Miscible Blends Containing Bacterial Poly(3hydroxyvalerate) and Poly(*p*-vinyl phenol)

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ABSTRACT: The miscibility of poly(3-hydroxyvalerate) (PHV)/poly(*p*-vinyl phenol) (PVPh) blends has been studied by differential scanning calorimetry (DSC) and Fourier transform infrared (FTIR) spectroscopy. The blends are miscible as shown by the existence of a single glass transition temperature (T_g) and a depression of the equilibrium melting temperature of PHV in each blend. The interaction parameter was found to be -1.2 based on the analysis of melting point depression data using the Nishi–Wang equation. Hydrogen-bonding interactions exist between the carbonyl groups of PHV and the hydroxyl groups of PVPh as evidenced by FTIR spectra. The crystallization of PHV is significantly hindered by the addition of PVPh. The addition of 50 wt % PVPh can totally prevent PHV from cold crystallization. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 383–388, 1999

Key words: poly(3-hydroxyvalerate); poly(*p*-vinyl phenol); miscibility

INTRODUCTION

Bacterial polyhydroxyalkanoates (PHAs) have received much attention in the past decade owing to their biodegradability.^{1,2} They are biosynthesized in a large number of bacteria as intracellular carbon and energy storage compounds, analogous to starch in plants, and glycogen in mammalian systems.^{3,4} The most well-known PHAs are poly(3-hydroxybutyrate) (PHB) and poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) copolymers; both of them are commercially available.

The most exciting development in PHA synthesis is the transfer of PHA biosynthetic genes into bacteria and plants to produce polymers.^{5–7} The engineered strains or transplants are able to produce PHAs efficiently, or to achieve PHAs with tailored structure. Meanwhile, the breakthrough

of fermentation engineering has also led to new members of the PHA family. During the past decade, a large number of nonnatural PHAs have been made by supplying a variety of compounds to microorganisms in feeding experiments.⁸ Recently, a new member of the PHA family, poly(3hydroxyvalerate) (PHV) was synthesized from the bacterium *Chromobacterium violaceum* by Steinbüchel et al.⁹ Similar to PHB and PHBV, PHV is a crystalline polyester with an isotactic chain configuration.

On the other hand, blending of bacterial polyesters with other polymers has received keen interest. This methodology may improve the properties, enlarge the applications, and lower the costs of these polyesters. A large number of polymer blends containing PHAs have been studied in recent years.¹⁰ PHB is miscible with poly(ethylene oxide),¹¹ poly(vinyl acetate) (PVAc),¹² poly(vinylidene fluoride),¹³ poly(epichlorohydrin),¹⁴ and poly(vinylidene chloride-*co*-acrylonitrile).¹⁵ PHBV9 (9 mol % 3-hydroxyvalerate content) is also miscible with PVAc.¹⁶ PHBV10 is miscible with synthetic atactic poly(3-hydroxybutyrate) (*a*-PHB).¹⁷

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PHBV16 and PHBV18 are miscible with poly(vinyl chloride).¹⁸

Poly(*p*-vinyl phenol) (PVPh) is miscible with various polymers such as poly(ethylene oxide),¹⁹ polyacrylates,²⁰ polymethacrylates,²¹ and polyesters including *a*-PHB, PHB, and PHBV15.^{22,23} We have recently studied the miscibility of poly(Llactide) and poly(D,L-lactide) with PVPh.^{24,25} It is interesting to investigate the miscibility of bacterial PHV/PVPh blends and the nature of specific interactions involved.

EXPERIMENTAL

Materials

PHV, produced by the microorganism *C. violaceum*,⁹ was kindly supplied by Prof. A. Steinbüchel. The weight-average molecular weight and polydispersity of PHV are 1.2×10^5 and 2.3, respectively, as determined by gel permeation chromatography using a Waters 600E system controller and Model 410 differential refractometer with tetrahydrofuran (THF) as the eluent. PVPh with a weight-average molecular weight of 3.0×10^4 was obtained from Polysciences, Inc., Warrington, PA.

Preparation of Blends

All the blends were prepared by casting from 1% (w/v) THF solution. The solvent was allowed to evaporate at room temperature overnight, followed by drying at 40°C *in vacuo* for 48 h, and finally dried at 70°C *in vacuo* for another 48 h.

Differential Scanning Calorimetry

DSC measurements were performed on a TA Instruments 2920 DSC. The instrument was calibrated with an indium standard and a nitrogen atmosphere was used throughout.

