Crystallization behaviour of polyethylene and i-polybutene-1 blends

K. Kishore and R. Vasanthakumari
Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India

The mutual influence of the components on the crystallization behaviour of polyblends, namely, isotactic polybutene-1 (PB) with low-density and high-density polyethylene (LDPE and HDPE), has been studied using techniques such as differential scanning calorimetry, infra-red spectroscopy, wide-angle X-ray diffraction, scanning electron microscopy, etc. Each component in the blend is observed to crystallize independently. There is phase separation and incompatibility, as shown from tensile properties and scanning electron microscopic observation of the fracture surface of the blend. For HDPE–PE blends (< 30% HDPE), unusual form I' crystals of PB are observed along with the usual form II.

INTRODUCTION

The concept of physical blending of two or more polymers to obtain new products is now attracting widespread interest[1]. Blending provides a method for changing the physical and mechanical properties of polymers[2]. However, compatibility decides the ultimate properties of the blend, the major controlling factors being composition, morphology, molecular weight, crystal structure, etc. A lot of work has been carried out on polymer blends in recent years and excellent reviews are available[1,3,4]. Most of the studies on polyblends are on non-crystalline polymers and the crystalline polyblends have received relatively little attention. Blends of crystalline polymers in which one or both of the components crystallize contain both compatible and incompatible pairs[5-19]. Various methods have been proposed to determine the extent of compatibility and each method has its own standard and sensitivity[20,21].

Isotactic polybutene-1 (PB) is known to crystallize in different polymorphic modifications, namely, form I (hexagonal), form II (tetragonal), form III (orthorhombic) and yet another form I' (hexagonal, but with a different melting point from that of form I)[22-25]. The blend system of polyethylene (PE) and PB has not so far been studied. In the present investigation, the crystallization behaviour of blends of PB with low-density polyethylene (LDPE) and high-density polyethylene (HDPE) has been studied to understand (i) the structure–property relationships of the system, (ii) the form in which PB crystallizes in the blend and (iii) compatibility of the blend.

EXPERIMENTAL

The polymers used in the present study were as follows: LDPE, WIG-11, obtained from AR & D Plastics, Hoogly, India; HDPE, Sholex F5012, from Sholex, Japan; and PB, Shell 0400, from Plastics Dept., Shell Chemical Co., Houston). The crystallinity and melting point of LDPE, HDPE and PB were 47% and 110°C, 65% and 140°C, and 35% and 114°C, respectively. Blends of various compositions were prepared by dissolving weighed amounts of the components in hot xylene and precipitating the polymer from methanol. The samples were filtered and dried in vacuum.

A Du Pont 990 differential scanning calorimeter was employed to study the crystallization and melting behaviour of the blends: 5–10 mg of the sample (in aluminium pans) was heated to 180°C, kept for 5 min at that temperature, followed by scanning at a cooling rate of 3–5°C min^{-1} to determine the crystallization exotherms. After the completion of crystallization in the differential scanning calorimeter itself, melting endotherms were obtained by rescanning the crystallized samples at a heating rate of 5°C min^{-1}. The temperature axis and the enthalpy output were calibrated with indium, tin and benzoic acid. From the areas of the crystallization and melting peaks, the heats of crystallization ΔH_c and fusion ΔH_f were determined.

Wide-angle X-ray diffraction (WAXD) scans were obtained with a Philips PW1050/70 vertical goniometer using CuKα radiation. Blends of different composition for WAXD studies were obtained by hot pressing the samples at 180°C and allowing to cool to room temperature at a rate of 4°C min^{-1} to obtain circular specimens with a thickness of 0.5 mm. The intensities of the prominent peaks were obtained from the peak heights. The degree of crystallinity was calculated from the diffraction peaks by taking the ratio of the crystalline area to the total area[26].

Bulk crystallization growth experiments were conducted on thin films of polymer samples of different composition. The samples were heated to 160°C on a Mettler hot stage (FP 52), maintained at that temperature for 5 min, and then cooled down rapidly to the required isothermal crystallization temperature. Radial growth rates G ($G = dx/dt$, where t is the time and x the radius of the spherulite) were measured by means of an ocular micrometer and a Zeiss optical microscope. The

error in the G measurements were between 0.5 and 1%. Photomicrographs of the crystals were taken whenever required.

Scanning electron microscopic (SEM) photographs were taken on a Cambridge Stereoscan 150 of the fracture surface of the blend samples crystallized from the melt at room temperature.

Tensile strength and elongation at break of the blends were measured at room temperature using an Instron testing machine at a crosshead speed of 0.2 cm min^{-1}. Microtensile specimens (ASTM D1708) of the samples were obtained by compression moulding. The error in the measurement was between 3–4%.

I.r. spectra were taken with a Perkin–Elmer i.r. spectrophotometer (model 597) on thin films of the blend samples crystallized at 90°C.

RESULTS AND DISCUSSION

Crystallization of LDPE–PB blend

Tensile properties. The tensile strength and elongation at break are plotted as functions of composition in *Figure 1*. The tensile strength of the blend decreases with increasing concentration of LDPE, reaches a minimum at 40% LDPE, and then increases. The elongation at break also follows the same trend. It has been shown[5,27] that blends of compatible polymers exhibit good mechanical properties; especially, tensile strength shows a near-linear

dependence with composition. In contrast, blends of incompatible polymers exhibit a broad minimum[28–31]. The results of the present investigation (*Figure 1*) suggest that the LDPE–PB blend is incompatible.

