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Miscibility of poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) and poly(vinyl chloride) blends

Soonja Choe* **and Yoon-Jong Cha**
Department of Chemical Engineering, Polymer Science and Engineering Research Institute, Inha University, Inchon 402-751, Korea

and Han-Sup Lee
Department of Textile Engineering, Inha University, Inchon 402-751, Korea

and Jin San Yoon and Hyoung Jin Choi
Department of Polymer Science and Engineering, Inha University, Inchon 402-751, Korea
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The miscibility behaviour of biodegradable poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHB-HV) blended with poly(vinyl chloride) (PVC) was investigated by using differential scanning calorimetry, dynamic mechanical thermal analysis, Fourier-transform infra-red spectroscopy and a mechanical testing system. A blend of PHB-HV containing 8% HV (PHB-8HV) with PVC was immiscible, showing two separate T_g values in all compositions; whereas a blend of PHB-HV containing 18% HV (PHB-18HV) with PVC was miscible, showing a melting-point depression and a single T_g in the whole range of compositions. For the PHB-18HV/PVC system, the C–O–C stretching vibration at 1183 cm^{-1} of PHB-18HV and the CH–Cl deformation at 1254 cm^{-1} of PVC were shifted, indicating that there exists a specific intermolecular interaction between the two components. In addition, as the PVC component was increased, tensile strength and Young's modulus were increased, while the inverse behaviour was observed in elongation at break.

(Keywords: PHB-HV/PBC blends; miscibility; specific interactions)

INTRODUCTION

Owing to improved mechanical properties and easy processibility, thermoplastics have been widely used in various fields of daily commodities, medical materials and so forth. However, much attention has been focused on pollution problems caused by plastic waste. As a result, biodegradable polymers have become a common interest all over the world.

Poly(3-hydroxybutyrate) (PHB), which is widely known as a thermoplastic biodegradable polymer, is a biosynthetic aliphatic polyester obtained by bacterial fermentation, and is a highly crystalline polymer with a melting point of about 180°C[1–3]. Poly(3-hydroxybutyrate-*co*-hydroxyvalerate) (PHB-HV) copolymer is also a biodegradable polymer and shows a wide range of mechanical and physical properties depending on the hydroxyvalerate (HV) content[4]. Thus, PHB and PHB-HV have attracted much attention as applications of thermoplastic biopolyesters. On the other hand, these materials suffer from the disadvantages of relatively high cost of production, low mechanical properties and limited processing temperature compared to conventional thermoplastics such as poly(vinyl chloride) (PVC), polystyrene (PS) or polyethylene (PE). By blending this biodegradable material with conventional thermoplastics, low-cost materials with improved properties may possibly be produced. Avella and Martuscelli have reported that PHB is miscible with poly(ethylene oxide) (PEO) in the melt state[5], and Yoon *et al.*[6] and Lee *et al.*[7] have recently reported various blend systems with PHB.

In this paper, we have investigated a way of possibly improving the miscibility and the poor conditions in production, such as high cost, low mechanical properties or limited processability, by using a blend of PHB-HV and PVC. The experimental techniques were differential scanning calorimetry (d.s.c.), dynamic mechanical thermal analysis (d.m.t.a.), Fourier-transform infra-red (*FT*i.r.) spectroscopy, thermogravimetric analysis (t.g.a.) and a mechanical testing system (m.t.s.).

EXPERIMENTAL

Materials

Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHB-HV) copolymers containing 8% and 18% HV (which are called PHB-8HV and PHB-18HV respectively in this text) were kindly provided by ICI Biological Products Division, Billingham, UK. Poly(vinyl chloride) (PVC) was purchased from Junsei Chemical Co., Japan. *N*,*N*′-Dimethylformamide (DMF) obtained from Junsei

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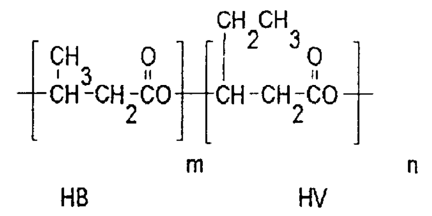
* To whom correspondence should be addressed

