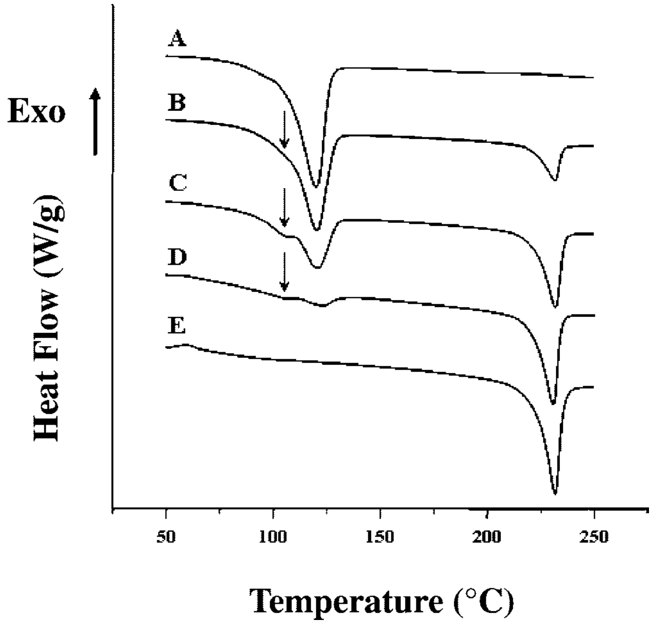


Figure 4. DSC thermograms acquired during heating of the electrospun (A) pure PB (100/0), (B) PB/PMP = 75/25, (C) PB/PMP = 50/50 (D) PB/PMP = 25/75, and pure PMP (0/100) fibrous membranes.

PMP (Figure 3E). Interestingly, although the metastable tetragonal crystals transform into stable hexagonal crystals in pure PB,[19,26] they still remain in the blends even after 1 year of aging at room temperature. This transformation can be observed in Figure 5, which shows that the intensity of the peaks corresponding to form II of PB decrease slightly over time with a corresponding increase in the peaks corresponding to form I of PB. This demonstrates that the metastable form II crystals of PB are stabilized in the presence of form I crystals of PMP.

For all blends, there is a main endothermic peak near 120 °C, corresponding to the melting temperature for PB of form I, and a smaller peak at 104 °C, corresponding to the melting temperature of form II (figure 4). The reason that the endotherms for form II are smaller than expected from the X-ray results is due to the accelerated transformation of some of the metastable form II crystals into form I during the heating ramp. This behavior has been previously observed in electrospun fibers of pure PB.[9]

The WAXD profile of the pure PMP fibrous membrane (Figure 3E) demonstrates that only form I is present and is the predominant crystal form in the blends, as evidenced by the reflections at $2\theta = 9.5°$, 16.8°, 18.3°, and 20.7°. Additionally, the melting temperature of PMP remains constant at 232 °C for both pure PMP fibers and blend fibers.

When the PB/PMP blends crystallize from the molten state, PMP first crystallizes in the presence of melted PB chains and then the molten PB crystallizes in the presence of PMP crystals. Figure 6 shows the thermograms obtained during crystallization of all blends. The crystallization temperatures (T_c) of pure PB and PB in the 75/25 and 50/50 blends were found to be 63, 76, and 75 °C, respectively (Figure 6A−C), and the temperature was seen to decrease to 31 °C for the 25/75 blend (Figure 6D). A possible explanation for the increased T_c of PB in the 75/25 and 50/50 blends is that the PMP crystals can act as nucleating agents during the crystallization of PB. Similar results have been observed in blends of PB with polypropylene prepared from the melt.[27] Furthermore, there are two crystallization temperatures at 75 and 33 °C in the 50/50 blend. This arises from the two different crystal forms of PB crystallizing during cooling and can be seen upon reheating the sample again, as shown in Figure 7. During the second heating scan of the 50/50 blend, there are two endothermic peaks, a main peak at 111 °C from form II and a small secondary peak at 132 °C, resulting from form I.

The stabilization of metastable form II of PB in PB/PMP blends is also observed in the FTIR spectra, as shown in Figure 8. Infrared spectroscopy is sensitive to changes in polymer backbone conformation and can exhibit different spectral absorption bands for different crystalline forms of polymers. For pure PB, this behavior is seen in the CH_2 and CH_3 rocking band, which appears at 925 cm^{-1} for form I and 900 cm^{-1} for form II.[28,29] This band is also present in PMP and appears at 918 cm^{-1} (CH_3 rocking)[30] in form I. The results

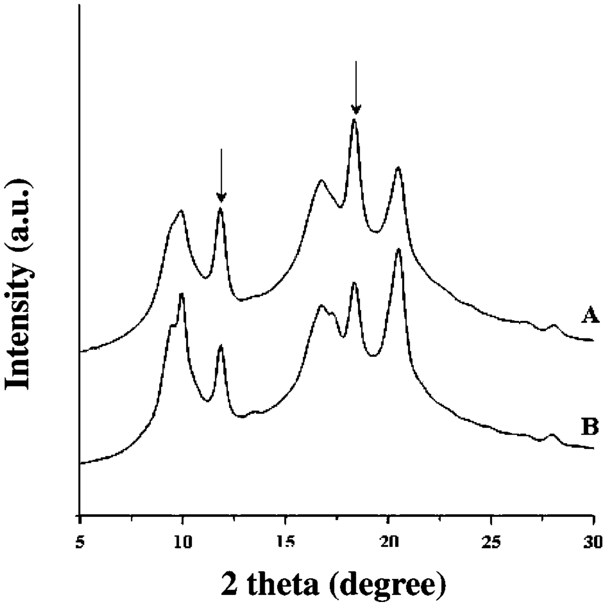


Figure 5. WAXD profiles of the electrospun 50/50 blend fibrous membrane after (A) 2 months and (B) 1 year aging time.