Thermal analysis. Crystallization and melting temperatures obtained for different compositions are plotted in *Figure 2*, which shows that the components crystallize independently. *Figure 2* also shows that the crystallization temperature of LDPE is not much affected, but for PB it is lowered. The PB that is crystallized is in form II, which is evident from the melting temperatures. There is an overlap of the endotherms corresponding to the melting of LDPE and PB at different compositions of the blend except at the composition of 40% LDPE, wherein two endotherms are obtained for the two components.

Experimental and calculated (from the upper and lower bounds of the pure components) ΔH_f and ΔH_c values are presented in *Table 1*. There is fairly good agreement between the experimental and calculated values at lower concentrations of LDPE, while there is a large deviation when the LDPE concentration is increased. This is
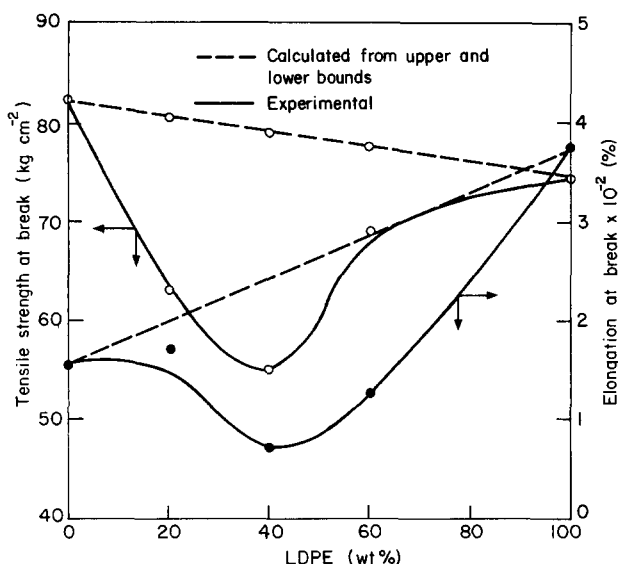

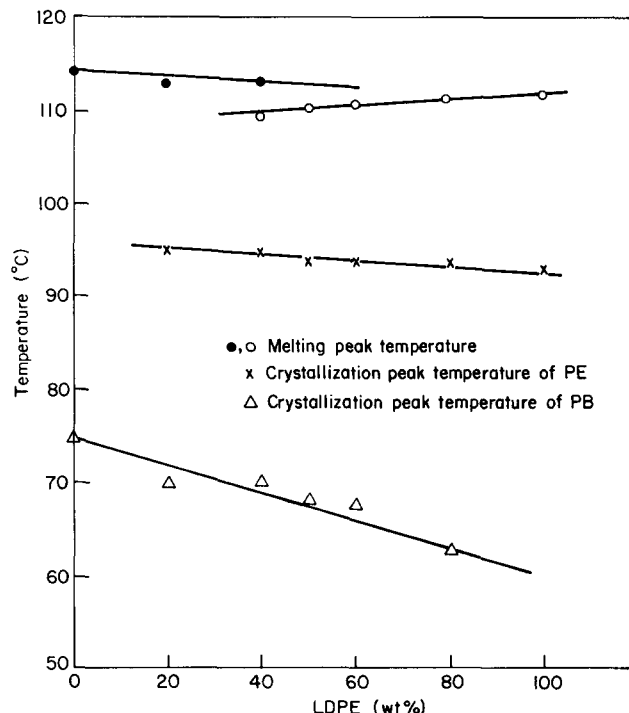**Figure 1** Tensile properties as a function of concentration of PE in the blend

Figure 2 Variation of crystallization and melting temperature of polyblend with composition

Table 1 Enthalpy data for the blend

| Blend composition | Heat of crystallization (J g^{-1}) | | | | | | Total heat of fusion (J g^{-1}) | |
| | Experimental | | | Calculated | | | | |
	ΔH_1	ΔH_2	ΔH_t	ΔH_1	ΔH_2	ΔH_t	Experimental	Calculated
80% PE	52.9	2.4	55.3	75.9	5.4	81.3	91.1	109.6
60% PE	45.6	6.1	51.7	57.1	10.6	67.7	80.0	90.7
50% PE	34.6	10.0	44.6	47.7	13.3	61.0	71.2	81.4
40% PE	26.4	14.1	40.5	38.1	15.9	54.0	61.9	71.9
20% PE	16.2	19.6	35.8	19.1	21.3	40.4	52.9	52.9

ΔH_1 is the heat of crystallization of PE
ΔH_2 is the heat of crystallization of PB
ΔH_t is the total heat of crystallization

because PB crystallizes at relatively low rates[7] at rather high degrees of supercooling compared with PE.

Wide-angle X-ray diffraction. WAXD scans of the blends show the diffraction characteristics of pure homopolymers. For all the blend compositions, the WAXD scan was found to be a superposition of PB and PE scans, i.e. the 2θ values for LDPE and PB do not change. The peak widths are observed to be independent of composition, suggesting that there is no change in the crystallite size. *Figure 3* shows the plot of the relative intensities of the main X-ray diffraction peaks as a function of the composition. The peak intensities change gradually with composition as if each phase crystallizes independently. The data suggest that this blend system is incompatible.

