PII: S0032-3861(97)00556-9

Polymer Vol. 39 No. 12, pp. 2479–2487, 1998
© 1998 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/98/$19.00+0.00

Compatibility of poly(3-hydroxybutyrate)/poly(ethylene-*co*-vinyl acetate) blends

Jin-San Yoon[a],*, Seong-Hwan Oh[a] and Mal-Nam Kim[b]
[a]*School of Chemical Science and Engineering, Inha University, Inchon 402-751, Korea*
[b]*Department of Biology, Sangmyung University, Seoul 110-743, Korea*
(Received 27 March 1997)

The miscibility of poly(3-hydroxybutyrate) (PHB) with ethylene–vinyl acetate (EVA) copolymers containing 70 or 85 wt% of vinyl acetate was investigated. The blend of PHB and EVA70 was found to be immiscible, because the glass transition temperature, the melting temperature and the spherulite growth rate under the isothermal crystallization conditions were independent of the blend composition. However, the melting temperature, the spherulite growth rate and the equilibrium melting temperature of the PHB/EVA85 blend decreased with an increase in the EVA85 content and the Flory–Huggins interaction parameter of the blend was negative. Therefore, PHB was found to be miscible with EVA85. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: polymer blend; poly(3-hydroxybutyrate); poly(ethylene-*co*-vinyl acetate))

INTRODUCTION

Poly(hydroxybutyrate) (PHB) is a microbially produced crystalline polymer which can be completely degraded in nature. The mechanical properties of PHB are very similar to those of polypropylene; however, PHB is quite brittle, expensive, and easily decomposed at high temperatures near its melting temperature[1–3].

In an attempt to improve the processibility of PHB, copolymerization of 3-hydroxybutyrate with either 3-hydroxyvalerate or 4-hydroxybutyrate using the microbial fermentation method[3–7] was developed. However, it is difficult to utilize these copolymers for diverse applications because the fermentation medium is rather limited and costly. To alleviate these problems PHB is blended with various commodity thermoplastics, thereby improving the mechanical properties, controlling the biodegradation rate, and reducing the cost of PHB. Poly(ethylene oxide)[8], poly(epichlorohydrin)[9], poly(vinyl acetate)[10] and poly(vinylidene fluoride)[11] have been found to be miscible with PHB, while ethylene–propylene rubber[10] and poly(lactic acid)[12] have been found to be immiscible.

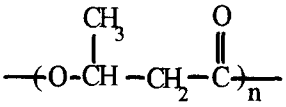
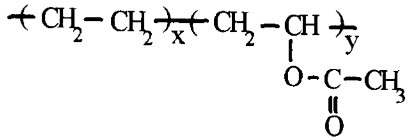
Since PHB was confirmed to be miscible with poly(vinyl acetate), we blended PHB with ethylene–vinyl acetate (EVA) copolymers, whose vinyl acetate content was 70 and 85 wt%, respectively. The thermal properties, crystallization behaviour and morphology of the blends were investigated.

EXPERIMENTAL

Materials

PHB was provided in powder form by the Biological Products Division of ICI, UK. EVA70, containing 70 wt% vinyl acetate, was purchased from Scientific Polymer Products. TAEVALON latex of Tae Young Chemical Co. was dried, cleaned by methanol soxhlet for 1 week and extracted in chloroform to produce EVA85 which contained 85 wt% vinyl acetate. Absence of any methanolysis of EVA during the soxhlet procedure was confirmed from the *FT*i.r. spectra. The content of vinyl acetate in EVA was measured by proton n.m.r. spectroscopy. The characteristics of the polymers are summarized in *Table 1*.

Table 1 Characteristics of the polymers

Polymer	Structural formula	$\bar{M}_w^a$	Vinyl acetate content^b (wt%)
PHB	 $-\!\!\left(O-\overset{CH_3}{\overset{\vert}{C}H}-CH_2-\overset{O}{\overset{\Vert}{C}}\right)_n\!\!-$	470 000	–
EVA70	 $-\!\left(CH_2-CH_2\right)_x\!\left(CH_2-\underset{\underset{\underset{O}{\Vert}}{O-C-CH_3}}{\overset{\vert}{C}H}\right)_y$	285 000	69.1
EVA85		646 000	85.8

^{a}Measured by g.p.c. in chloroform at 30°C
^{b}Measured by ^{1}H n.m.r.

---

* To whom correspondence should be addressed

Sample preparation

EVA (3 wt%) in chloroform was mixed with 3 wt% of PHB in chloroform in the pre-determined weight ratios by stirring for 24 h. The mixture was dried in vacuum at 40°C to produce films.

Analysis

A Perkin-Elmer DSC-7 was used to measure T_m and T_g and kept at 190°C for 1 min, then they were cooled to −50°C at −100°C $\min^{-1}$ to measure T_g by reheating those samples to 190°C at 20°C $\min^{-1}$. The equilibrium melting temperature of each blend was obtained as follows: heating the sample to 190°C at 20°C $\min^{-1}$, holding it at 190°C for 1 min, quenching the sample to the pre-determined crystallization temperature (T_c) at −100°C $\min^{-1}$, crystallizing for 30 min at the T_c, and heating at 20°C $\min^{-1}$ to monitor the melting temperature. E', E'' and $\tan\delta$ were measured by Rheovibron DDV-II-C, while heating the sample (50 × 4 × 0.03 mm) at 10°C $\min^{-1}$ from −50°C.