Blend samples were first heated from -80 to 160° C at a rate of 20° C/min. The samples were kept at 160° C for 1 min and were then rapidly quenched to -80° C. The samples were heated again to 160° C at a rate of 20° C/min. The glass transition temperatures (T_g 's), melting temperatures (T_m 's), enthalpies of fusion (ΔH_f), cold crystallization temperatures (T_{cc} 's), and enthalpies of cold crystallization (ΔH_{cc}) were determined from the DSC curves. The T_m and T_{cc} were taken as the peak values of the respective endotherm and exotherm in the DSC curve. The T_g was taken as

the midpoint of the specific heat increment. The reported T_g 's are based on the second heating runs unless otherwise stated.

For the determination of the equilibrium melting temperature (T_m^0) of PHV in the pure sample and the blends, the melting temperature of PHV in each blend was obtained by heating the sample to 160°C after being crystallized at different crystallization temperatures $(T_c$'s) according to the procedure of Pearce and Marchessault.²⁶ The T_m^0 of PHV cannot be determined for the blends containing 50 wt % or more of PVPh because no fusion process was detected after isothermal crystallization in all T_c 's studied.

Fourier Transform Infrared Spectroscopy

FTIR spectra were obtained with a Bio-Rad 165 FTIR spectrophotometer. A total of 64 scans were taken with a resolution of 2 cm⁻¹ in all cases. Samples were prepared by casting the THF solutions directly onto KBr discs. The discs were dried under the same condition as the cast films mentioned earlier. Spectra recorded at an elevated temperature were obtained using a Specac hightemperature cell mounted inside the sample chamber. All the films used in this study were sufficiently thin to be within an absorbance range where the Beer–Lambert law is obeyed.



Figure 1 DSC curves of PHV/PVPh blends after quenching from 160°C: (a) PHV, (b) 90/10, (c) 75/25, (d) 50/50, (e) 25/75, (f) 10/90, and (g) PVPh.



Figure 2 Phase diagram of PHV/PVPh blends. T_g composition curve was drawn using the Kwei equation with k = 0.45 and q = -38.

RESULTS AND DISCUSSION

Blend Miscibility

Figure 1 shows the DSC curves of quenched samples of PHV, PVPh, and the blends. PHV is a semicrystalline polymer with a T_g of -14° C and a T_m of 110°C for quenched sample; PVPh has a T_g of 143°C. For the entire blend composition, each PHV/PVPh blend shows only one T_g , which increases with increasing PVPh content, indicating the miscibility of the PHV/PVPh blends. The T_g 's of the blends containing 50 and 75 wt % of PVPh are rather broad. As shown in Figure 2, the T_g composition relationship can be described by the Kwei equation²⁷

$$T_{g} = \frac{w_{1}T_{g1} + kw_{2}T_{g2}}{w_{1} + kw_{2}} + qw_{1}w_{2}$$
(1)

where T_g , T_{g1} , T_{g2} are the T_g 's of the blend, PVPh, and PHV, respectively; w_1 and w_2 are the weight fractions of PVPh and PHV; and k and qare fitting constants. The best fit values of k and q for the miscible PHV/PVPh blend system are 0.45 and -38, respectively.

For the quenched sample of PHV, an exothermic peak corresponding to the cold crystallization of amorphous PHV is present at 58°C (Fig. 1). PHV/PVPh 90/10 blend shows a similar feature as that of pure PHV, but the cold crystallization peak appeared at a higher temperature (73°C). The peak is not detectable for the blends with PVPh content above 10 wt %. Moreover, the enthalpy of cold crystallization, ΔH_{cc} , is significantly lowered by the addition of PVPh. ΔH_{cc} is -48.4 J/g for pure PHV and -4.5 J/g for the 90/10 blend (Table I). The results indicate that the crystallization of PHV is markedly hindered by the presence of PVPh. The high T_g of PVPh and thus higher T_g 's for the miscible PHV/PVPh blends may account for this. As a result, the enthalpy of fusion, ΔH_f , decreases from 57.6 J/g for pure PHV to 4.7 J/g for the 90/10 blend.

