On phase separation in high- and low-density polyethylene blends: 2. A working model

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Some experimental evidence has recently been reported supporting the view of a phase-segregated melt in high-density/low-density polyethylene blends. Dispersive interaction between components makes it reasonable for segregation to occur. A simple model is proposed that allows one qualitatively to understand compatability as a function of the degree of branching. A critical branch content, ε_c, below which compatibility is assured for all compositions, is predicted. The model is based on thermodynamic mixing concepts of lattice theory, assuming an increasing presence of holes with branching, according to specific-volume changes derived from X-ray data.

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

INTRODUCTION

In previous studies[1,2] we reported experimental melting-point depression data that support the view of phase separation in high-density (HD) and low-density (LD) polyethylene (PE) blends. We also showed that the observed depression was dependent both on the relative concentration of the two polymers and on the branching content of the LDPE, being more relevant for higher concentrations of LDPE and for the blend containing the lower branching content. These phenomena are connected to the more general unsolved problem of understanding the dependence of the free energy of mixing with branching content and temperature. Phase diagrams might then be derived and the range of degree of branching in which segregation occurs could also be predicted. Two recent publications are also related to this topic. Keller *et al.*[3] have reported morphological evidence for phase separation in blends of HDPE/LDPE with concentration higher than 50% of the latter. A second publication[4] also challenges molecular segregation effects observed in linear low-density PE (LLDPE). The aim of the present study is to offer a simple justification of why the HDPE/LDPE system could undergo phase separation. As a matter of fact one would expect that dispersive interaction between components prevents miscibility because of the extremely low entropy gain associated with the mixing of long chains. This is in contrast with the well known criterion or requirement of a negative interaction parameter for compatibility in polymer blends[5].

THE THEORETICAL MODEL

The forthcoming presentation is an attempt to understand in a simple way the thermodynamic mixing behaviour of HDPE/LDPE blends. Volume changes, due to branching[6] and upon mixing, have to be taken into account. In order to use lattice model concepts we are going to simulate such effects by allowing the presence of holes with a concentration ϕ_h within the lattice. Scott's equation[7] for the mixing of a ternary system will then be used with holes instead of solvent.

Entropy of mixing

Accordingly, the entropic part of the partial molar free energy of mixing per mole of structural units of the polymer is given by:

$$\Delta\mu_s = RT[\ln \phi_2/x_2 + (1/x_2 - 1/x_1)\phi_1 + (1/x_2 - 1/x_h)\phi_h] \tag{1}$$

where $x_h = v_h/v_u$ and v_u are the volumes of a hole and one structural unit respectively. The combinatorial entropy contribution to the chemical potential in equation (1) involves: (i) the usual combinatorial entropy due to the polymer chains and (ii) the entropic contribution associated with the free volume (simulated by the presence of holes) due to a less dense packing.

The first contribution, i.e. the usual one, can be calculated following the treatment described by Flory and Scott[8,9] for the case of linear polymers. The only difference in our mean-field statistical calculations will concern the segments next to branch–backbone cross-points. However, for low ε values one can assume that branches are not located at consecutive segments of the backbone. Bearing in mind this hypothesis and assuming total chain flexibility, one can simply evaluate the mixing entropy following analogous steps as Flory[8] and Scott[9]. The resulting configurational entropy of mixing is equivalent to the case of mixing a linear component 2

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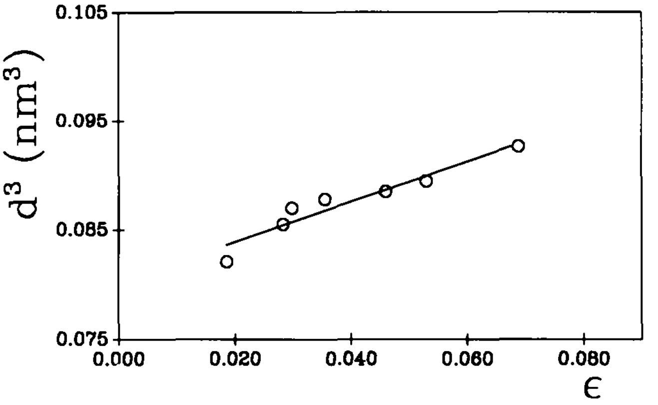

Figure 1 Cubic mean amorphous intermolecular distance d^3 as a function of branch content. The data are derived from the positions of the X-ray diffraction amorphous halos taken from ref. 6. The parameter α can be derived from the slope to intercept ratio, assuming linearity

with an also linear component 1 but of effective length $\tilde{x}_1 = x_1(1+\varepsilon r)$, where $\tilde{x}_1$ is the total number of repeat units irrespective of their location (backbone or branches).