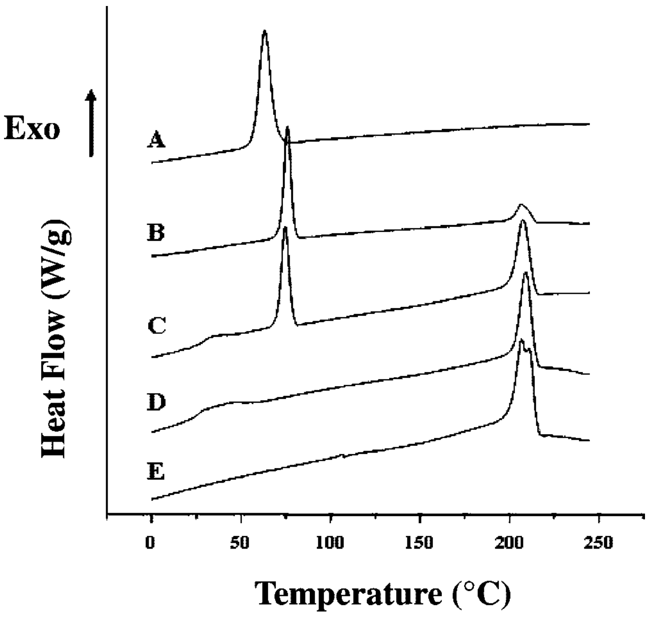


Figure 6. DSC thermograms acquired during cooling of the electrospun (A) pure PB (100/0), (B) PB/PMP = 75/25, (C) PB/PMP = 50/50 (D) PB/PMP = 25/75, and pure PMP (0/100) fibrous membrane.

presented in Figure 8 corroborate the results obtained from WAXD and DSC and provide additional evidence that polymer chains with chain conformations indicative of form II are present in the blends.

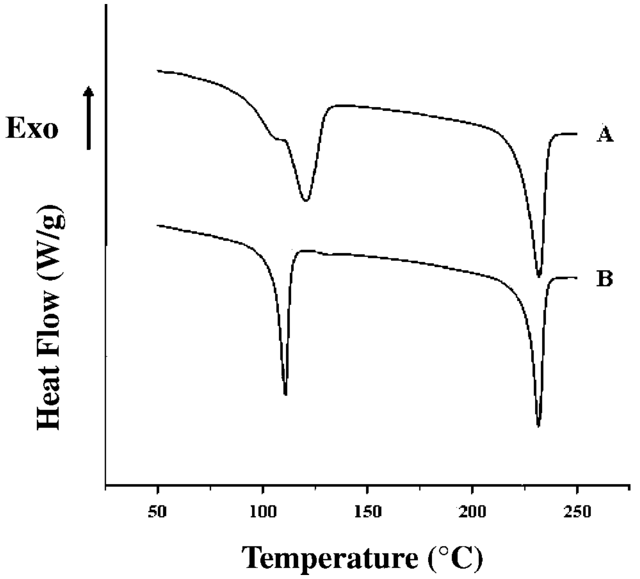


Figure 7. DSC thermograms of the electrospun 50/50 blend fibrous membrane: (A) first heating scan and (B) second heating scan.

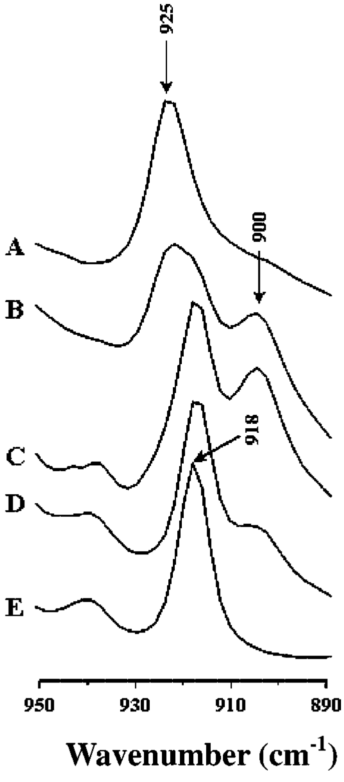


Figure 8. FTIR spectra of the electrospun (A) pure PB (100/0), (B) PB/PMP = 75/25, (C) PB/PMP = 50/50, (D) PB/PMP = 25/75, and pure PMP (0/100) fibrous membranes in the range of 950−890 cm^{-1}.

Conclusions

The crystallization behavior of electrospun PB/PMP blends was investigated. The results of WAXD, DSC, and FTIR spectroscopy show that the transformation of form II to form I of PB is severly restricited in the blends, most likely due to the interchain or crystal/crystal interactions between the PB and PMP. The PMP component in the blends shows behavior similar to that of pure PMP regardless of blend composition. The fact that only one component of the blend is affected is due to the wide disparity of the melting temperatures of the two components, Upon cooling, the PMP crystallizes first and can therefore act as a nucleation agent for PB without itself being affected by the presence of the PB within the blend.

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