The total degree of crystallinity (*Figure 4*) as determined from the WAXD scans shows that it is maintained almost constant (55%) up to the blend
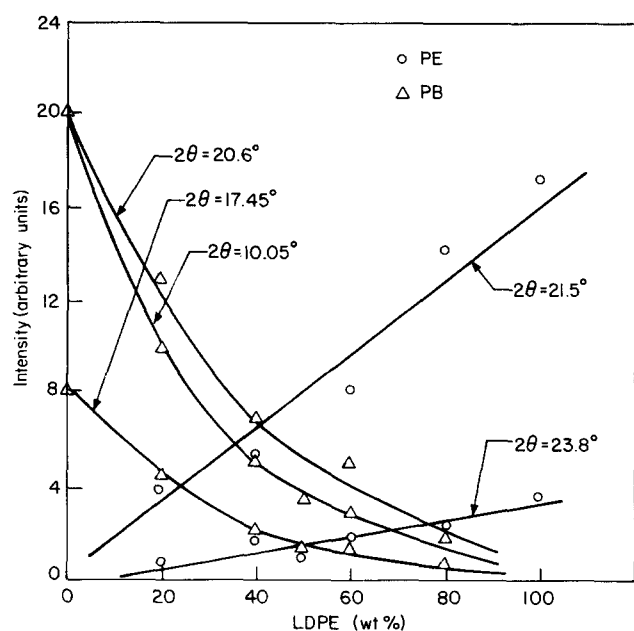

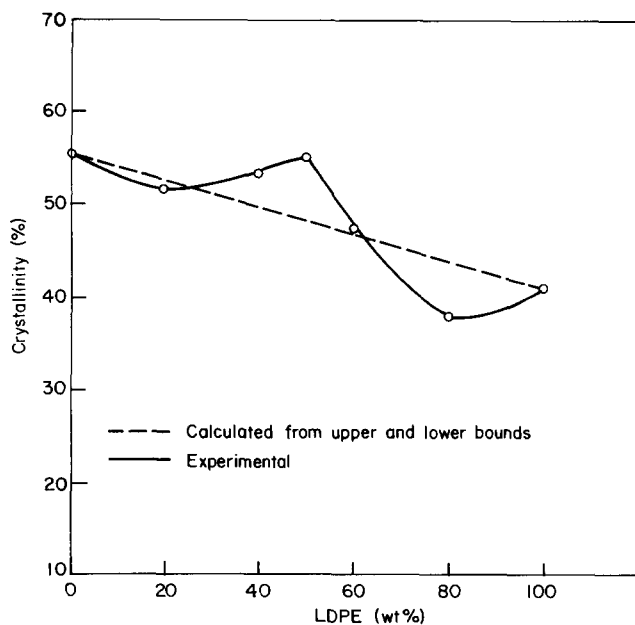**Figure 3** Intensity of WAXD peaks vs. concentration of PE in the blend

Figure 4 X-ray total crystallinity of PE–PB blends
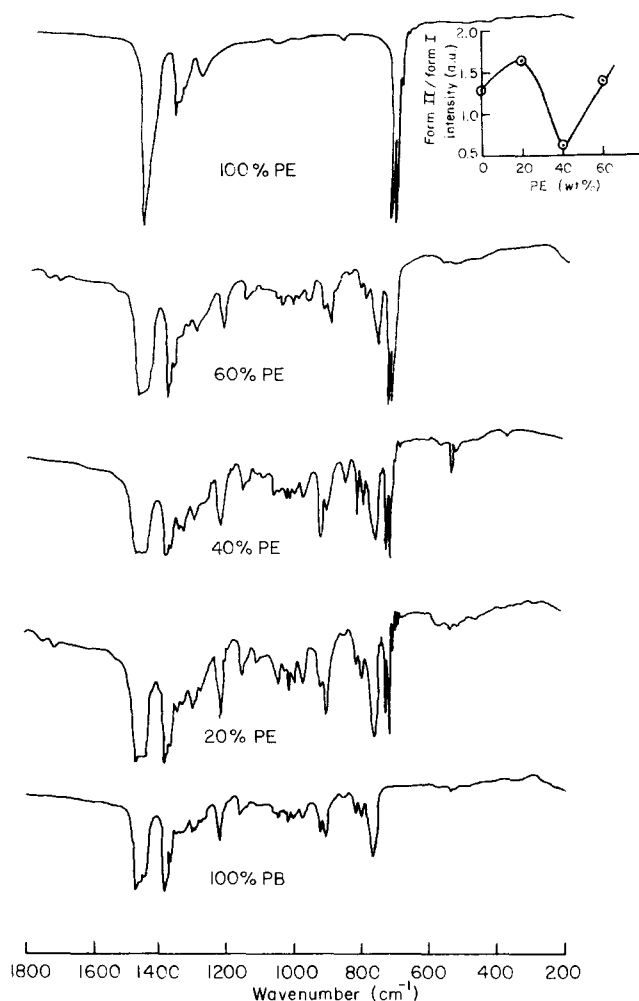

Figure 5 I.r. spectra of PE–BP blends

containing 50% LDPE. Further increase in LDPE concentration decreases the crystallinity to 38%. It appears therefore that the presence of two components in the system hinders to some extent the crystallization process of both phases.