Melting Point Depression

According to the Nishi–Wang equation,²⁸ the melting point depression for the miscible PHV/ PVPh blend system can be expressed by

$$-\left[\frac{\Delta H^{0}V_{1}}{RV_{2}}\left(\frac{1}{T_{mb}^{0}}-\frac{1}{T_{m}^{0}}\right)+\frac{\ln \phi_{2}}{N_{2}}+\left(\frac{1}{N_{2}}-\frac{1}{N_{1}}\right)\phi_{1}\right]$$
$$=\beta=\chi_{12}\phi_{1}^{2} \quad (2)$$

where χ_{12} is the Flory–Huggins interaction parameter, T_m^0 and T_{mb}^0 are the equilibrium melting points of PHV in the pure state and in the blend, respectively; ΔH^0 is the enthalpy of fusion of PHV (131 J/g)²⁹; V_1 and V_2 are the molar volumes of the repeat units of PVPh (100 cm³/mol)²⁰ and PHV (86.3 cm³/mol),³⁰ respectively; and ϕ_1 and ϕ_2 are the volume fractions of PVPh and PHV. The

Table I	Thermal Properties of PHV and PHV/PVPh Blends	
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Sample	T_g (°C)	$\begin{array}{c} T_{cc} \\ (^{\circ}\mathrm{C}) \end{array}$	ΔH_{cc} (J/g)	T_m (°C)	ΔH_f (J/g)	T_m^0 (°C)
PHV	-14.4	57.6	-48.4	109.9	57.9	132.5
90/10	-11.1	72.6	-4.5	109.3	4.66	131.3
75/25	-0.9		_	106.4	0.77	125.9



Figure 3 Hoffman–Weeks plot for PHV/PVPh blends: (a) PHV, (b) 90/10, and (c) 75/25.

 T_m^0 and T_{mb}^0 are determined by extrapolation to the line of $T_m=T_c$ according to the Hoffman–Weeks equation 31

$$T_m = \frac{1}{\gamma} T_C + \left(1 - \frac{1}{\gamma} \right) T_m^0 \tag{3}$$

where γ is the ratio of the initial to the final lamellar thickness. From Figure 3, the T_m^0 of pure PHV is determined to be 132.5°C, in good agreement with the literature value of 130°C.²⁶ The



Figure 4 Nishi–Wang plot for PHV/PVPh blends.



Wavenumber (cm⁻¹)

Figure 5 FTIR spectra in the hydroxyl stretching region for PHV/PVPh blends recorded at 160°C: (a) PVPh, (b) 10/90, (c) 25/75, (d) 50/50, (e) 75/25, and (f) 90/10.

equilibrium melting points of PHV in the blends are 131.3 and 125.9°C for the 90/10 and 75/25 blends, respectively.

Based on eq. (2), a negative χ_{12} value of -1.2 is obtained from Figure 4, which is consistent with a miscible blend system. As compared to a larger negative interaction parameter (-1.4) for the PHB/PVPh blend system,³² it appears that the interaction between PHV and PVPh is slightly weaker than the interaction between PHB and PVPh.

Hydrogen-Bonding Interaction

Figure 5 shows the FTIR spectra in the hydroxyl stretching region for the PHV/PVPh blends. The stretching band of hydrogen-bonded hydroxyl groups (self-association) of PVPh is broad and centered at 3396 cm^{-1} , and the stretching band of the free hydroxyl groups is evident as a shoulder at 3520 cm^{-1} at 160° C. The absorption of hydrogen-bonded hydroxyl band of PVPh progressively shifts to higher frequencies with increasing PHV content. The intensities of the free hydroxyl absorption bands of the blends are lower as compared to that of pure PVPh.



Wavenumber (cm⁻¹)

Figure 6 FTIR spectra in the carbonyl stretching region for PHV/PVPh blends recorded at 160°C: (a) PHV, (b) 90/10, (c) 75/25, (d) 50/50, (e) 25/75, and (f) 10/90.

The FTIR spectra in the carbonyl stretching region for PHV/PVPh blends recorded at 160°C are shown in Figure 6. The carbonyl stretching band of PHV appears at 1741 cm⁻¹. On the other hand, a notable new band located at 1715 cm^{-1} is found in the blends, attributed to the hydrogenbonded carbonyl groups. The intensity of the new absorption band increases with increasing PVPh content. The results indicate that hydrogen-bonding interactions between carbonyl groups of PHV and hydroxyl groups of PVPh are present in the blends. Moreover, it can be concluded that the interassociation is weaker than the self-association of PVPh as shown by the high-frequency shifts of the hydrogen-bonded hydroxyl band. Similarly, the hydrogen-bonded hydroxyl band of PVPh also showed high-frequency shifts in miscible PHBV15/PVPh²³ and a-PHB/PVPh²² blends.

CONCLUSIONS

PHV and PVPh are miscible over the whole composition range. The interaction parameter obtained from melting point depression analysis is -1.2. Hydrogen-bonding interactions between the carbonyl groups of PHV and hydroxyl groups of PVPh are shown by FTIR. The absorption band of hydrogen-bonded hydroxyl groups of PVPh shifts to higher frequencies on blending with PHV. The addition of PVPh leads to the development of hydrogen-bonded carbonyl band at a lower frequency.

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