

The effect of mixing on the properties of polyethylene blends

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A linear low-density polyethylene (LLDPE) with hexyl branches has been blended with high-density polyethylene (HDPE) and a comparison has been made of the effects of three methods of blending on the quality of the blends produced. A twin-screw extruder, roll mills and solution precipitation have been compared for their effectiveness in producing a uniform blend. Compositional variations have been measured by Fourier-transform infra-red spectroscopy, crystallization and melting characteristics have been studied using differential scanning calorimetry, and the morphology has been examined by wide-angle X-ray scattering and scanning electron microscopy. In general, it is concluded that in the melt the two grades of PE are compatible and co-crystallize on quenching. The most uniform product is produced by the twin-screw extruder, since the blends have higher melting points, crystallinity, yield stress and elongation at break. The solution-blended product crystallizes at a lower temperature than the others, consistent with a reduction in heterogeneous nucleation.

(Keywords: linear low-density polyethylene; high-density polyethylene; hexyl branches; blends; differential scanning calorimetry; wide-angle X-ray scattering)

INTRODUCTION

In recent years there has been considerable interest in the development of polymer blends derived from large-volume commodity plastics. More than 60% of linear low-density polyethylenes (LLDPE), for example, have been blended with other polyolefins: polypropylene (PP), polyethylene (PE) and copolymers such as ethylene-vinyl acetate (EVA)¹. It has been well demonstrated that a number of physical properties and the processability of polyolefins can be improved by blending.

The methods usually employed in the large-scale production of blends are those of mechanical shearing on either heated roller mills or extruders. Solution mixing is invariably limited to laboratory scale, where there is some limitation on volume of materials available. The presence of a solvent, however, can alter the morphology of the blends, as a three-component system is present during phase development, and the solvent can act as a compatibilizer during precipitation².

In this paper a comparative study has been made of the effect of mixing method on the crystallization and melting behaviour, morphology and mechanical properties of LLDPE blends with high-density polyethylene (HDPE). The blending methods used were heated roll mill, twin-screw extruder and solution blending.

EXPERIMENTAL

The characteristics of the polyethylene samples used are listed in *Table 1*. Molar-mass averages were determined by gel permeation chromatography, using a Waters 150C GPC operating at 135°C with *o*-dichlorobenzene

as the mobile phase. The amount of short-chain branching in LLDPE samples was determined by ¹³C n.m.r. spectroscopy, using a Bruker WH400 ¹³C n.m.r. spectrometer and the experimental conditions outlined previously³. Peak assignments were those suggested by Randall⁴. Melt index and density were measured adopting standard procedures for polyethylene.

Blends of various compositions were prepared from solution and melt mixing. One per cent solutions of LLDPE and HDPE in xylene using 1% 2,6-di-*t*-butyl-4-methylphenol as an oxygen inhibitor were made by dissolution at 130°C for 30 min and mixed in appropriate volumes. The solutions were precipitated into methanol, filtered and the blends washed with acetone. The polymer blends were dried *in vacuo* at 50°C for 48 h. Milling was carried out on a Schwabenthan roll mill at 140°C for 15 min with a roller velocity ratio of 1.2:1 to encourage shear mixing. The film of polymer melt was confined to a narrow band in the middle of the rollers. This band was cut diagonally and folded over repeatedly to encourage mixing. Circumferential cuts were also pushed into the nip at a skew angle. An APV 2000 twin-screw compounder was also used with a high shear setting. All zones of the compounder, die, die head and barrel zones were set to 200°C. Melting and crystallization rate studies were made on a Perkin-Elmer differential scanning calorimeter, DSC-2, interfaced to a BBC Master computer. The temperature scale of the calorimeter was calibrated from the melting points of indium, tin and zone-refined stearic acid, and the thermal response from the enthalpy of fusion of indium. Corrections were made for thermal lag, as described elsewhere⁵.

A JEOL model J5200 scanning electron microscope was used to examine blend morphology. Blends were

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Table 1 Polymer characteristics

Type	M_n (kg mol^{-1})	M_w (kg mol^{-1})	Branch		Density (kg m^{-3})	Melt index (dg min^{-1})
			Type	Conc. $\text{CH}_3/1000$		
HDPE	26	160	—	—	965	6.44
LLDPE	17	210	Hexyl	14.0	920	1.15

fractured at liquid-nitrogen temperature and etched with permanganic acid⁶.