Infra-red. For all the blend compositions the spectra (*Figure 5*) are essentially a superposition of contributions from the individual components, except for the composition 40% LDPE. There is a change in the intensities of the peaks at 905 and 925 cm^{-1}. It has been shown[22] that the absorption at 925 cm^{-1} corresponds to form I while that at 905 cm^{-1} corresponds to form II. In 100% LDPE, 100% PB, 20% LDPE + 80% PB and 60% LDPE + 40%PB samples, the intensity of 905 cm^{-1} absorption suggests that the concentration of form II of PB is more than that of form I. However, in 40% LDPE + 60% PB blend, the 905 cm^{-1} absorption suggests that PB is present more in form I than in form II. The ratio of the intensities of form I and form II peaks is plotted as a function of composition in the inset of *Figure 5*, which shows that the proportion of form II increases as the concentration of LDPE is increased up to 20%, between 20% and 40% LDPE there is a drastic decrease, and beyond 40% there is again an increasing trend.

The maximum incompatibility at 40% LDPE as shown by tensile measurements, d.s.c. and X-ray diffraction data is thus attributed to the presence of a larger proportion of form I relative to form II.
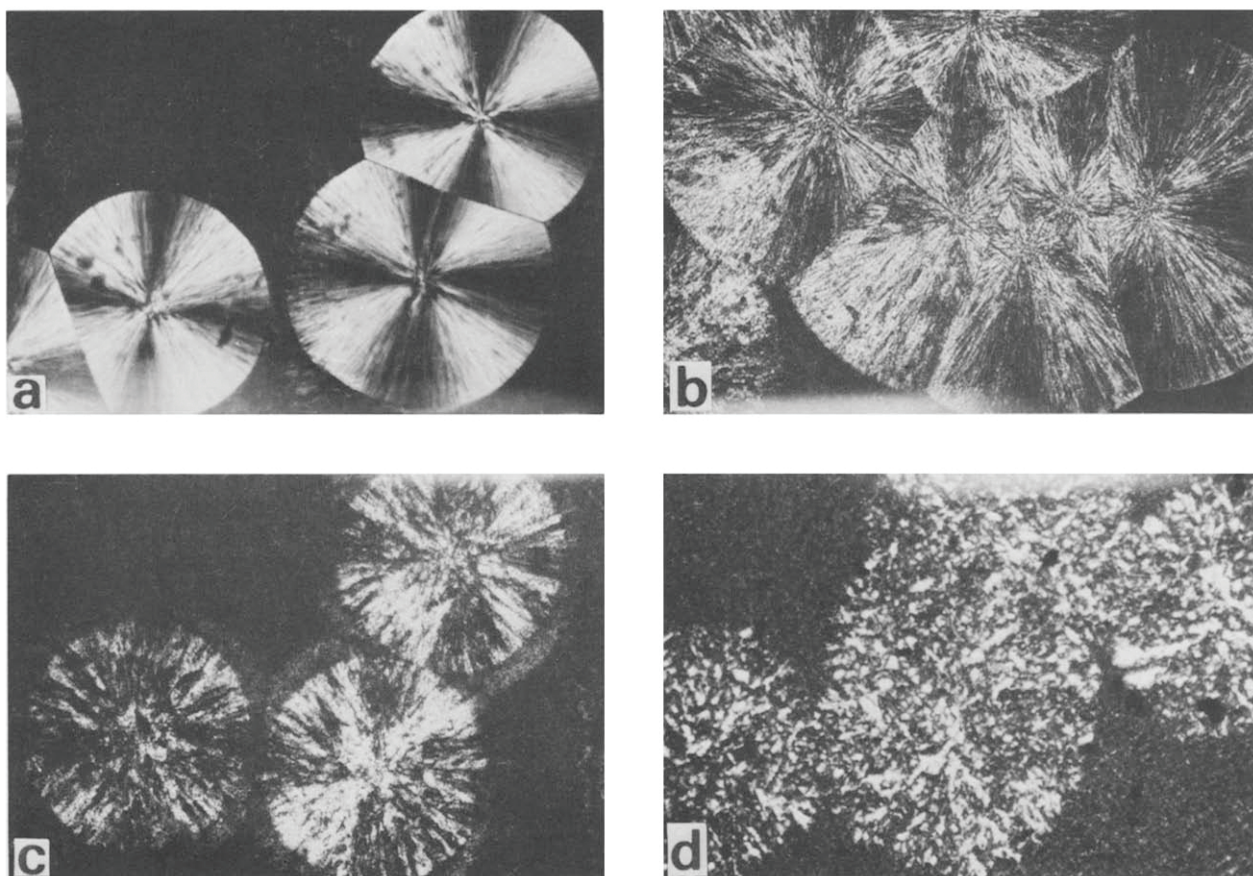
Figure 6 Optical photomicrographs of LDPE–PB blends: (a) 100% PB; (b) 9% PE; (c) 20% PE; (d) 40% PE

Morphology studies. (i) Hot stage microscopy: The samples were heated to 160°C, maintained at that temperature for 5 min, and then cooled rapidly to 90°C, when numerous nuclei were formed and PB spherulites started growing. As the composition of LDPE was increased in the blend, more and more LDPE nuclei appeared, obscuring the growing spherulites of PB.