Change in morphology of the blend as a function of the composition was monitored by a polarizing microscope (NIKON OPTIPHOT2-POL). Spherulite growth rate was measured by analysing the spherulite size using a CCD camera. Films were heated to 190°C at 20°C $\min^{-1}$, held at 190°C for 1 min, and quenched to the pre-determined T_c at −100°C $\min^{-1}$.

RESULTS AND DISCUSSION

It has been shown by d.s.c. that the melting endotherm of PHB had a bimodal shape. When the d.s.c. heating rate was increased, the intensity of the melting peak appearing at the higher temperature was reduced compared to that of the melting peak at the lower temperature. Organ and Barham[13] found that the melting peak at the lower temperature was due to the crystallites formed during the sample preparation and the one at the higher temperature was due to those recrystallized during the heating in d.s.c. However, the lower melting peak disappeared when the PHB was crystallized by quenching from the melt state to the crystallization temperature.

Figure 1 shows the first scan melting temperature of the PHB/EVA70 blends, which were prepared by the method described in the experimental section. Two melting temperatures of PHB in the blend appeared at around 165 and 178°C and they were nearly independent of the blend composition. The melting temperatures of PHB in the PHB/EVA85 blends were also bimodal, as shown in *Figure 2*. Both melting temperatures were decreased, as the EVA85 content in the blend was increased (*Figure 3*). The size of each endotherm was gradually decreased with the EVA85 content.

Equilibrium melting temperature, which may be defined as the melting point of the infinitely large lamella, can be derived by the following Hoffman–Weeks equation[14]

$$T'_m = \frac{T_c}{\gamma} + \left(1 - \frac{1}{\gamma}\right) T_m^0 \qquad (1)$$

where T'_m is the observed melting temperature, γ is the ratio of the initial to the final lamellar thicknesses. The equilibrium melting temperature, T_m^0, was obtained by extrapolation of T'_m to the line where $T'_m = T_c$. *Figure 4* describes the procedure of determining the equilibrium melting temperature of the blend according to the Hoffman–Weeks equation. The equilibrium melting temperatures decreased steadily with the increasing amount of EVA85, as depicted in *Figure 5*. This reduction in the equilibrium melting temperature means that the blend is thermodynamically miscible.

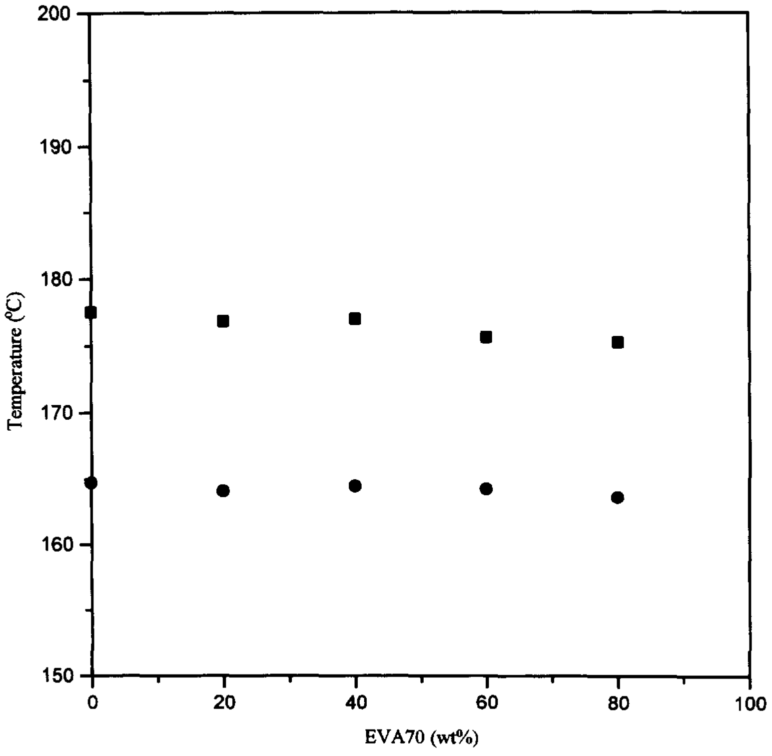


Figure 1 Melting temperature of PHB/EVA70 blends measured by DSC: (■) melting peak for crystals crystallized during heating stage; (●) melting peak for crystals formed during solvent casting stage

