On phase separation in high- and low-density polyethylene blends:
1. Melting-point depression analysis

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(Received 2 May 1990; revised 11 September 1990; accepted 8 October 1990)

A melting-point depression analysis of high-density polyethylene crystals embedded in molten branched polyethylene is presented. The results indicate that the melting temperature of the crystals is influenced by both the branching content of the low-density polyethylene and the relative volume concentration of the two polymers. The results are critically discussed in terms of the Flory–Huggins approximation for polymer–polymer mixtures.

(Keywords: high-density polyethylene; low-density polyethylene; mixtures; melting-point depression; compatibility; phase separation)

INTRODUCTION

The aim of physical characterization of polymers is to minimize molecular heterogeneity and impurities existing in commercial samples. Polyethylene (PE) is undoubtedly a very good example; indeed most experimental data, except those obtained from selected expensive fractions, are spread around some commonly accepted average values. From this point of view, any conventional PE sample may actually be contemplated as a molecular blend in which the tails of the molecular-weight distribution and the presence of a small proportion of branches could substantially shift the expected values. On the other hand, blending of PE of different degrees of branching has long been employed either to balance the properties of the final product or to improve the melt processing. While an extensive literature concerning molecular-weight effects is available, information related to branching effects is more limited. In this paper we focus our attention on the possible effects that branched molecules might have on the crystallization and melting behaviour of linear PE. Leaving aside the long-standing controversy on the location of the branches, outside[1] or inside[2] the crystals, it is a well established fact that increasing the number of branches along the main PE chain causes an expansion of the unit-cell parameters[3], an increase in lattice distortions[4], a decrease in crystallinity and crystal dimensions[5,6] and a severe reduction in the melting temperature and enthalpy of fusion of the crystals[7]. In this work we are mostly concerned with two main questions: (a) How does branching affect molecular compatibility? (b) Could linear and branched PE form an isomorphic system? If so, under what crystallization conditions and up to what degree of branching? A few recent publications are somehow connected to these questions. Keller *et al.*[8] have reported experimental data that support the view of a phase-segregated melt in blends of high-density and low-density polyethylene (HDPE/LDPE) with concentration higher than 50% of the latter. The branching content (ε) of the LDPE is close to one branch per hundred CH_2. A second publication[9] also envisages molecular segregation effects observed in linear low-density polyethylene (LLDPE) prior to crystallization. Furthermore while Edward[10] concludes that LLDPE and HDPE are fully compatible, Malavasic *et al.*[11] show that HDPE/LDPE are fully incompatible. Co-crystallization phenomena have received more attention. Some authors have shown evidence of co-crystallization in ternary and binary blends[12,13] although the crystallization conditions have generally been overlooked. Low-molecular-weight linear PE and LDPE blends have also been reported to co-crystallize within the narrow temperature range 387–389 K[14]. The possibility of co-crystallization under heavy quenching conditions will be analysed in a separate[15] publication. In this paper melting data of HDPE crystals grown isothermally from HDPE/LDPE blends together with melting data of HDPE single crystals immersed in LDPE matrix will be presented. It will be shown how the concentration and branching of the LDPE material affect the crystallization and melting of the linear crystals. A theoretical justification of the experimental results will be treated separately in a forthcoming publication[16].

EXPERIMENTAL

Four different commercial PE grades, one linear and three branched, have been used. Data on molecular weight and branching content of these samples are collected in *Table 1*. More details on sample characterization can be found elsewhere[4].

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0032-3861/91/162984-05

Table 1 Commercial name, molecular weight and fraction of branches for the PE samples

Sample	Name	$M_w \times 10^3$	ε(CH_3/100 C)
A	Lupolen 6011L	100.0	0
B	Hostalen GF	120.0	0.70
C	Epolene C11	10.0	1.21
D	Lupolen KR 1051	51.0	1.76