In order to observe the growth of PB alone, the temperature was raised from 90 to 105°C, when the PB nuclei disappeared, leaving behind the PB crystals. 100% PB crystallizes in the form of well defined spherulites at 90°C and, with the increase of LDPE concentration, the spherulites become less perfect with coarse fine structure (*Figure 6*). As the concentration of LDPE was increased further up to 80%, the morphology of PB becomes non-spherulitic, which is in agreement with earlier studies[9,16,32,33].

Table 2 summarizes the radial growth rates G for four compositions of polyblend in the temperature range 85–98°C. For PB spherulites, G decreases as the concentration of LDPE is increased at all crystallization temperatures. The number of spherulites at a given crystallization temperature also increases with the increase of LDPE concentration. The temperature dependence of G for the blend is found to be very similar to that of homopolymers (*Table 2*), suggesting that the process is nucleation-controlled. This indicates clearly that the two polymer melts are incompatible.

(ii) Scanning electron microscopy: In order to confirm the incompatible nature of the blend, SEM studies were carried out. SEM examination at room temperature of the surfaces formed by fracture of the blend showed phase

Table 2 Growth rate data of PE/PB blend

T (°C)	Radius growth rate, G, (μm min^{-1})			
	40% PE	20% PE	9% PE	0% PE
85	16.8	16.8	22.0	22.4
90	11.0	11.0	13.8	13.8
93	7.3	7.6	8.2	8.4
95	4.8	4.8	5.9	5.9
98	2.4	2.6	3.1	3.9

separation. At low composition of each polymer (below 30%), isolated spherical domains were observed. At higher compositions (40–60%), the morphology changed into that of rods. *Figures 7a* and *b* reveal the discrete LDPE matrix respectively and *Figure 7c* the rods of LDPE and PB. Further, the discrete spheres of PE embedded in the matrix of PB increased in number and decreased in size as the PE concentration decreased, and vice versa. These results show the incompatible nature of LDPE and PB blend.

Crystallization of HDPE–PB blend

Crystallization of HDPE–PB blend was characterized using thermal analysis, WAXD and SEM. The results obtained in WAXD and SEM are quite similar to those observed with LDPE–PB blend, supporting the incompatible nature of the blend. On the other hand, a new observation was found from d.s.c. studies for HDPE–PB blend.

Figures 8a and *b* show that the d.s.c. thermograms for crystallization peak temperatures around 70 and 120°C
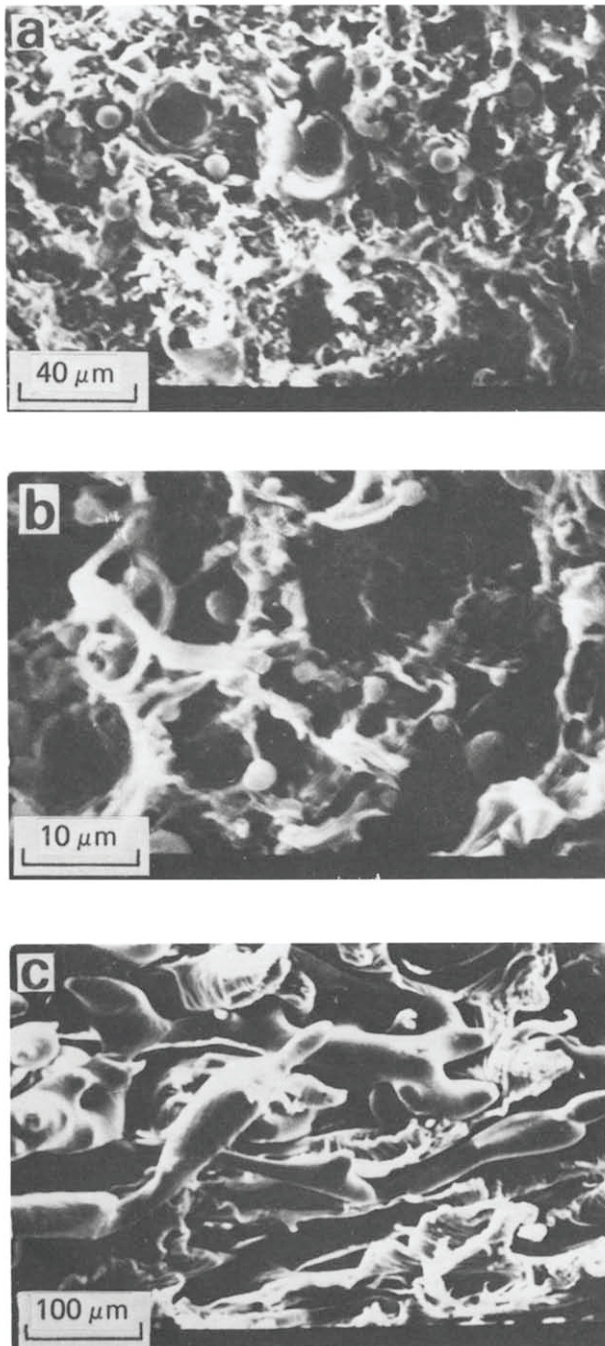
Figure 7 SEM photographs of fracture of LDPE–PB blends: (a) 20% PE; (b) 80% PE; (c) 60% PE
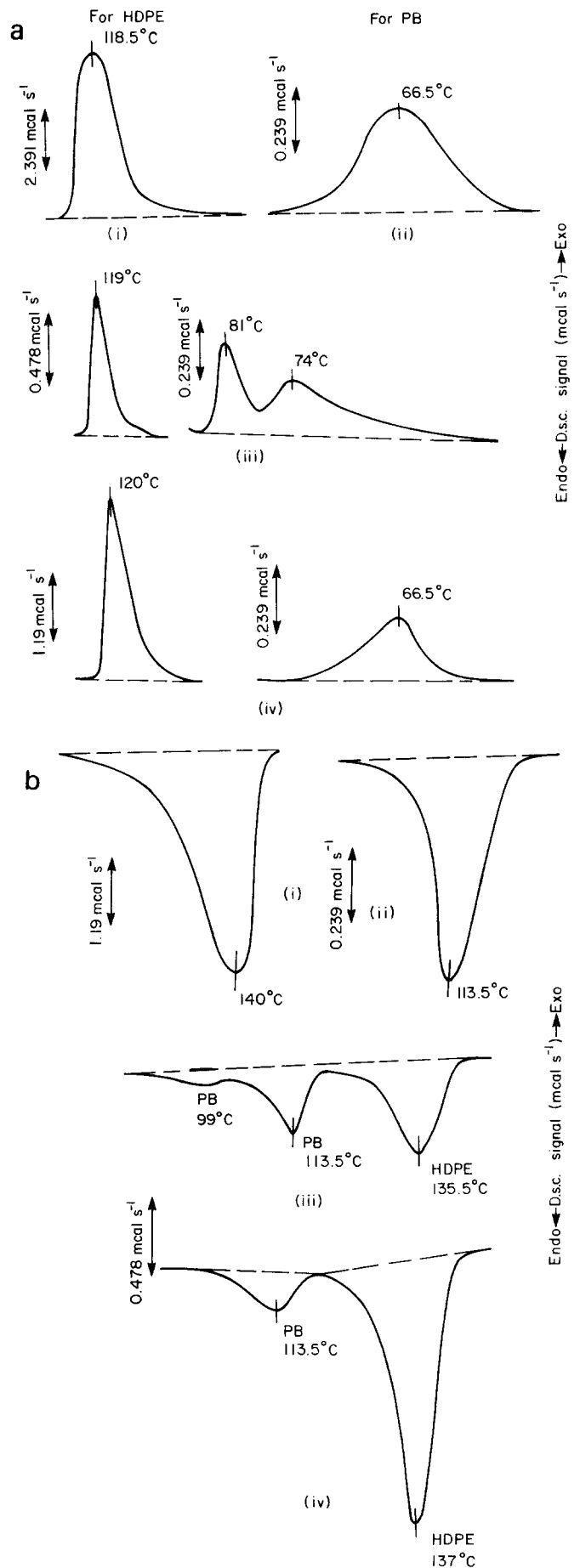