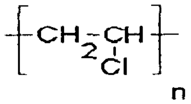
Table 1 Characteristics of poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHB-HV) and poly(vinyl chloride) (PVC)

Polymer	Source	Code	Molecular weight ($\overline{M}_n$)
PHB-HV	ICI	PHB-8HV PHB-18HV	492000^a 461500^a
PVC	Junsei Chemical	PVC	68750^b

^{a} By g.p.c. in chloroform at 30°C
^{b} By g.p.c. in THF at 30°C

Chemical Co. was used without further purification. The chemical structures of PHB-HV copolymers and PVC are shown below and their characteristics are described in *Table 1*. The molecular weight of the PHB-HV copolymers and PVC was measured in this laboratory using a Waters GPC model 510 in chloroform and tetrahydrofuran (THF) as mobile phase, respectively.


$$\left[\overset{\mathrm{CH_3}}{\mathrm{CH}}-\mathrm{CH_2}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{O}\right]_m\left[\overset{\mathrm{CH_2CH_3}}{\mathrm{CH}}-\mathrm{CH_2}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{O}\right]_n$$


$$\left[\mathrm{CH_2}-\underset{\mathrm{Cl}}{\mathrm{CH}}\right]_n$$

Sample preparation

PHB-8HV and PHB-18HV are soluble in chloroform, *N,N'*-dimethylacetamide (DMAc) and *N,N'*-dimethylformamide (DMF); and PVC is soluble in tetrahydrofuran (THF) and *N,N'*-dimethylformamide (DMF). DMF (ρ 0.952 g cm^{-3}, *RI* 1.428) was used as a co-solvent. PHB-HV copolymers were dissolved in a high-pressure reactor (Parr Instruments, USA) at 80°C for 2 h and filtered. PVC homopolymer was also dissolved in DMF at room temperature for 2 h. Polymer solutions (3 wt%) were mixed by weight ratio and stirred in a thermostated water bath at 80°C for 4–5 h. Films were cast from the 3 wt% polymer mixtures on a Petri dish under a nitrogen atmosphere at 80°C for 24 h. The cast film was dried in a vacuum oven at 120°C for 24 h. Films of 90–100 μm thickness were cast for d.s.c. or t.g.a. experiments, 120–150 μm for d.m.t.a. or m.t.s., and 8–10 μm for *FT*i.r.

Analysis

D.s.c. experiments were carried out using a Perkin-Elmer DSC-7 controlled by a 7500 PC. The sealed sample in an aluminium pan was heated from 30 to 170°C at a heating rate of 10°C min^{-1} under a nitrogen atmosphere and annealed for 5 min at that temperature. The sample was then quench-cooled to −40°C and rescanned up to 180°C at a heating rate of 10°C min^{-1} (this is called run II in this experiment).

Rheological properties were measured by using Polymer Laboratories DMTA model Mk II with a low-temperature head. The experiments were performed in a tensile mode from −60 to 120°C at a frequency of 2 Hz at a heating rate of 4°C min^{-1}. The scanning was repeated several times for comparison with the d.s.c. results.

Thermal properties were studied using a Perkin-Elmer TGA-7 from 50 to 700°C under a nitrogen atmosphere at a heating rate of 10°C min^{-1}.

Thin films were used for *FT*i.r. studies at room temperature. A Bruker IFS-48 spectrophotometer was used and the spectra were averaged from 32 scans at a frequency resolution of 2 cm^{-1}.

Mechanical tests were performed on a table model Instron 4200. Approximately ten measurements were averaged for each blend specimen with a 50 mm min^{-1} crosshead speed and 60% relative humidity at 25°C.

RESULTS AND DISCUSSION

Differential scanning calorimetry

Pure PHB-8HV and PHB-18HV were opaque with a light grey colour, while PVC itself is transparent. Blends of PHB-8HV and PHB-18HV with PVC were only optically clear when more than 70 wt% PVC was used.