Single crystals

HDPE single crystals were grown from 0.2% solution in *p*-xylene at 349 K. Solutions in *p*-xylene of the different LDPE samples were then added to the suspension of the HDPE crystals so as to make mixtures of the two polymers at concentrations of 25, 50 and 75% by weight of LDPE. The mixtures were separated from the liquid by centrifuge and the remaining slurry was cast on d.s.c. pans and fully dried at 343 K under vacuum for 24 h. D.s.c. runs were carried out at heating rates of 10, 20 and 40 K min^{-1}. Instrumental corrections were applied using indium as a standard. Melting temperatures were taken at the maximum of each HDPE endothermic peak. Typical d.s.c. traces exhibited by the samples studied are displayed in *Figure 1*. In order to inspect the contact between the two polymers the following experiment was carried out with the blend of polymer A and polymer C: the samples were held in the temperature range defined by the single-crystal melting temperature of the HDPE and the melting temperature of the LDPE and then they were cooled down. The resulting thermograms are identical to those exhibited by the original preparations.

Melt-crystallized blends

Binary solution-mixed blends of HDPE and LDPE were prepared using the samples described in *Table 1*. Samples containing 25, 50 and 75% of linear PE were prepared by dissolving the polymer pellets in hot *p*-xylene followed by acetone precipitation. Where the C component was involved, additional 15, 40, 60 and 85% mixtures were prepared. The filtered material was then dried in a vacuum oven at 343 K over 24 h to ensure complete removal of the liquids. Films (25 μm thick) of resulting materials were melted at 443 K for 5 min between glass plates and rapidly crystallized at room temperature. Each sample was then placed in a hot-stage microscope. To derive the equilibrium melting temperatures T_m^0, optical melting points were determined using a Leitz Laborlux microscope in conjunction with a Mettler hot stage. The thickness of the sample has been found to be very critical. Indeed variations of less than 10% in the thickness provide deviations in the measured temperatures of 0.2°C. Thus special care was taken to work within the limits of 25 ± 1 μm in thickness for each sample. The experimental T_m values for each blend as a function of T_c were determined as follows: The melt-crystallized sample within the hot stage was brought to 443 K to ensure total melting of residual nuclei, then the sample was cooled at the maximum rate available (30 K min^{-1}) till the selected crystallization temperature T_c. Crystal growth was then observed, under polarized light, and stopped when the spherulites were of the order of 3 μm diameter. Heterogeneous nucleation with density values of ≈ 2500 nuclei/mm^2 was generally found. In the crystallization range used in this work the appearance of the spherulites was almost simultaneous. T_m was determined by heating up the samples, at a rate of 10 K min^{-1}, till total disappearance of birefringence was achieved. Here we are measuring the final melting temperature, which corresponds to the old (first crystallized) crystals. We should point out that the measured T_m values correspond to the original crystals but possibly modified by isothermal thickening and annealing effects during the heating process. Plotting the observed T_m as a function of T_c one goes from less perfect crystals grown at higher supercooling to crystals of higher perfection grown at lower supercooling. The value at $T_m = T_c$ yields the extrapolated equilibrium melting temperature, T_m^0, for each sample.

RESULTS

Figure 2 shows the plots of T_m *versus* T_c for the different blends used. The lower limit of the range of crystallization (393–398 K) is caused by the rapid crystallization rate of PE at that temperature. Below that temperature the process of growth can no longer be isothermally controlled unless removal of nucleating agents through a tedious cleaning procedure has been carried out[17]. The upper limit, 398 K, has been chosen to minimize isothermal thickening effects[18], which might perturb the melting values of the original grown crystals. As can be observed, an excellent linear relationship between T_m and T_c is obtained. The extrapolated values T_m^0, obtained by a least-squares fitting of the experimental points, are collected in *Table 2*. The data clearly show that the melting point of the HDPE crystals varies with both the degree of branching of LDPE and with its concentration in the blend. In order to characterize better the dependence of ΔT with the concentration ϕ, we have prepared additional blends with sample C. The obtained T_m^0 values are shown in *Figure 3*. It is clear that T_m^0 of the HDPE decreases almost linearly with increasing concentration of LDPE. This plasticizing effect has already been described by other authors[13] although this is the first time that a systematic dependence of ΔT with ϕ has been reported. However, the T_m^0 data have to be cautiously analysed. Although the T_m vs. T_c method is widely accepted to calculate T_m^0 values, the possible curvature of the T_m vs. T_c lines at low undercooling might affect the results[19]. Thus, we have employed an