Figure 8 (a) D.s.c. crystallization thermograms of: (i) 100% HDPE; (ii) 100% PB; (iii) 20% HDPE; (iv) 40% HDPE. (b) D.s.c. melting thermograms of: (i) 100% HDPE; (ii) 100% PB; (iii) 20% HDPE; (iv) 40% HDPE

and melting temperatures around 114 and 140°C correspond to PB (form II) and HDPE respectively. An additional crystallization peak around 80°C and a corresponding melting peak at 100°C are observed for the blend composition having less than 30% HDPE. These peaks correspond to a new form of PB, which could be either form III or form I'. To decide between the two forms, WAXD patterns were obtained (*Figure 9*). It may be recalled that the blend samples used for crystallization and melting studies contained PB mainly in form I. *Figure 9* shows that the 2θ values of PB do not change even at low concentrations of HDPE (< 30%), where additional crystallization and melting peaks were observed. This goes to show that the crystal structure of the new form is similar to form I of PB, suggesting that it is form I' and not form III.

Since PB and HDPE crystallize independently at different temperatures (*Figure 10*), it suggests that cocrystallization does not occur and the blend is incompatible. However, the crystallization temperature of form II of PB shows an increase up to 10% HDPE, followed by a gradual decrease; the initial increase in T_c is attributed to the nucleating effect of HDPE[34]. The
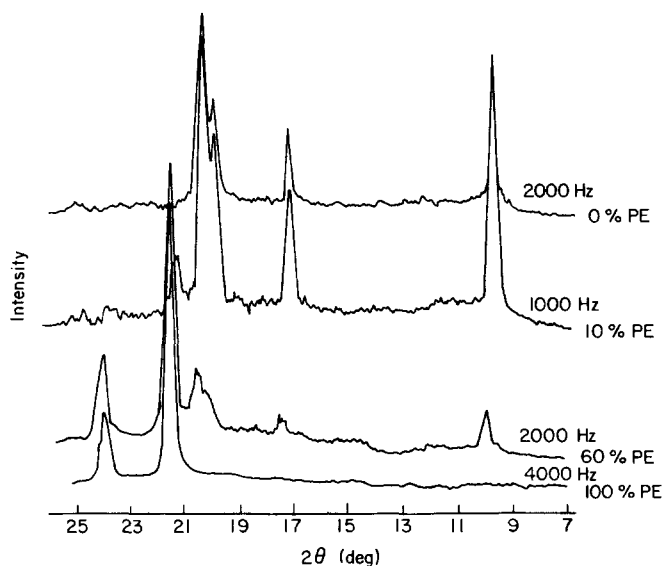