The observed T_g values of the pure polymers, PHB-8HV, PHB-18HV and PVC, were 3.2, −2.5 and 80.8°C, respectively. The effect of PVC on PHB-HV was investigated by measuring the melting point (T_m) or the glass transition temperature (T_g) over the temperature range of −40 to 180°C (run II). *Figure 1* shows the d.s.c. thermograms of PHB-8HV/PVC blends. The blend containing 30 wt% PVC showed a T_g near that of PHB-8HV, while the T_g values of the blends containing 50 wt% or more PVC were close to that of PVC. As the PVC content was increased, a slightly lowered melting point (T_m) was observed, but this was too small to treat quantitatively. Although this system is believed to be immiscible, incorporation of PVC into PHB-8HV may cause a depression in crystal size or may affect the crystallinity of PHB-8HV.

On the other hand, the d.s.c. thermograms of the PHB-18HV/PVC blend system exhibit a linear lowering of the melting point with incorporation of PVC as shown in *Figure 2*. In addition, a single composition-dependent T_g indicative of miscibility was observed. The experimental values of T_m and T_g of PHB-8HV/PVC and PHB-18HV/PVC using d.s.c. are plotted in *Figures 3a* and *3b*, respectively. *Figures 3a* and *3b* show contrasting trends: in *Figure 3b* melting-point depression and increased T_g values of PHB-18HV/PVC are observed with PVC

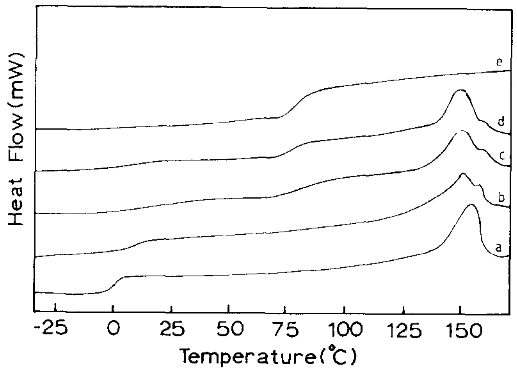


Figure 1 D.s.c. thermograms of pure PHB-8HV, pure PVC and PHB-8HV/PVC blends (run II): (a) pure PHB-8HV; (b) 70/30 wt% PHB-8HV/PVC, (c) 50/50 and (d) 30/70; and (e) pure PVC

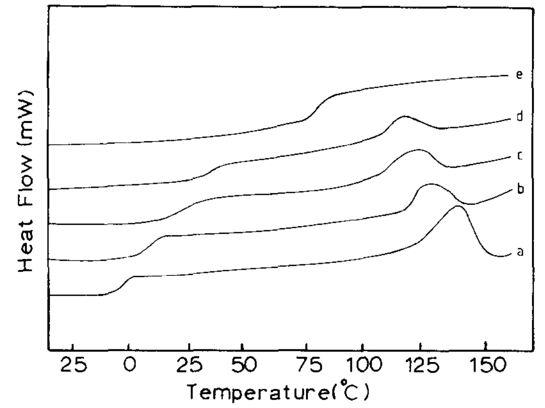


Figure 2 D.s.c. thermograms of pure PHB-18HV, pure PVC and PHB-18HV/PVC blends (run II): (a) pure PHB-18HV; (b) 70/30 wt% PHB-18HV/PVC, (c) 50/50, (d) 30/70; and (e) pure PVC

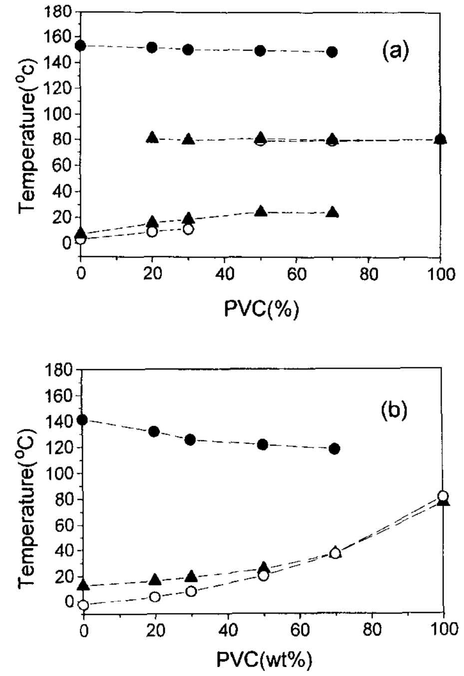


Figure 3 Glass transition temperature T_g (○), dynamic loss modulus E'' maximum (▲) and melting point T_m (●) of: (a) pure PHB-8HV, pure PVC and PHB-8HV/PVC blends; (b) pure PHB-18HV, pure PVC and PHB-18HV/PVC blends