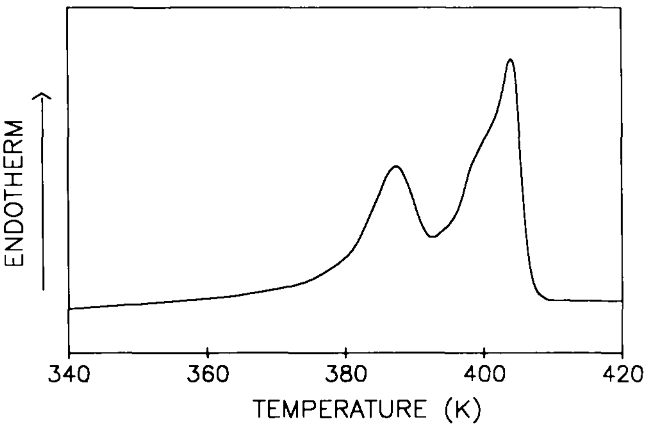

Figure 1 Typical d.s.c. trace obtained for one of the HDPE/LDPE investigated mixtures (A/C, 50:50) showing the two characteristic melting peaks

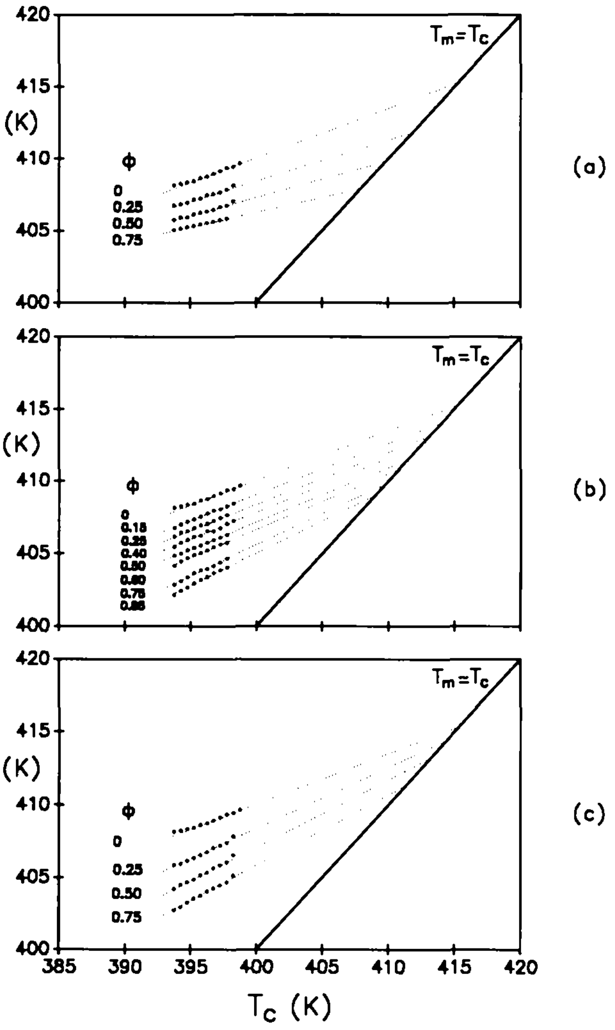

Figure 2 Plots of $T_m - T_c$ for the different blends: (a) A/B, (b) A/C and (c) A/D. The volume concentration ϕ of the low-density component is indicated in each plot

Table 2 Equilibrium melting temperature $T_m^0(\phi)$ of HDPE crystals in the different melt-crystallized blends. The values have been obtained for three different LDPE concentrations ϕ