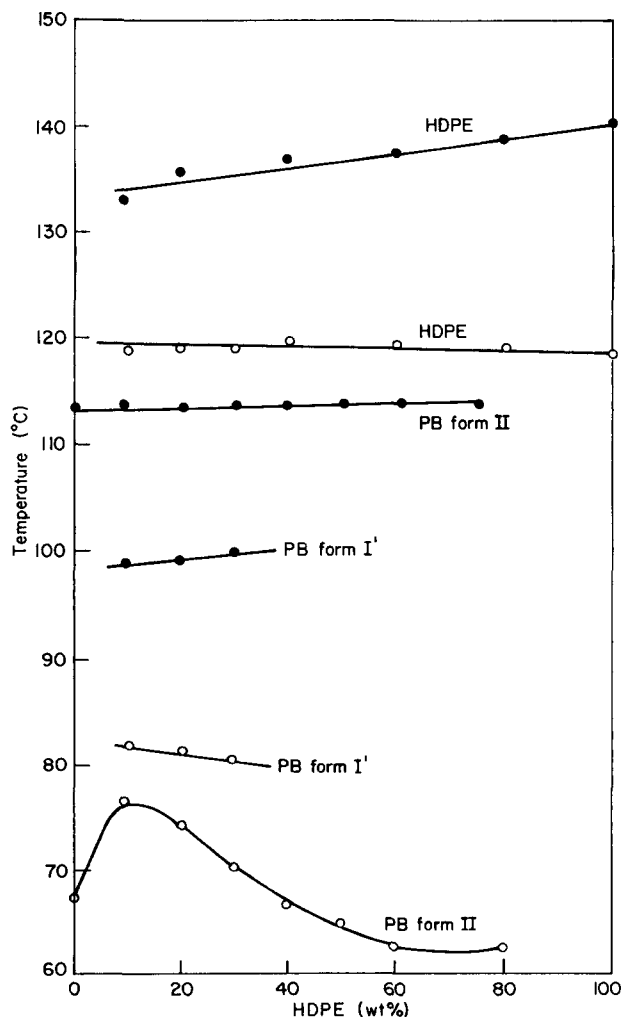**Figure 9** X-ray diffraction scans of the blends

Figure 10 Crystallization and melting temperatures as a function of composition: (O), crystallization; (●), melting
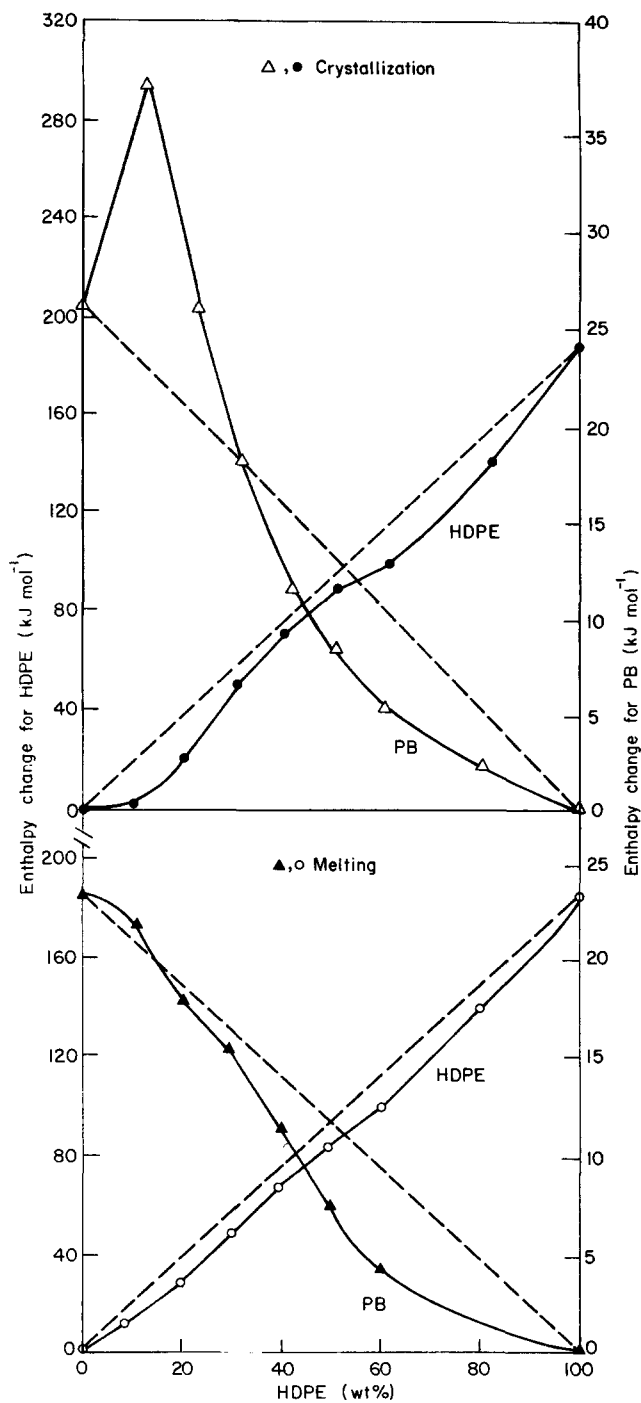

Figure 11 Variation of enthalpy with composition

decrease in T_c beyond 10% is due to the fact that HDPE crystallizes[24] at low undercooling, thereby hindering the crystallization of PB. The melting temperature of form II of PB does not show any appreciable change with composition.