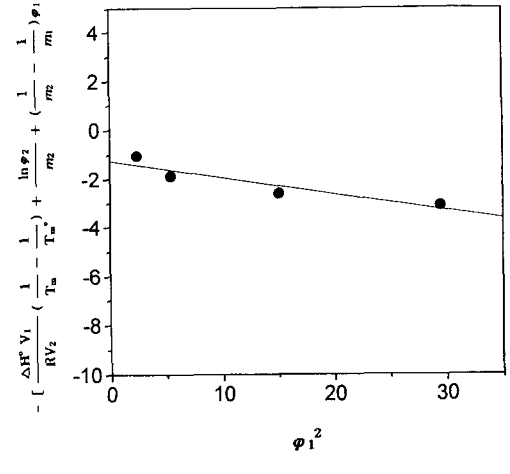


Figure 4 Melting-point depression for PHB-18HV/PVC blends. Application of the Flory–Huggins equation (2) given in the text. The left-hand side of equation (2) ($\times 10^2$) is plotted as a function of φ_1^2 ($\times 10^2$)

content, while no appreciable T_m change and the two T_g values of each component were observed in *Figure 3a*. Miscibility of blends where one component is semicrystalline can be measured by melting-point depression. Dilution of amorphous polymer into crystalline polymer gives rise to melting-point depression. In general, melting-point depression of blends can arise from a decrease of crystalline size, formation of co-crystal or dilution by amorphous phase. The expression for melting-point depression of blends can arise from a decrease of crystalline size, formation of co-crystal or dilution by amorphous phase. The expression for melting-point depression due to thermodynamic effects in accordance with the Flory–Huggins theory[8,9] is:

$$\frac{1}{T_m}-\frac{1}{T_m^\circ}= -\frac{RV_2}{\Delta H^\circ V_1}\left[\frac{\ln\varphi_2}{m_2}+\left(\frac{1}{m_2}-\frac{1}{m_1}\right)\varphi_1+\chi_{12}\varphi_1^2\right] \qquad (1)$$

where the subscripts 1 and 2 represent the amorphous and the crystalline polymer respectively, χ_{12} is the polymer–polymer interaction parameter, V is the molar volume of the polymer repeat unit at the equilibrium melting point, m and φ are the degree of polymerization and the volume fraction of the polymers in the blend, ΔH° is the heat of fusion of perfect crystalline polymer, and T_m and T_m° are the melting point of the blend and of pure crystalline polymer respectively. The melting-point depression is argued to arise from the intermolecular interaction in miscible mixtures[8,9]. By rearranging the terms, equation (1) can be written as:

$$-\left[\frac{\Delta H^\circ V_1}{RV_2}\left(\frac{1}{T_m}-\frac{1}{T_m^\circ}\right)+\frac{\ln\varphi_2}{m_2}+\left(\frac{1}{m_2}-\frac{1}{m_1}\right)\varphi_1\right]=\varphi_1^2\chi_{12} \qquad (2)$$

This equation can be used to estimate the interaction parameter χ_{12}. If χ_{12} is composition-independent and the melting-point depression is not influenced by morphological effects, then a plot of the left-hand side of equation (2) *versus* φ_1^2 should give a straight line passing through the origin[10,11]. From the slope of such a straight line, χ_{12} can be calculated. In order to calculate the left-hand side of equation (2), the following parameter values have been used: ΔH° (PHB-18HV) = 723 cal mol^{-1}, $T_m^\circ = 415$ K, $V_1 = 48.49$ cm^3 mol^{-1}, $V_2 = 87.49$ cm^3 mol^{-1}, $m_1 = 1100$, $m_2 = 4615$, $\rho_1 = 1.289$ g cm^{-3} and $\rho_2 = 1.143$ g cm^{-3}. A plot of equation (2) using the above and experimental values is shown in *Figure 4*. The experimental points may be extrapolated by a line with an intercept of about -1.2259 at $\varphi_1^2 = 0$ and a slope of -0.068. The fact that this line does not pass through the origin can be attributed to a possible composition dependence of χ_{12}. The interaction parameter χ_{12} plays a decisive role in the melting behaviour of crystalline polymer–amorphous polymer systems. The negative value for χ_{12} obtained indicates that the polymer pairs can form a thermodynamically stable solution at temperatures above the melting point, and thus this blend is thermodynamically miscible.