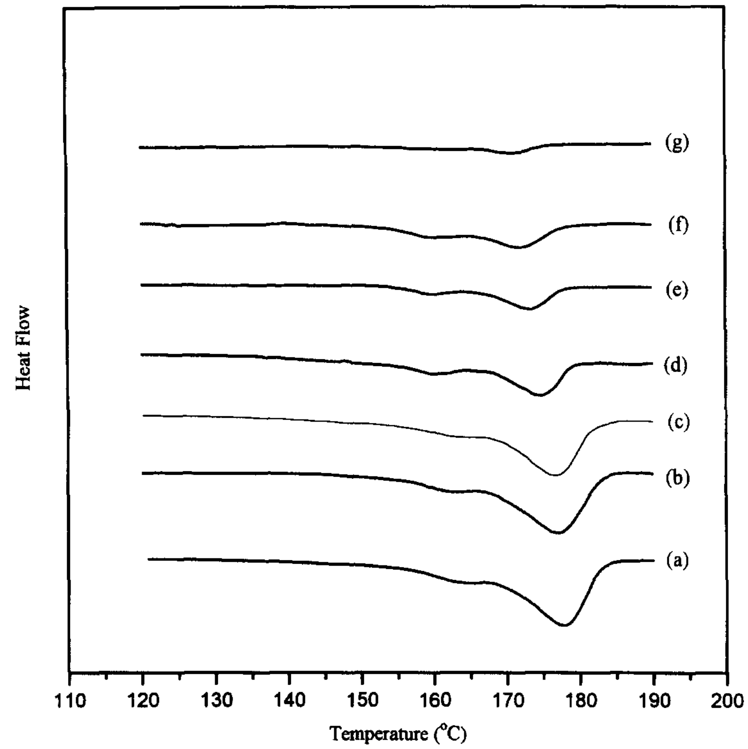


Figure 2 DSC thermogram of PHB/EVA85 blends: (a) PHB100%; (b) PHB 80%; (c)PHB60%; (d) PHB40%; (e) PHB30%; (f)PHB20%; (g) PHB10%

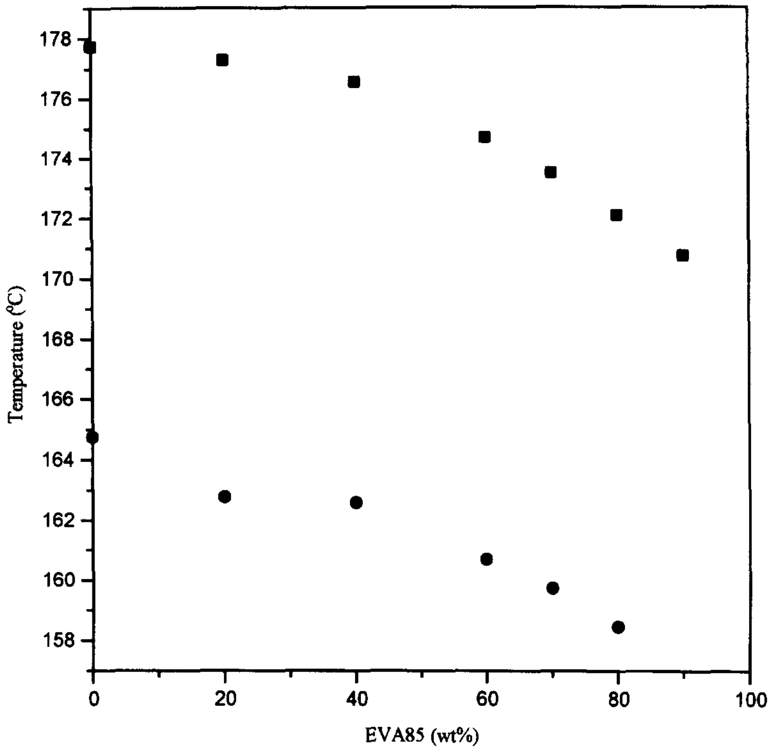


Figure 3 Melting temperature of PHB/EVA85 blends: (■) melting peak for crystals crystallized during heating stage; (●) melting peak for crystals formed during solvent casting stage

Equilibrium melting temperature depression can be predicted by the Flory–Huggins theory as follows[15,16]

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{RV_2}{\Delta H^0 V_1}\left[\frac{\ln \phi_2}{m_2} + \left(\frac{1}{m_2} - \frac{1}{m_1}\right)\phi_1 + \chi_{12}\phi_1^2\right] \tag{2}$$

where the subscript 1 means the amorphous component and the subscript 2 means the crystalline component of the blend. χ_{12} is the interaction parameter between the constituent polymers, V is the molar volume of the repeat unit at the equilibrium melting temperature, ϕ is the volume fraction, m is the degree of polymerization, ΔH^0 is the heat of fusion for the perfect crystalline polymer, and T_m and T_m^0 are