	ϕ		
Sample	0.25	0.50	0.75
A/B	411.8	409.8	407.8
A/C	413.1	411.4	409.8
A/D	414.5	413.2	411.3

alternative method to determine the depression of HDPE crystals while immersed in a LDPE matrix. In this case the same batch of HDPE single crystals was mixed with different LDPE. Here we are measuring the variation in the melting temperature $T_m(\phi)$ of a single crystal of lamellar thickness l in a molten matrix of LDPE. The value for an infinite crystal can be derived from the well known Thomson–Gibbs equation:

$$T_m = T_m^0\left(1 - \frac{2\sigma_e}{\Delta H^0 l}\right) \tag{1}$$

where ΔH^0, σ_e and T_m^0 are the bulk enthalpy, the surface free energy and the equilibrium melting temperature of an infinite crystal and T_m is the melting temperature of a crystal of thickness l. If the crystal melts in a matrix of LDPE of concentration $(1-\phi)$ the equivalent equation will be:

$$T_m(\phi) = T_m^0(\phi)\left(1 - \frac{2\sigma_e}{\Delta H^0 l}\right) \tag{2}$$

Dividing equation (1) and (2) one obtains that:

$$T_m^0(\phi) = \frac{T_m^0 T_m(\phi)}{T_m}$$

Now by using the experimental values T_m^0, $T_m(\phi)$ and T_m one can derive $T_m^0(\phi)$. The values thus obtained are plotted in *Figure 4*. Again we find that T_m^0 decreases with increasing concentration of LDPE and also that this depression is more conspicuous for the mixtures containing the lower branching material.

DISCUSSION

Phase segregation

The melting-point depression values $\Delta T = T_m^0(\phi = 0) - T_m^0(\phi)$ observed in the investigated samples are plotted in *Figure 5*. One can clearly observe that the ΔT variations with ϕ and ε show a parallel and systematic behaviour in both systems, melt-crystallized (m.c.) and single crystals (s.c.). However, the level of the experimental

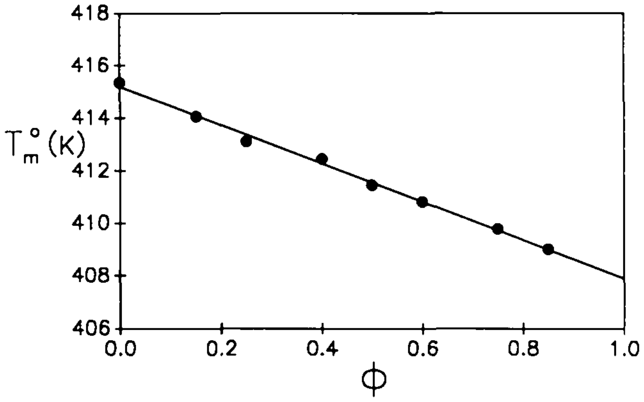

Figure 3 Variation of the equilibrium melting point of HDPE crystals with low-density material of volume concentration ϕ. Data shown are for the blend A/C

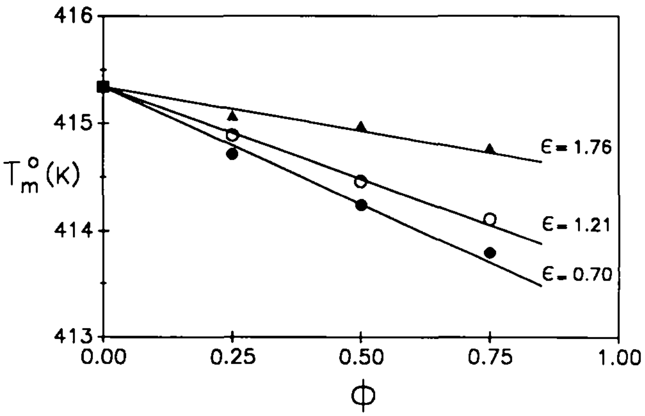

Figure 4 Variations of the equilibrium melting point of a HDPE single crystal in a mixture with low-density material of volume concentration ϕ. The branching content of the low-density material is indicated in the plot