Dynamic mechanical properties

Figure 5 shows dynamic loss modulus (E'') of PHB-8HV/PVC blends as a function of temperature. PVC

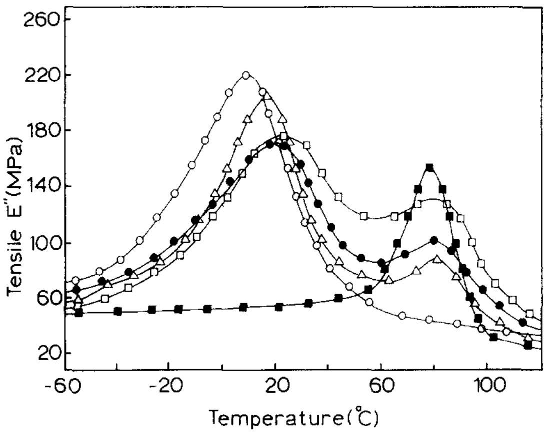


Figure 5 Dynamic loss modulus (E'') curves of various PHB-8HV/PVC blends: (○) pure PHB-8HV; (△) 70/30 wt% PHB-8HV/PVC, (□) 50/50, (●) 30/70; and (■) pure PVC

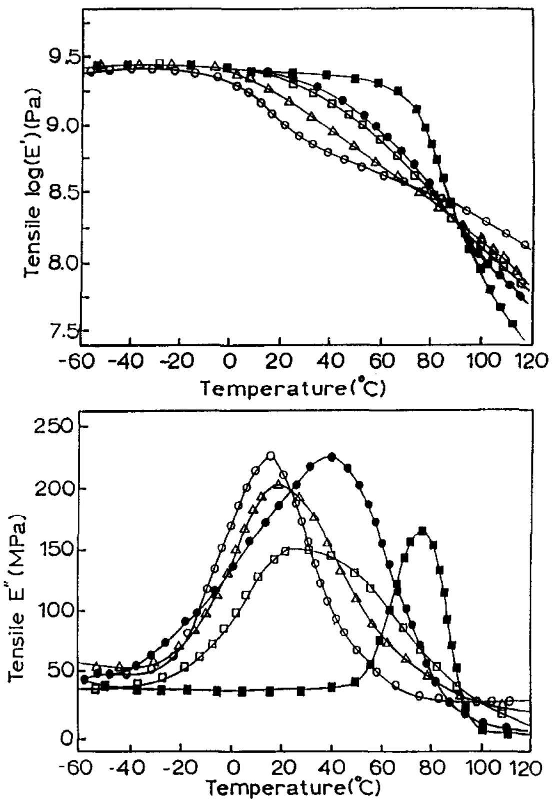


Figure 6 Dynamic storage modulus and loss modulus of various PHB-18HV/PVC blends: (○) pure PHB-18HV; (△) 70/30 wt% PHB-18HV/PVC, (□) 50/50, (●) 30/70; and (■) pure PVC

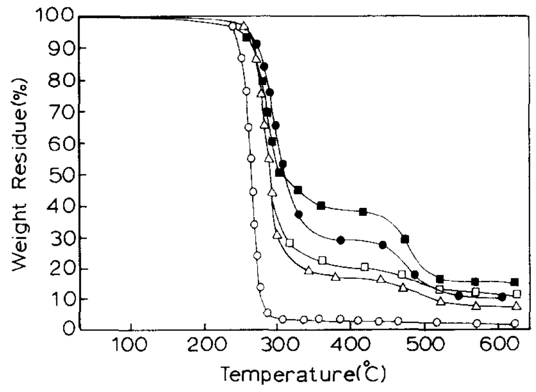


Figure 7 T.g.a. thermograms of PHB-18HV/PVC blends in nitrogen atmosphere: (○) pure PHB-18HV; (△) 70/30 wt% PHB-18HV/PVC, (□) 50/50, (●) 30/70; and (■) pure PVC