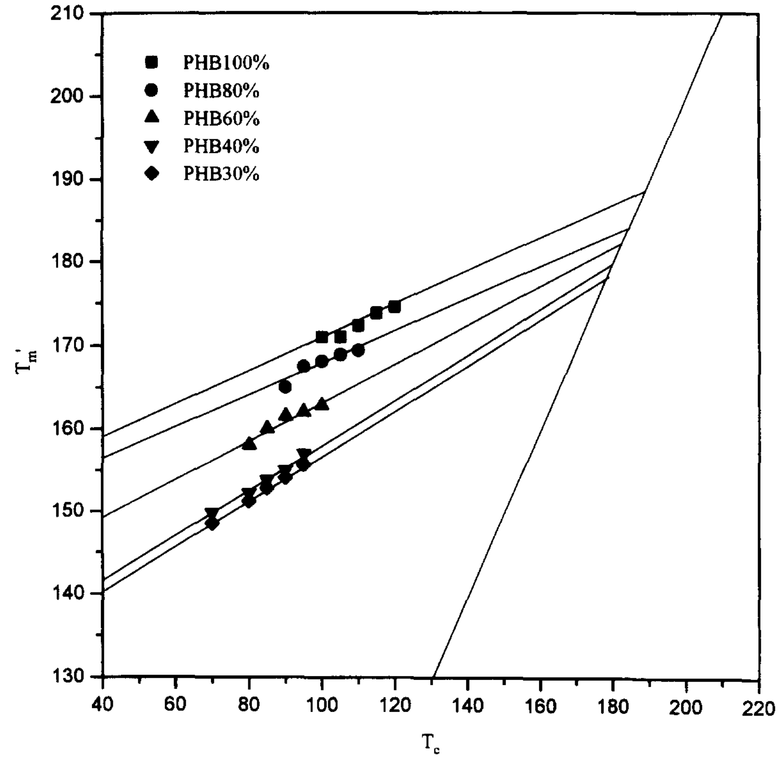


Figure 4 Observed melting temperature (T_m') as a function of crystallization temperature (T_c) for PHB/EVA85 blends

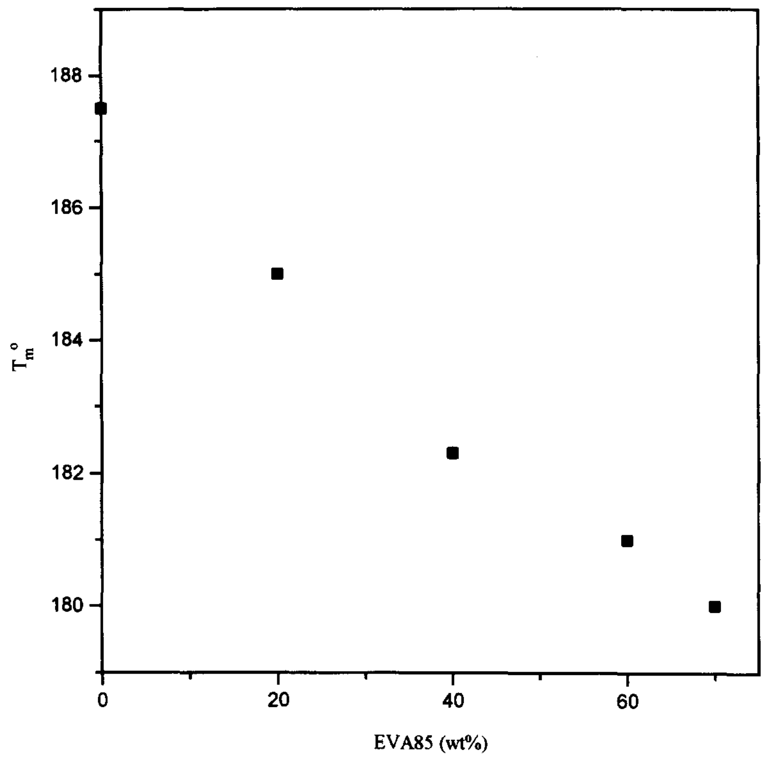


Figure 5 Equilibrium melting temperature of PHB/EVA85 blends

the equilibrium melting temperature of the blend and the crystalline polymer, respectively.

Equation (2) can be rearranged as follows[8-10]

$$-\left[\frac{\Delta H^{\circ}V_1}{RV_2}\left(\frac{1}{T_m}-\frac{1}{T_m^{\circ}}\right)+\frac{\ln\phi_2}{m_2}+\left(\frac{1}{m_2}-\frac{1}{m_1}\right)\phi_1\right]=\phi_1^2\chi_{12} \tag{3}$$

If χ_{12} is independent of the blend composition and if the melting-point depression is independent of the morphological effects, there will be a linear relationship between ϕ_1^2 and the left-hand side of equation (3). Thus, the interaction parameter χ_{12} is obtained from the slope of the straight line. In *Figure 6*, equation (3) was plotted by utilizing the equilibrium melting temperatures at each blend composition. Numerical values of the parameters in the left-hand