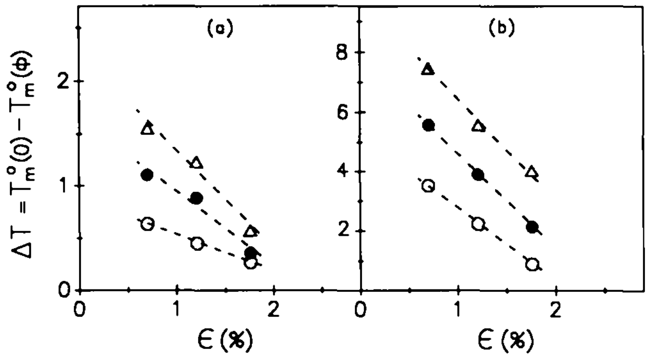

Figure 5 Equilibrium melting-point depressions observed in mixtures of high-density PE crystals and low-density material: (a) single crystals; (b) melt-crystallized samples

depression is much more conspicuous in m.c. (7.5 K $\geqslant \Delta T \geqslant$ 4 K, for sample A/B) that in s.c. (1.6 K $\geqslant \Delta T \geqslant$ 0.6 K) material. Although we do not have a clear explanation for this discrepancy, one might think of several factors that could be underlining the observed phenomenon. A first consideration has to be based on the experimental details involved in the determination of the T^0_m values. The data in m.c. samples have been obtained as linear extrapolations of the corresponding $T_m - T_c$ points. It might be argued that a shift of T_m towards higher values at very low undercoolings could yield higher extrapolated points. This possible curvature of the $T_m - T_c$ lines has already been discussed by other authors[19]. A second consideration is based upon morphological factors. Indeed, in all cases of m.c. and s.c. materials, we are measuring melting at temperatures far from equilibrium and hence kinetic factors such as diffusion rates should be taken into consideration. Consequently, crystals grown from the melt generally exhibit smaller lateral dimensions[20] than s.c., favouring the mixing as compared to the larger s.c. A third point to be raised is the incorporation of some branched segments into the crystals while growing from the melt. The inclusion of branch segments would generate local lattice defects within the crystals[3] or at the surfaces[7,21], reducing the thermal stability of the crystals. To summarize this point, both sets of ΔT data, which show qualitatively the same experimental evidence, have to be taken as limiting values for a given concentration and degree of branching. What is more important is that the extrapolation of ΔT to zero seems to indicate that phase segregation of the HDPE/LDPE system may occur with LDPE having branching content higher than $\simeq 2\%$.

Flory–Huggins approximation

The analysis of crystal melting point provides a valid route to determine the compatibility of a polymer blend when at least one crystallizable component is used[22]. The classical Flory–Huggins approach for polymer–solvent systems[23] has been successfully extended by Nishi and Wang[24] to polymer–polymer mixtures. In fact, this approach is the only existing model that might provide an explanation of the observed melting behaviour. The thermodynamic mixing of two polymers was first treated by Scott[25] using the classical Flory–Huggins approximation[23]. By equating the chemical potential differences due to the mixing and to the melting of the crystals one obtains for each CH_2 unit:

$$\frac{1}{T^0_m(\phi)} - \frac{1}{T^0_m(0)} = \frac{-Rv_2}{\Delta H^0_u v_1}\left[\frac{\ln(1-\phi)}{m_2} + \left(\frac{1}{m_2} - \frac{1}{m_1}\right)\phi + \chi\phi^2\right] \tag{3}$$

where v and m refer to the molar volume of the repeat unit and degree of polymerization respectively and the subscripts 1 and 2 to the liquid (LDPE) and crystalline (HDPE) phases. R is the gas constant, and ϕ the volume concentration of the LDPE phase. The first two terms are entropic and depend on the molecular lengths. The third term is enthalpic and is governed by the interaction parameter χ. By taking the average molecular-weight values one can estimate the contribution of the first two terms. The calculated results, using a value of 1 kcal mol^{-1} for ΔH^0_u, are collected in *Table 3*. To evaluate the enthalpic contribution one needs an independent determination of χ. Freytag *et al.*[26] have calculated χ from solubility measurements in the HDPE/LDPE system. The values reported by these authors range from 0.0013 to 0.0053 depending on the method used to determine the solubility parameters. The branching content is not reported and the temperature of determination is close to 423 K. By taking for χ the average value 0.0033 we have calculated the enthalpic terms for the different concentrations. The values are also collected in *Table 3*. By inspecting this table one can draw several conclusions. The most striking one is that even in the most favourable case (sample A/C and s.c. material) equation (3) cannot explain the observed level of melting-point depressions. What is more the blends should be incompatible at all concentrations and branching values. In order to find out the dependence of the depression with concentration it is worth while plotting the values $1/T^0_m(\phi) - 1/T^0_m(0)$ as a function of ϕ for the samples A/C. It is clear that, in a first approximation, a linear correlation is observed (*Figure 6*). Hence, the entropic terms that depend on ϕ are predominant in the observed depression. The mixing might then be enhanced by the volume excess created by the branches. This effect would result in an increase of entropy on mixing. Nevertheless, to explain the tendency to phase separation with branching one has to admit that χ must increase with branching. This hypothesis has already been used by other authors[27] in copolymer materials where the interaction parameter increases with increasing content of non-crystallizable units. A tentative