A Mattson Polaris FTi.r. spectrometer was used, interfaced to an IBM-PC computer. A minimum of 50 scans were signal averaged at a resolution of 1 cm^{-1} .

Wide-angle X-ray scattering was measured with a Picker automated powder diffractometer. Data collection was controlled with a Phillips PW1710 diffractometer control unit, and this in turn was controlled remotely by a Brother PCAT microcomputer. The data were transferred to an IBM 4340 mainframe computer for further analysis. The blends were moulded into $45 \times 25 \times 3 \text{ mm}^3$ flat plates and directly mounted into the diffractometer without a sample holder. The diffractometer was calibrated using a sample coated with a thin layer, 0.01 mm thick, of $\text{Pd}(\text{NO}_3)_2$ powder. The powder was removed and the sample rescanned without repositioning. Sample transparency corrections were made, as suggested by Langford *et al.*⁷.

Dumbbell-shaped specimens were cut from moulded sheets and tensile properties measured on an Instron testing machine, model TM-BM, at 20°C . The gauge length was 21 mm and width 4 mm. An average of five specimens were taken in reporting the yield stress and elongation at break.

RESULTS AND DISCUSSION

Initial considerations

Before studies were made on the blends, compositional variations between the mixing techniques were measured by FTi.r. spectroscopy. The ratio of absorbance at 1378 cm^{-1} to that at 1368 cm^{-1} was used as a measure of the methyl group content and so of the LLDPE content. The peak at 1378 cm^{-1} is attributed to a symmetrical deformation of the methyl group and that at 1368 cm^{-1} to the wagging of the methylene groups⁸. The latter acted as an internal standard. The ratio decreased with HDPE content and was linear between the two limits. Blends produced by all three methods, roll mill (RMM), twin-screw extruder (TSEM) and solution precipitation (SM), had very similar compositions (see *Figure 1*), implying that each was equally effective and there was no systematic loss of material in any mixing method.

All the blends produced by the various methods of mixing were considered to be equivalent as far as overall composition was concerned.

Co-crystallization

The similarity in chain structure between HDPE, LLDPE and LDPE implies the possibility not only of compatible mixtures but also of their co-crystallization. However, the evidence is that blends of LLDPE and

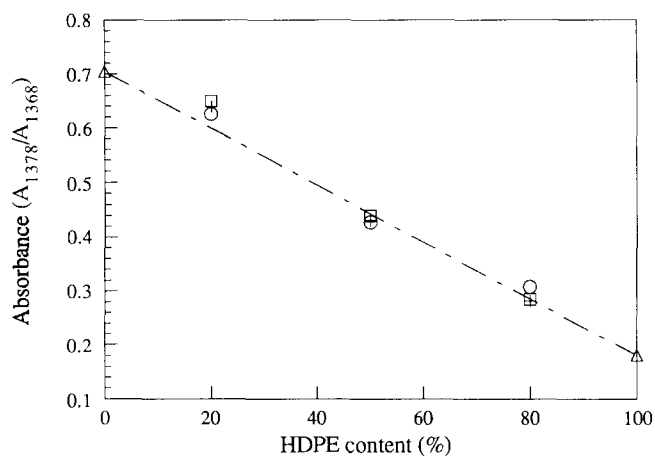


Figure 1 Absorbance ratio against blend composition: (+) TSEM, (O) RMM and (□) SM blends

LDPE are incompatible⁹ and two different crystal structures, identified as 'LLDPE' and 'LDPE' structures, exist in the crystalline phase, with different crystallization kinetic characteristics and melting behaviour.

The compatibility of LLDPE and HDPE has been the subject of considerable debate, in that several authors^{10,11} have concluded that they are incompatible while others, on the basis of WAXS, Raman spectroscopy and thermal analysis, have concluded that they are compatible¹², in exhibiting a single melting point (m.p.) and the same WAXS pattern. *Figure 2* exhibits the cooling and melting d.s.c. thermograms of a 50:50 blend and also of the LLDPE and HDPE samples. Only single crystallization and melting peaks were observed for the blends, irrespective of the experimental conditions adopted, although the LLDPE exhibited three melting peaks. The melting range and the crystallinity that developed in the 50:50 blend were intermediate between HDPE and LLDPE, and there was some melting in the lower m.p. range of LLDPE consistent with proportion present. There is clearly considerable superposition of the two melting exotherms of the components in the blends. The crystal structures of the blends were investigated by WAXS to determine if any co-crystallization had occurred. All the PE crystallized samples were orthorhombic (see *Table 2*), but the unit-cell volume decreased linearly with LLDPE content (see *Figure 3a*) and as fewer hexyl groups were incorporated into the unit cell. There was no broadening of the WAXS lines, as measured by the half-widths of the diffraction lines (see *Figure 3b*), consistent with both LLDPE and HDPE crystals coexisting together in proportion to their composition. Instead, the half-widths increased continuously with branch content, and co-crystallization of HDPE and LLDPE must have taken place to produce