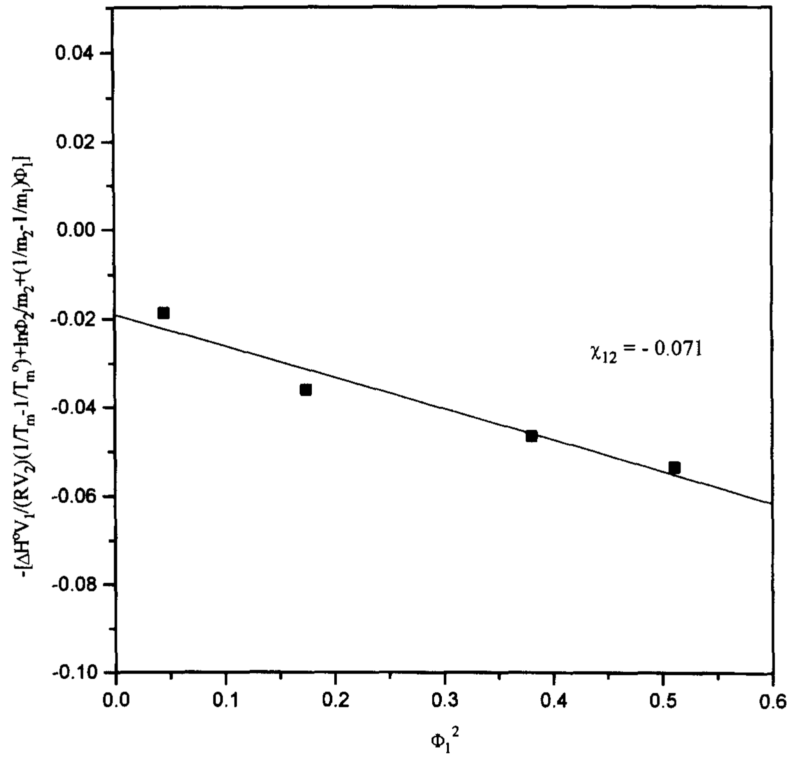


Figure 6 Melting-point depression for PHB/EVA85 blends with the Flory–Huggins equation results

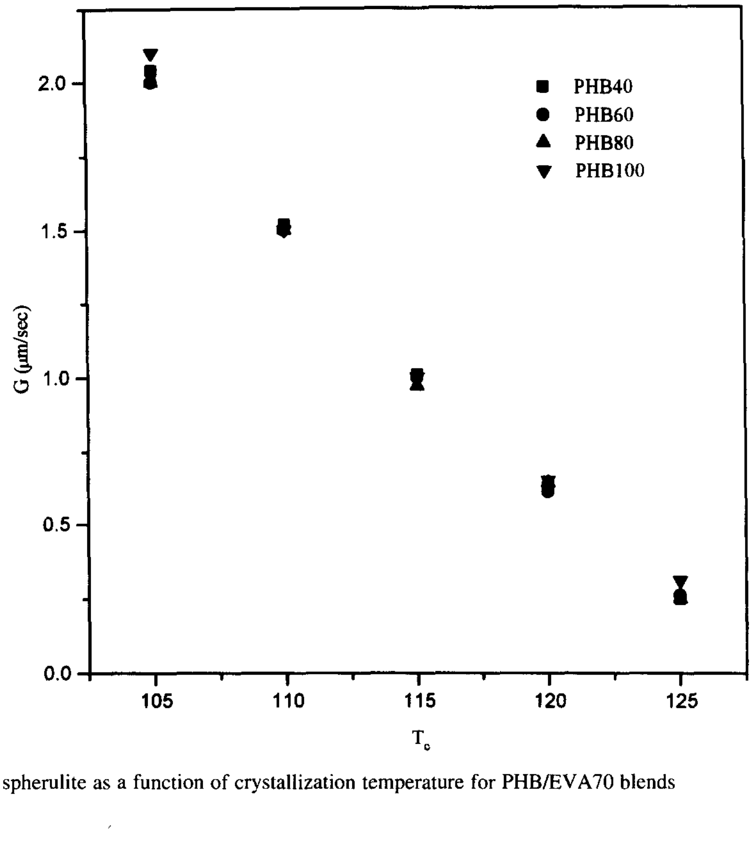


Figure 7 Radial growth rate of spherulite as a function of crystallization temperature for PHB/EVA70 blends

side of equation (3) were[8,17]: $\Delta H^o = 3001$ cal mol^{-1}, $T_m^o = 460.7$ K, $V_1 = 72.2$ cm^3 mol^{-1}, $V_2 = 75.0$ cm^3 mol^{-1}, $m_1 = 8357$, and $m_2 = 5477$. χ_{12} between PHB and EVA85 was found to be -0.071. Greco and Martuscelli[10] reported that the interaction parameter for the PHB/PVAc blend was -0.073. It has been shown[8–10] that the blend with a negative interaction parameter formed a thermodynamically stable mixture in the melt state.

Spherulite radii of both PHB/EVA70 and PHB/EVA85 blends increased linearly with the crystallization time when crystallized at various crystallization temperatures. As shown in *Figure 7*, the spherulite growth rate of the PHB/EVA70 blend was decreased with the crystallization temperature, yet the growth rate was independent of the blend composition, as long as the crystallization temperature remained constant.