Table 3 Experimental $1/T^0_m(\phi) - 1/T^0_m(0)$ values for melt-crystallized (m.c.) and single crystal (s.c.) samples. Entropic and enthalpic calculated contributions from equation (3)

		$\Delta(1/T)$				
Sample	ϕ	m.c.	s.c.	$\frac{\ln(1-\phi)}{m_2}$	$\left(\frac{1}{m_2} - \frac{1}{m_1}\right)\phi$	$\chi\phi^2$
A/B	0.25	20.4	3.6	0.08	−0.01	−0.41
	0.50	32.3	6.6	0.19	−0.02	−1.65
	0.75	44.2	9.0	0.39	−0.03	−3.71
A/C	0.25	12.8	2.4	0.08	+0.63	−0.41
	0.50	22.8	4.8	0.19	+1.26	−1.65
	0.75	32.3	7.2	0.39	+1.89	−3.71
A/D	0.25	4.6	1.2	0.08	−0.06	−0.41
	0.50	12.2	2.4	0.19	−0.13	−1.65
	0.75	23.4	3.6	0.39	+0.20	−3.71

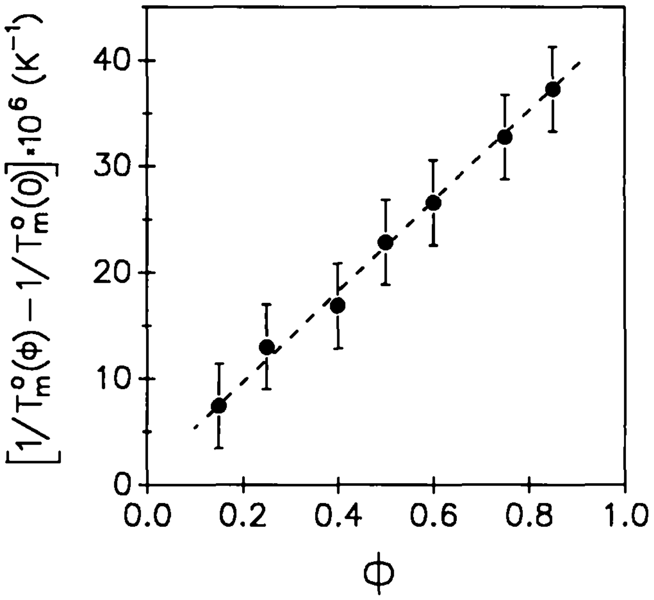

Figure 6 Plot of $\Delta T/T^0_m(\phi)T^0_m(0)$ against ϕ for the blends A/C

justification of this behaviour will be given in a forthcoming publication[16].

CONCLUDING REMARKS

One can draw some conclusions from this study. The presence of branched material reduces the melting point of the PE crystals. The level of this depression is much more relevant in melt-crystallized blends than in mixtures of single crystals with low-density material. Nevertheless, the qualitative behaviour of this depression is identical in both methods. These depressions, which cannot be explained with the classical Flory–Huggins approximation, seem to indicate that mixing of the two polymers at the melting point (≈400 K) takes place whenever the branching content is lower than 2%. Above 3% of branching phase segregation might occur.

ACKNOWLEDGEMENTS

This work was generously supported by the CICYT grants MAT90-0832 and PB86-0559. Thanks are due to Drs F. Ania and D. R. Rueda for revision of the manuscript.

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