The second contribution, i.e. the free-volume contribution associated with branches, is implicit in the hole concentration ϕ_h. On the other hand such hole concentration is expected to result from a balance between two counter-effects: (i) a positive contribution ϕ_h^+ of holes inherent in the pure LDPE matrix and (ii) a negative contribution ϕ_h^- associated with the volume contraction of the total system upon mixing. From X-ray diffraction measurements a plot of the mean intermolecular distance as a function of branch content ε was obtained[6]. The cube of such a distance is proportional to the specific volume. It is reasonable to assume the concentration of holes inherent in the pure LDPE matrix as:

$$\phi_h(\text{pure LDPE}) = \Delta V/V_0 = \alpha\varepsilon \qquad (2)$$

which has been taken proportional to the branch content according to the experimental plot of *Figure 1*, the proportionality constant being $\alpha \simeq 2$. The positive contribution of holes to the total system will be:

$$\phi_h^+ = \alpha\varepsilon\phi_1 \qquad (3)$$

On the other hand, annihilation of holes will take place upon mixing because of the accessibility of HDPE chain segments to LDPE holes. We take this negative contribution proportional to the probability of meeting between linear polymer and holes, i.e.:

$$\phi_h^- = \beta\phi_h^+\phi_2 = \alpha\beta\varepsilon\phi_1\phi_2 \qquad (4)$$

The limit value $\beta = 1$ corresponds to the case of certain annihilation per meeting, in contrast to the opposite limit case $\beta = 0$. A net hole contribution will be used for equation (1):

$$\phi_h = \phi_h^+ - \phi_h^- = \alpha\varepsilon\phi_1 - \alpha\beta\varepsilon\phi_1\phi_2 \qquad (5)$$

which yields the effective level of holes favouring mixing around given values of ϕ_1 and ϕ_2.

Heat of mixing

Let us assume a Van Laar type of expression for the heat of mixing[5,10]:

$$\Delta H_m = (V_1 + V_2)B\phi_1\phi_2 \qquad (6)$$

where B is the binary interaction energy density, and V_1 and V_2 are the actual volumes of the components. Additional terms in equation (6) involving ϕ_h as a factor have been neglected owing to their low values ($\phi_h \ll \alpha\varepsilon\phi_1$) compared to the usual ϕ_1 and ϕ_2 values. This kind of expression has already been discussed by other authors for the case of random copolymer/homopolymer systems[5,10]. We shall use their conclusions for the HDPE/LDPE mixtures, assuming as a first approximation that we can consider LDPE chains as random copolymeric chains with randomly distributed branches along the backbone. The energy density interaction parameter B can be written as:

$$B = B_{lb}\phi_{lb}^2 \qquad (7)$$

where B_{lb} is the corresponding interaction energy density between segments—CH$_2$ units—located respectively at the linear and branched parts of the molecules, and ϕ_{lb} represents the volume fraction of branch segments relative to the whole number of segments forming the chain. The volume fraction ϕ_{lb} can be expressed as:

$$\phi_{lb} = \varepsilon r/(1+\varepsilon r) \approx \varepsilon r \qquad (8)$$

where r is the average number of segments of each branch (in our case $r \approx 4$–5). For low ε values, i.e. $\varepsilon r \ll 1$, $\phi_{lb} \approx \varepsilon r$. On the other hand the actual volumes of the components are given by $V_2 = N_2 x_2 v_u$ and $V_1 = N_1 x_1(1+\varepsilon r)v_u$, N_i being the number of molecules of polymer i. From equation (6) we can easily derive the enthalpic contribution to the free energy of mixing:

$$\Delta\mu_H = N_A\,\partial\Delta H_m/\partial(N_2 x_2) = RT\gamma\varepsilon^2\phi_1^2 \qquad (9)$$

where $\gamma = r^2 B_{lb} v_u/kT$ and $RT\gamma\varepsilon^2$ represent the energy difference per mole of segment of polymer 2 immersed in a pure matrix of polymer 1 and in its own matrix respectively. Similarly one can derive the energy difference $kT\tilde{x}_1\gamma\varepsilon^2$ per molecule of polymer 1 immersed in a pure matrix of linear polymer and in its own matrix, from where it is straightforward to derive an approximate value for the energy difference per mole of branches

$$\Delta E_{\text{branch}} = RT\gamma\varepsilon \qquad (10)$$

Free energy of mixing: outcomes of the model

Taking $x_h \simeq 1$ and neglecting the terms associated with long chains one can write a simplified expression for the free energy of mixing per mole of segments:

$$\Delta\mu_2 = -RT(\alpha\varepsilon\phi_1 - \beta\alpha\varepsilon\phi_1\phi_2 - \gamma\varepsilon^2\phi_1^2) \qquad (11)$$

which for the limit case of $\beta = 1$ takes the following very simple form:

$$\Delta\mu_2 = -RT(\alpha - \gamma\varepsilon)\varepsilon\phi_1^2 \qquad (12)$$

The criterion for phase separation to occur is given in this case either by the condition $\Delta\mu_2 > 0$ or by $\partial\Delta\mu_2/\partial\phi_1 > 0$. Compatibility is assured for all compositions below a critical branching content, i.e. if $\varepsilon < \varepsilon_c$, with $\varepsilon_c = \alpha/\gamma$. The stability condition $\partial\Delta\mu_2/\partial\phi_1 > 0$ applied to the counter limit case, i.e. $\beta = 0$, yields a stability boundary and a critical branch content $\varepsilon_c = \alpha/2\gamma\phi_1$, which lowers with composition at a given temperature. The real situation is expected to be between both extreme cases.