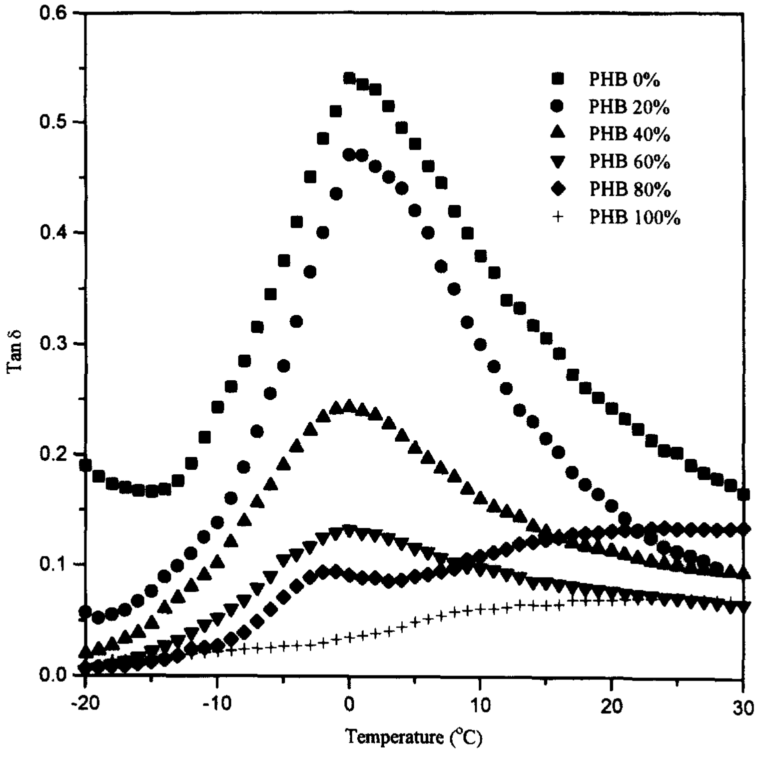


Figure 8 Tran δ curve of PHB/EVA70 blends

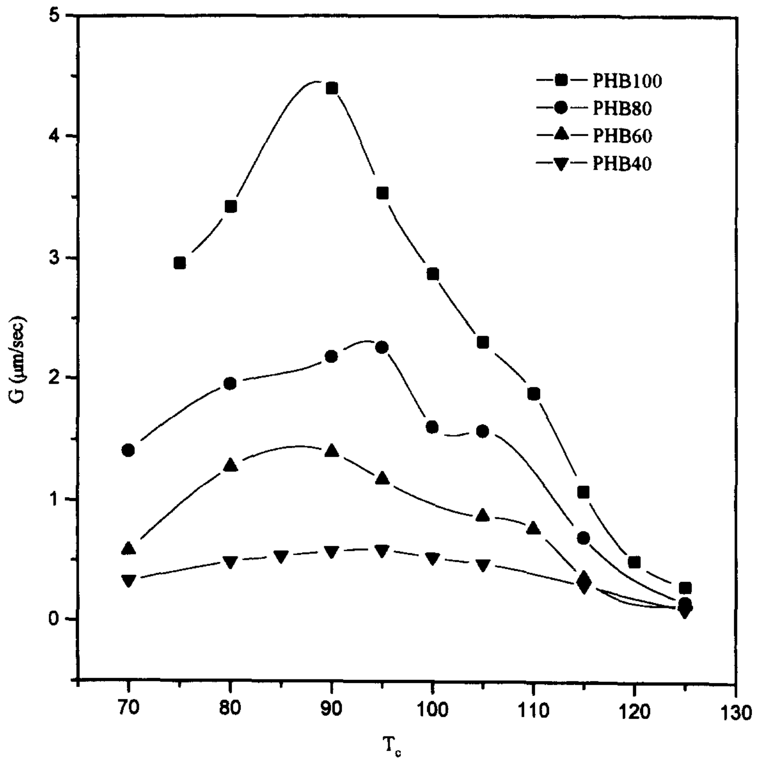


Figure 9 Radial growth rate of spherulite as a function of crystallization temperature for PHB/EVA85 blends

Loss tangent of the PHB/EVA70 blend was measured by Rheovibron and plotted in *Figure 8*. At all blend compositions loss peak was obtained at around 0°C, which coincides with the glass transition temperature of EVA70. As the PHB content in the blend was increased, the intensity of the loss peak was decreased. Loss peak was determined by heating the blend films which were cast from chloroform solution at room temperature. Since the PHB/EVA70 blends showed a constant T_g irrespective of the blend composition, the PHB/EVA70 blend could be assumed to be immiscible at room temperature. Moreover, the melting temperature of the PHB/EVA70 blend in *Figure 1* was also independent of the composition, and the growth rate of the spherulite was independent of the composition, when the blend was