Figure 11 shows the variation of enthalpy of crystallization ΔH_c and melting ΔH_f as functions of composition. The prominent observation is the pronounced increase in ΔH_c of PB at low concentration of HDPE as compared to the expected value with respect to the pure components in the blend. This is attributed to the crystallization of form I' in addition to form II. Since ΔH_f of form I' as evident from *Figure 8* is very much less than that for form II, the total ΔH_f of PB does not show any significant deviation from the calculated value (*Figure 11*).

For blends having higher concentration of HDPE, ΔH_f and ΔH_c are lower than the expected value because the crystallization of PB is hindered by HDPE. However, the ΔH_c and ΔH_f of HDPE are not affected by PB.

CONCLUSIONS

WAXD, i.r. and d.s.c. studies on PE–PB blends show that each phase crystallizes independently of the other. Tensile properties show incompatibility, which is further supported by the phase separation as observed by SEM of the fracture surface. For the blends containing <30% HDPE, form I' crystals of PB are obtained along with the usual form II, which may be due to the high nucleating effect of HDPE.

ACKNOWLEDGEMENTS

REFERENCES

1   Paul, D. R. and Newman, S., 'Polymer Blends', Academic Press, New York, 1978, Vols. 1 and 2
2   Jalbert, R. L. and Smajkal, J. P., 'Modern Plastic Encyclopedia', McGraw-Hill, New York, 1976
3   Shen, M. and Kawai, H., *AIChE J.* 1978, **24**, 1
4   Cooper, S. L. and Estes, G. M., 'Multiphase Polymers', *Adv. Chem. Ser.* 1979, **176**; *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* 1978, **19**, 5
5   Krausse, S. *J. Macromol. Sci. Rev. Macromol. Chem.* 1972, **7**, 251
6   Weing, W. and Meyer, K. *Colloid Polym. Sci.* 1980, **258**(9), 1009
7   Foglia, A. J. *Appl. Polym. Symp.* 1969, **11**, 1
8   Aref, A. A., Hay, J. N., Marsdon, B. J. and Walker, N. *J. Polym. Sci., Polym. Phys. Edn.* 1980, **18**(3), 637
9   Siegmann, A. *J. Appl. Polym. Sci.* 1979, **24**, 233
10 Schneier, B. *J. Appl. Polym. Sci.* 1974, **18**(7), 1999
11 Schurer, J. W., De Boer, A. and Chulla, G. *Polymer* 1975, **16**(3), 201
12 Feldman, D. and Ghimpu, M. *Bull. Inst. Politech. Iasi Sect.* 1975, **21**(1–2), 75
13 Nishi, T. and Wang, T. T. *Macromolecules* 1975, **8**(6), 909
14 Wang, T. T. and Nishi, T. *Macromolecules* 1977, **10**(2), 421
15 Hourston, D. J. and Hughes, I. D. *Polymer* 1977, **18**(11), 1175
16 Stein, R. S., Khambatta, F. B., Warner, F. P., Russell, T., Escala, A. and Balizer, E. *J. Polym. Sci., Polym. Symp.* 1978, **63**, 313
17 Godovskii, Yu. K., Kharikova, Z. F. and Malinskii, Yu. H. *Vysokomol. Soed. A* 1981, **23**(1), 133
18 Blackadder, A. D., Richardson, M. J. and Sarill, G. N. *Makromol. Chem.* 1981, **182**(4), 1271
19 Slagowski, F. L., Chang, E. P. and Tkacik, J. J. *Polym. Eng. Sci.* 1981, **21**(9), 513
20 Bohn, L. *Rubber Chem. Technol.* 1978, **41**, 495
21 Rosen, S. L. *Polym. Eng. Sci.* 1967, **7**, 115
22 Boor, J. Jr and Mitchell, J. C. *J. Polym. Sci. A* 1963, **1**, 59
23 Zannetti, R., Manaresi, P. and Buzzori, G. C. *Chim. Ind.* 1961, **43**, 735
24 Danusso, F. and Cianolti, G. *Makromol. Chem.* 1963, **61**, 139
25 Armeniades, C. D. and Baer, E. *J. Macromol. Sci., Phys. B* 1967, **1**, 309
26 Ong, C. J. and Price, F. P. *J. Polym. Sci., Symp.* 1978, **63**, 45
27 Manson, J. A. and Sperling, L. H., 'Polymer Blends and Composites', Plenum, New York, 1976
28 Ferry, E. *J. Appl. Polym. Sci.* 1964, **8**, 2605
29 Fried, J. R. Ph.D. Thesis, University of Massachusetts, 1976
30 Agroldi, G., Gatta, G., Gugelmetto, P. D., Rettore, R. and Talamini, G. P. *Adv. Chem. Ser.* 1971, **99**, 119
31 Feldman, D. and Rusu, M. *Eur. Polym. J.* 1974, **10**, 41
32 Keith, H. D. and Padden, F. J. *Appl. Phys.* 1964, **35**, 1270
33 Hubbel, D. S. and Cooper, S. C. *J. Appl. Polym. Sci.* 1977, **21**, 3035
34 Wunderlich, B., 'Macromolecular Physics', Academic Press, New York, 1976, Vol. 2, Chap. 5