The chosen value $\gamma \simeq 100$ is in agreement with previous melting-point depression experiments[1], which show in a systematic and reproducible way the tendency of the free energy of mixing of this system to become zero or negligible for $\varepsilon > 0.02$, i.e. the critical branch content value to be around 2%. Such γ value yields $\Delta E_{\text{branch}} \simeq 600$ cal mol^{-1}, which is rather reasonable if one keeps in mind that the energy difference between the minimum *trans* overall potential energy of polyethylene and the position of the second minimum (*gauche*) is ~495 cal mol^{-1}. As a matter of fact it is known[11] that in PE the cohesive energy difference between the poorest and the best packing is around 300 cal mol^{-1} and hence it is reasonable to expect our interaction energy per branch to be somewhat higher but of the same order. Moreover the estimated value $\gamma \simeq 100$ is in accordance with the orders of magnitude and range of values obtained from solubility measurements[12] for the Flory interaction parameter.

Several factors modulate the critical branch content: branch size and temperature among others. Branch size was shown in the last section to be involved in the expression for γ, implying that the higher the size of branches the higher is the γ parameter and hence the lower is the critical branching content ε_c. In order to consider the influence of temperature one should know the variation of both parameters α and γ with temperature. As a rough approximation one can assume the former to increase linearly with temperature whereas the latter can be supposed to change with $(1/RT)$ as in the primitive lattice models. A critical temperature would hence be derived below which segregation occurs at a given branching content. Under this crude approximation increasing temperature always favours mixing.

MODEL PREDICTIONS: COMPARISON WITH SOME EXPERIMENTAL RESULTS

Melting-point depression

It is well known that melting-point depression measurements yield a direct estimation of the free energy of mixing around the melting temperature:

$$\Delta H_u\{[T_m^0 - T_m^0(\phi)]/T_m^0\} = -\Delta\mu_2 \qquad (13)$$

where ΔH_u is the heat of fusion per structural unit, $T_m^0(\phi)$ is the melting temperature of the crystal in the counter matrix and T_m^0 is the melting temperature of the crystal in the pure matrix. The determination of the T_m^0 values is ordinarily carried out on melt-crystallized blends. In the present case, besides melting shifts due to lamellar thickness, PE crystals might incorporate in them a certain amount of branched molecules. An alternative method was used[1], i.e. single HDPE crystals embedded in a LDPE matrix, avoiding the above-mentioned effects.

Rather low melting-point depressions are predicted from equation (13) for the systems under consideration. However depressions around 1°C are expected and confirmed by our previous experiments[1]. Accepting the rough values $\alpha = 2$ and $\gamma = 100$, one can derive the expected melting-point depression data for these two cases. Experimental results are compared with model predictions in *Table 1*.

Table 1 Experimental and predicted $[1/T_m^0 - 1/T_m^0(\phi)] \times 10^6$ (K^{-1}) values for various mixtures of HDPE single crystals and LDPE material of branching ε

ε	ϕ_1	Experimental	Predicted
0.007	0.25	3.6	1.1
	0.50	6.6	4.6
	0.75	9.0	10.2
0.0121	0.25	2.4	1.2
	0.50	4.8	4.8
	0.75	7.2	10.7
0.0176	0.25	1.6	0.5
	0.50	2.4	2.1
	0.75	3.6	4.7

CONCLUDING REMARKS

The phase-separation problem in HDPE/LDPE systems has been treated on the basis of simple thermodynamic mixing concepts of lattice theory. Volume changes have been simulated by the presence of holes, which play the role of a third component. The main outcomes of the work can be summed up in several points:

(i) Despite the dispersive character of the interaction between components, miscibility is expected owing to the supplementary configurational entropy associated with the holes (free volume) brought by the LDPE component (such holes are accessible to linear chain segments but not to the LDPE chains).

(ii) For a given temperature a critical degree of branching is predicted above which phase separation takes place because of the enhancement of the dispersive interaction, which varies with the square of branching content, as compared with the entropy associated with the presence of holes, which varies linearly with branching content.

(iii) The model explains satisfactorily the melting-point depression tendency of HDPE single crystals embedded in LDPE matrices and supports the idea of phase separation for $\varepsilon \geqslant 2\%$ around 400 K.

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