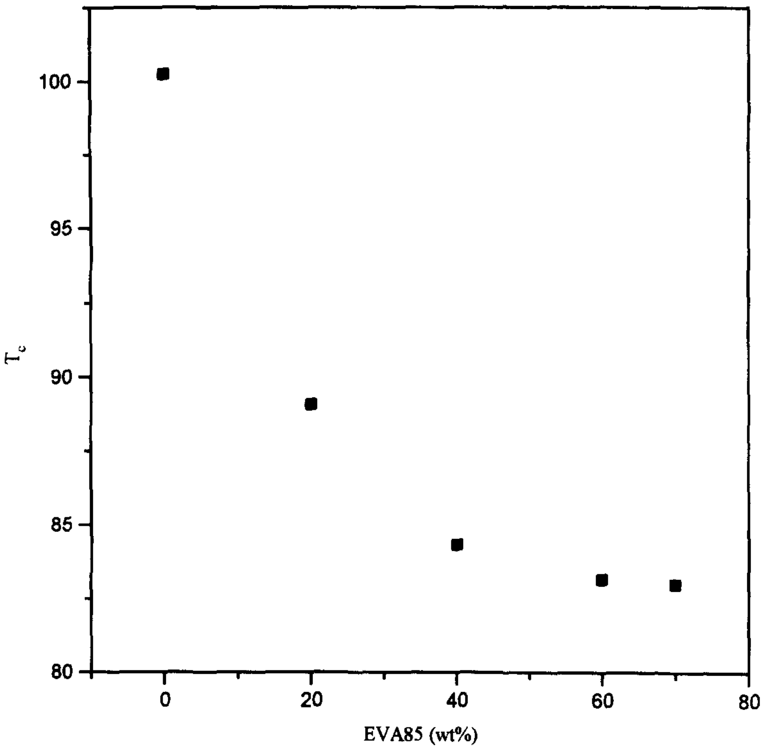


Figure 10 Non-isothermal crystallization temperature (T_c) of PHB/EVA85 blends

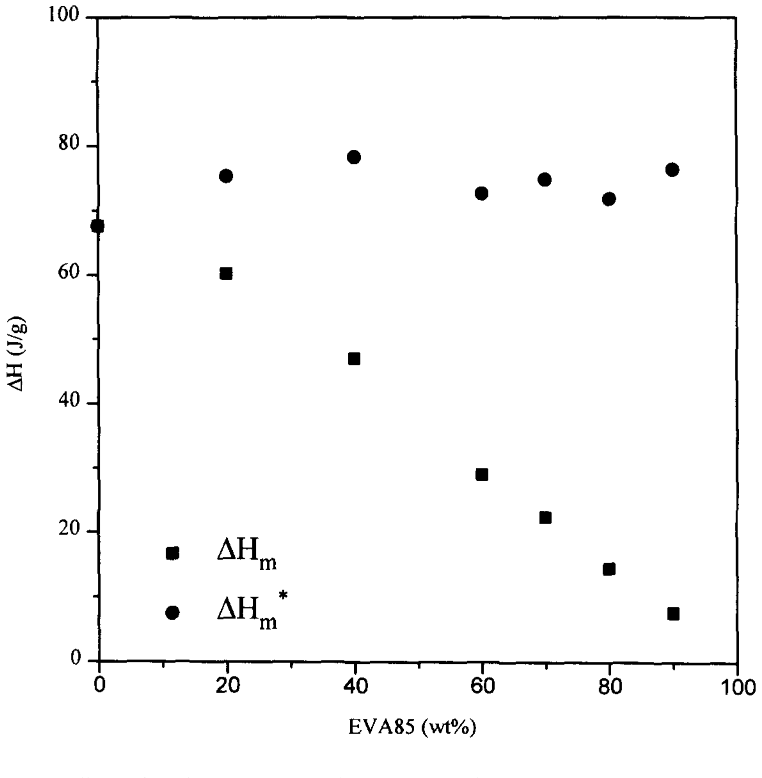


Figure 11 Non-isothermal 2_{nd} scan overall enthalpy of fusion based on the unit weight of the blends (ΔH_m) and enthalpy of fusion based on the unit weight of PHB in the blends (ΔH_m*)

quenched from the melt to the crystallization temperature (*Figure 7*). Therefore, the PHB/EVA70 blend is believed to be also immiscible in the melt as well.

It was difficult to measure the change in the T_g of the PHB/EVA85 blend, because the T_g of PHB and EVA85 appeared at 26 and 30°C, respectively, by Rheovibron. In *Figure 9* as the PHB content in the PHB/EVA85 blend was decreased, the growth rate of the spherulite was decreased at each crystallization temperature, which is quite different from the case for the PHB/EVA70 blend in *Figure 7*. Because the non-crystalline regions of PHB and EVA85 were mixed to form a homogeneous melt, the chemical potential for the crystallization of PHB became lower. However, the spherulite diameter increased linearly with

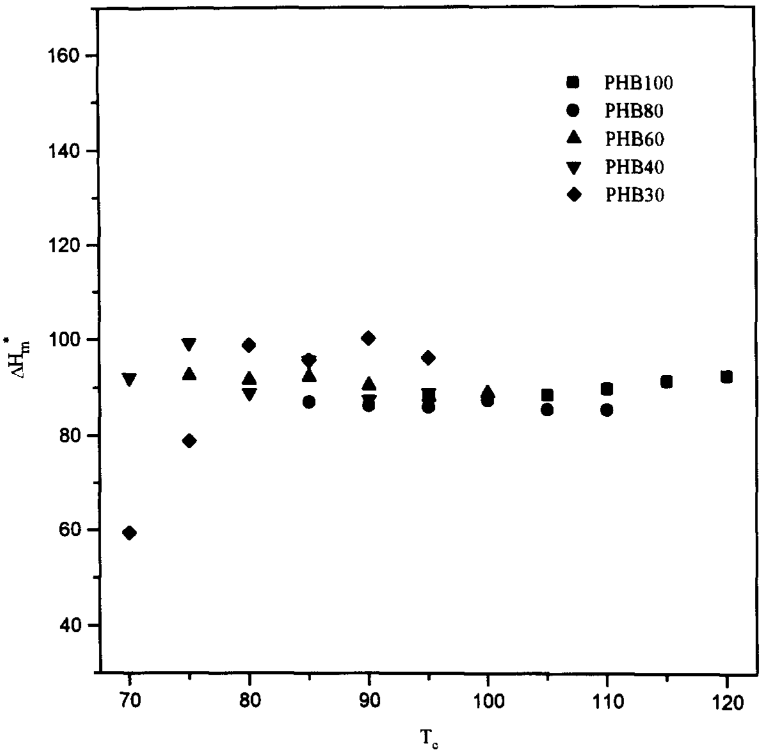


Figure 12 Enthalpy of fusion at the equilibrium melting temperature based on the unit weight of PHB in the blends as a function of T_c

crystallization time, and the amorphous component is believed to penetrate into the interlamellar region.