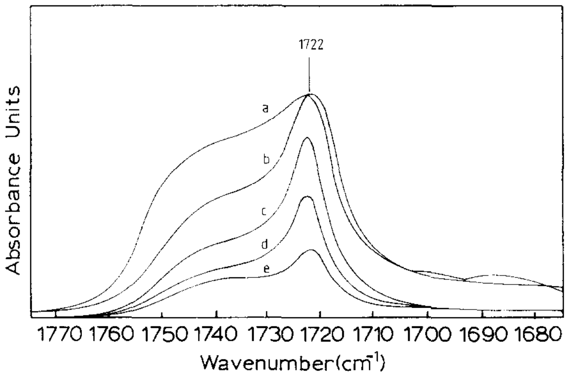


Figure 8 *FT*i.r. spectra of PHB-18HV/PVC blends in the region 1675–1775 cm^{-1} at room temperature: (a) pure PHB-18HV; (b) 70/30 wt% PHB-18HV/PVC, (c) 50/50, (d) 30/70 and (e) 20/80

exhibits a maximum in E'' at 76.4°C indicating the T_g, whereas PHB-8HV shows the glass transition temperature at 7.2°C. As seen in this figure, two distinct relaxation transitions representing the T_g of each component were observed at all compositions. This is evidence of immiscible behaviour and agrees with the d.s.c. result. In addition, a slight increase in the T_g of the PHB-8HV component is similar to the result of d.s.c. but this was again not considered as a characteristic of a miscible blend system.

Figure 6 shows the dynamic storage modulus (E') and loss modulus (E'') of PHB-18HV/PVC blends as a function of temperature. A proportional decrease in E' is observed with PHB-18HV content in the range 0–80°C. In addition, the maximum peak position of E'' is increased as PVC is incorporated, indicating that this system is miscible over the whole range of compositions. However, the intensity of the E'' peak shows that the transition is broad in the blend; the maximum broadness is observed for the 50/50 wt% blend of PHB-18HV/PVC. The T_g values observed from d.m.t.a. or d.s.c. are both described in *Figure 3a* for PHB-8HV/PVC and in *Figure 3b* for PHB-18HV/PVC. The miscibility behaviour of the two systems is distinctly described in these two figures and the T_g values observed between d.s.c. and d.m.t.a. agree well.

Thermogravimetric analysis

Weight loss and weight retention of the PHB-18HV/PVC blend are depicted in *Figure 7*. Here the curves represent pure PHB-18HV copolymer, PHB-18HV/PVC blend composition of 70/30, 50/50 and 30/70 wt%, and pure PVC. The 5% weight-loss temperature was at 240°C for PHB-18HV and at 250°C for PVC. At above 250°C, thermal stability of the blends was relatively improved by addition of PVC to PHB-18HV.

Fourier-transform infra-red spectroscopy

Figure 8 shows the *FT*i.r. spectra in the ester carbonyl stretching region of PHB-18HV/PVC blends in the solid state. The ester carbonyl stretching frequency (C=O) is