Non-isothermal crystallization temperature was measured as the PHB/EVA85 blend was cooled at a constant rate of 20°C min^{-1} from the melt (190°C). In *Figure 10*, as the amount of EVA85 in the blend was increased, the crystallization rate was more suppressed and so the non-isothermal crystallization temperature was decreased.

Figure 11 plots the second scan enthalpy of fusion of PHB in the PHB/EVA85 blend and *Figure 12* depicts the enthalpy of fusion at the equilibrium melting temperature as a function of the crystallization temperature. In *Figure 12*, except for very low crystallization temperatures, the enthalpy of fusion of the PHB/EVA85 blends crystallized for 30 min at a given T_c was independent of the crystallization temperature or of the blend composition. Even though PHB and EVA85 can form a miscible blend system as discussed earlier, the enthalpy of fusion based on the unit weight of PHB in the blend was nearly constant irrespective of the EVA85 content. Thus, it could be inferred that the composition independent heat of fusion during the non-isothermal crystallization was not kinetically driven. It has been also demonstrated for the PHB/PEO blend[8] and the PHB/poly(lactic acid-*co*-ethylene glycol-*co*-adipic acid) blend[19] that the non-isothermal enthalpy of fusion of PHB was independent of the blend composition. Indeed, these two blend systems were confirmed to be miscible because the blends had composition-dependent single glass transition temperatures and the growth rate of PHB spherulite and the equilibrium melting temperature were depressed with the change in the blend composition. The non-isothermal enthalpy of fusion of PHB in the miscible PHB/PVAc blend was decreased with the increasing amount of PVAc; however, the difference in the enthalpy of fusion was reported to be rather small[10].

CONCLUSIONS

For the PHB/EVA70 blend the glass transition temperature of the blend due to EVA70 and the melting temperature of the blend were almost constant, as the composition of the blend was changed. Thus, the PHB/EVA70 blend was determined to be immiscible. On the contrary, the melting temperature and the equilibrium melting temperature of the PHB/EVA85 blend were depressed with the increase in the EVA85 content. The growth rate of the PHB spherulite was also decreased with increasing amount of EVA85. Melting temperature depression analysis yielded the Flory interaction parameter, χ_{12}, of the PHB/EVA85 blend to be -0.071, indicative of miscibility.

ACKNOWLEDGEMENTS

This work was partly supported by grants from the Korea Science and Engineering Foundation (94-0900-07-01-3).

REFERENCES

1. Howells, E. M., *Chem. Ind.*, 1982, 508.
2. King, P. P., *J. Chem. Technol. Biotechnol.*, 1982, **32**, 2.
3. Holems, P. A., *Phys. Technol.*, 1985, **16**, 32.
4. Doi, Y., Tamaki, A., Kunioka, M. and Soga, K., *Appl. Microbiol. Biotechnol.*, 1988, **28**, 330.
5. Kamiya, N., Yamamoto, Y., Inoue, Y., Chujo, R. and Doi, Y., *Macromolecules*, 1989, **22**, 1676.
6. Inoue, Y., Kamiya, J., Yamamoto, Y., Chujo, R. and Doi, Y., *Macromolecules*, 1989, **22**, 3800.
7. Shimamura, E., Kasuya, K., Kobayashi, G., Shiotani, T., Shima, Y. and Doi, Y., *Macromolecules*, 1994, **27**, 878.
8. Avella, M. and Martuscelli, E., *Polymer*, 1988, **29**, 1731.
9. Paglia, E. D., Beltrame, P. L., Canetti, M., Seves, A., Martcandalli, B. and Martuscelli, E., *Polymer*, 1993, **34**, 996.
10. Greco, P. and Martuscelli, E., *Polymer*, 1989, **30**, 1475.
11. Marand, H. and Collins, M., *Polym. Prepr.*, 1990, **31**, 552.

12. Blümm, E. and Owen, A. J., *Polymer*, 1995, **36**, 4077.
13. Organ, S. J. and Barham, P. J., *Polymer*, 1993, **34**, 2169.
14. Hoffman, J. D. and Weeks, J. J., *J. Res. Natl. Bur. Stand.*, 1962, **66**, 13.
15. Flory, P. J., *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953.
16. Nishi, T. and Wang, T. T., *Macromolecules*, 1975, **8**, 809.
17. Barham, P. J., Keller, A., Otun, E. L. and Holmes, P. A., *J. Mater. Sci.*, 1984, **19**, 2781.
18. Cheo, S., Cha, Y. J., Lee, H. S., Yoon, J. S. and Choi, H. J., *Polymer*, 1995, **36**, 4977.
19. Yoon, J. S., Chang, M. C., Kim, M. N., Kim, C. and Chin, I. J., *J. Polym. Sci. Polym. Phys. Edn.*, 1996, **34**, 2543.