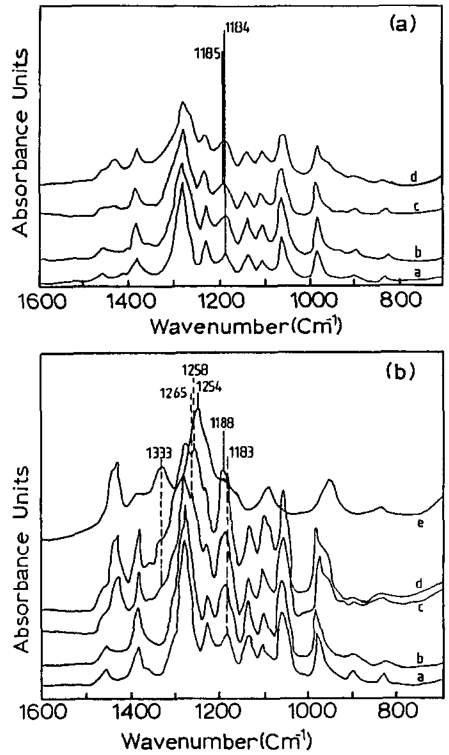


Figure 9 *FT*i.r. spectra of PHB-8HV/PVC blends in the region 700–1600 cm^{-1} at room temperature: (a) pure PHB-8HV; (b) 70/30 wt% PHB-8HV/PVC, (c) 50/50 and (d) 30/70. (**b**) *FT*i.r. spectra of PHB-18HV/PVC blends in the region 700–1600 cm^{-1} at room temperature: (a) pure PHB-18HV; (b) 70/30 wt% PHB-18HV/PVC, (c) 50/50, (d) 30/70; and (e) pure PVC

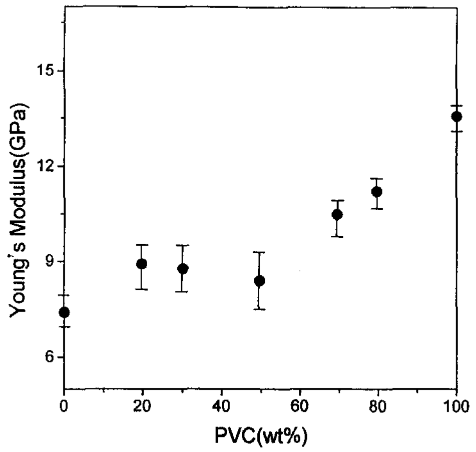


Figure 10 Young's modulus of PHB-18HV/PVC blends as a function of PVC content (circles are the average values with experimental error bars)

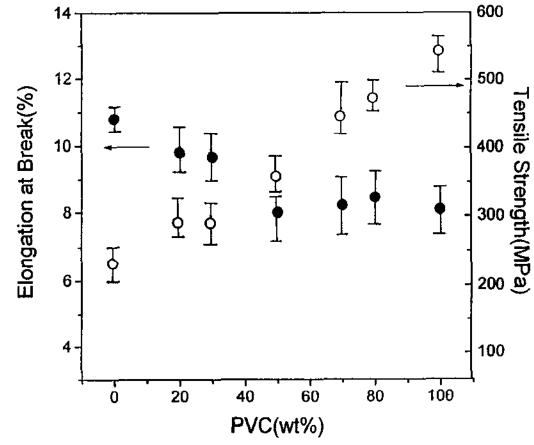


Figure 11 Tensile strength (○) and elongation at break (●) for various PHB-18HV/PVC blends (circles are the averages with experimental error bars)

observed at 1722 and 1740 cm^{-1} for the crystalline and amorphous phase respectively. The amorphous band is characteristically broader than that of the crystalline, which reflects an increase in conformational freedom. The width of the carbonyl peak is increased with increasing PHB-18HV content, leaving the peak maximum position unchanged. We believe that the carbonyl group of PHB-18HV is not involved for this system to be miscible with PVC.

Figures 9a and *9b* show the different spectral behaviours for the PHB-8HV/PVC and PHB-18HV/PVC systems respectively. Two bands at 1183 and 1254 cm^{-1} originating from PHB-18HV were chosen to differentiate from the PHB-8HV systems. The peak at 1184 cm^{-1} (or 1183 cm^{-1} is assigned to the oxygen between ester and carbonyl. The CH–Cl deformation of PVC is tentatively assigned at 1254 and 1333 cm^{-1}. Neither of the above two peak positions is shifted in *Figure 9a*. In comparison, as shown in *Figure 9b*, the peak at 1183 cm^{-1} in PHB-18HV blend is shifted to 1188 cm^{-1} with PVC content. Similarly, the CH–Cl deformation at 1254 cm^{-1} in PVC is shifted to 1265 cm^{-1} in the 50/50 wt% blend. Polymer–polymer miscibility generally requires specific interactions such as hydrogen bonding, dipole–dipole interaction, polar interaction or donor–acceptor interation, etc. If there exist specific interactions between two components, the spectrum of the blends should be shifted[12–15]. Thus, we believe that the C–O–C group in PHB-18HV and the CH–Cl group in PVC are responsible for this system to be miscible, giving rise to a polar interaction between two components. From the observed results, the possible rationalization may be that there is a critical amount of hydroxyvalerate in PHB-HV copolymers to bring about miscibility with PVC.

Mechanical behaviour

The stress–strain behaviour of the two blend systems was examined and the following characteristics were obtained.

Figure 10 shows the Young's modulus of PHB-18HV/PVC blend as a function of the PVC content. As the PVC content increases, the modulus of the blend increases within experimental error. Modulus values of all blends are higher than for pure PHB-18HV copolymer, which represents an improvement over the pure copolymer.

Figure 11 summarizes the results of tensile strength and elongation at break. As the PVC content is increased, considerable improvement in tensile strength is observed, while a relatively slight decrease in elongation at break is obtained. If experimental error is allowed, the blend with 80% PVC is optimum for improved characteristics.

CONCLUSIONS

The PHB-8HV/PVC blend system showed two T_g

values corresponding to those of the pure components. The partially crystalline blend of PHB-18HV/PVC exhibited a single composition-dependent T_g indicating a homogeneous miscible system. In the latter system, the T_m and ΔH_f (heat of fusion) were decreased as the PVC content was increased. The interaction parameter χ_{12} calculated using the theory of melting-point depression exhibited a negative value, which indicates that the PHB-18HV/PVC system is thermodynamically miscible.

The oxygen (C–O–C) stretching vibration band at 1184 cm^{-1} and CH–Cl deformation at 1254 cm^{-1} were unshifted in PHB-8HV/PVC, while those in PHB-18HV/PVC system were shifted with incorporation of PVC. We believe that there exists a critical quantity of hydroxyvalerate in PHB/HV copolymer necessary to bring about miscibility with PVC and that a polar interaction between C–O–C in PHB-18HV and the CH–Cl group in PVC is the possible interaction that gives miscibility.

The tensile strength and modulus were increased while elongation at break was slightly decreased with PVC.

Thus the PHB-18HV/PVC system is miscible; in particular, a 80 wt% PVC blend is recommended as an improved system with lower cost of production, processability and higher mechanical properties.

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REFERENCES

1 Bluhm, T. L., Hammer, G. K. and Marchessault, R. H. *Macromolecules* 1986, **19**, 2871

2 Bloembergen, S. and Holden, S. A. *Macromolecules* 1986, **19**, 2865

3 Organ, S. J. *Polymer* 1994, **35**, 86

4 Kamiya, N., Sakurai, M. and Inoue, Y. *Macromolecules* 1991, **24**, 2178

5 Avella, M. and Martuscelli, E. *Polymer* 1988, **29**, 1731

6 Yoon, J. S., Choi, C. S., Maing, S. J., Choi, H. J., Lee, H. S. and Choe, S. *Eur. Polym. J.* 1993, **29**(10), 1359

7 Lee, H. S., Lee, J. S., Yoon, J. S., Choi, H. Y. and Choe, S. *Polymer (Korea)* 1994, **18**(3), 338

8 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, NY, 1953

9 Nishi, T. and Wang, T. T. *Macromolecules* 1975, **8**, 809

10 Greco, P. and Martuscelli, E. *Polymer* 1989, **30**, 1475

11 Cimmino, S., Martuscelli, E. and Silvestre, C. *J. Polym. Sci., Polym. Phys. Edn* 1989, **27**, 1781

12 Fahrenholtz, S. F. and Kwei, T. K. *Macromolecules* 1981, **14**, 1076

13 Kwei, T. K., Nishi, T. and Robertz, R. F. *Macromolecules* 1974, **7**, 667

14 Coleman, M. M. and Zarian, J. *J. Polym. Sci., Polym. Phys. Edn* 1979, **17**, 837

15 Coleman, M. M., Zarian, J., Varnell, D. F. and Painter, P. C. *J. Polym. Sci., Polym. Lett. Edn* 1977, **15**, 745