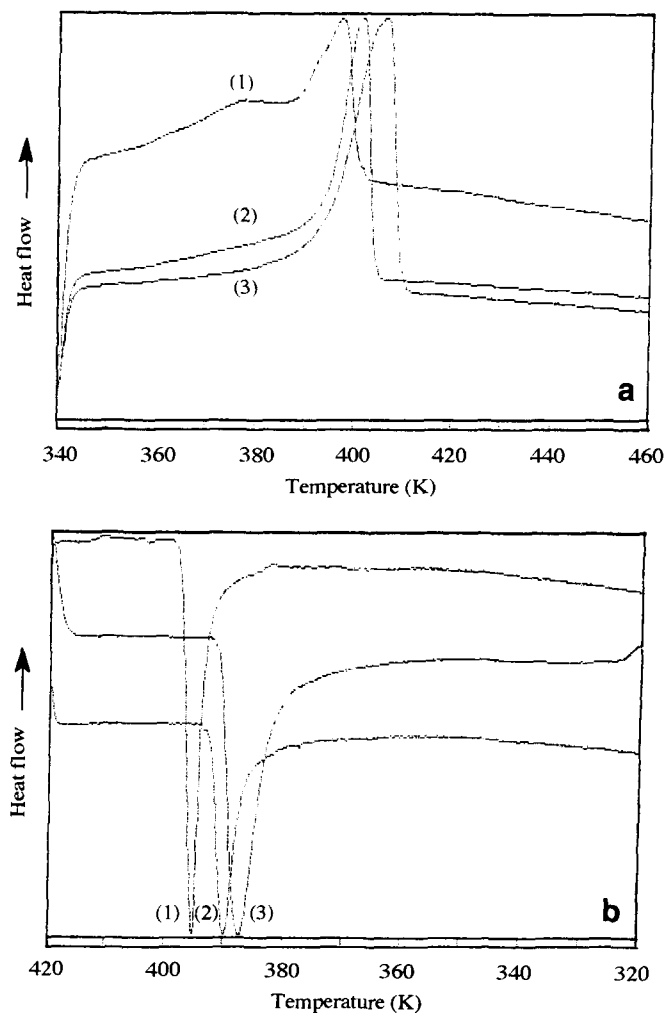


Figure 2 D.s.c. thermograms of (1) LLDPE, (2) 50:50 blend and (3) HDPE: (a) melting at 10 K min⁻¹; (b) crystallization of 50:50 blend on cooling at (1) 2.5, (2) 5.0 and (3) 10.0 K min⁻¹

Table 2 Comparison of observed 2θ values with calculated values assuming an orthorhombic unit cell

Plane index	Observed (deg)	Calculated (deg)
110	21.588	21.541
200	23.942	23.983
120	38.260	38.246
011	39.874	39.818
310	40.828	40.757
111	41.746	41.712
201	43.100	43.113
211	47.002	47.020
400	49.091	49.105
121	53.004	53.008
311	54.982	54.982
221	57.486	57.534

'mixed' crystals containing both HDPE and LLDPE. The unit-cell dimensions along the *a*, *b* and *c* axes all exhibited similar trends with composition, the *c* axis, i.e. the chain direction, decreasing less than the others (see Figure 3).

The overall crystallization kinetics

Isothermal crystallization kinetics of the blends were measured by d.s.c. as outlined before¹³. It was assumed that the extent of crystallinity, *X_t*, could be evaluated by

integrating the exotherm from the start to time *t*, i.e.

$$X_t = \int_0^t (dH/dt) dt / \int_0^\infty (dH/dt) dt \quad (1)$$

The development of crystallinity with *t* was then analysed with the Avrami equation:

$$-\ln(1 - X_t) = Zt^n \quad (2)$$

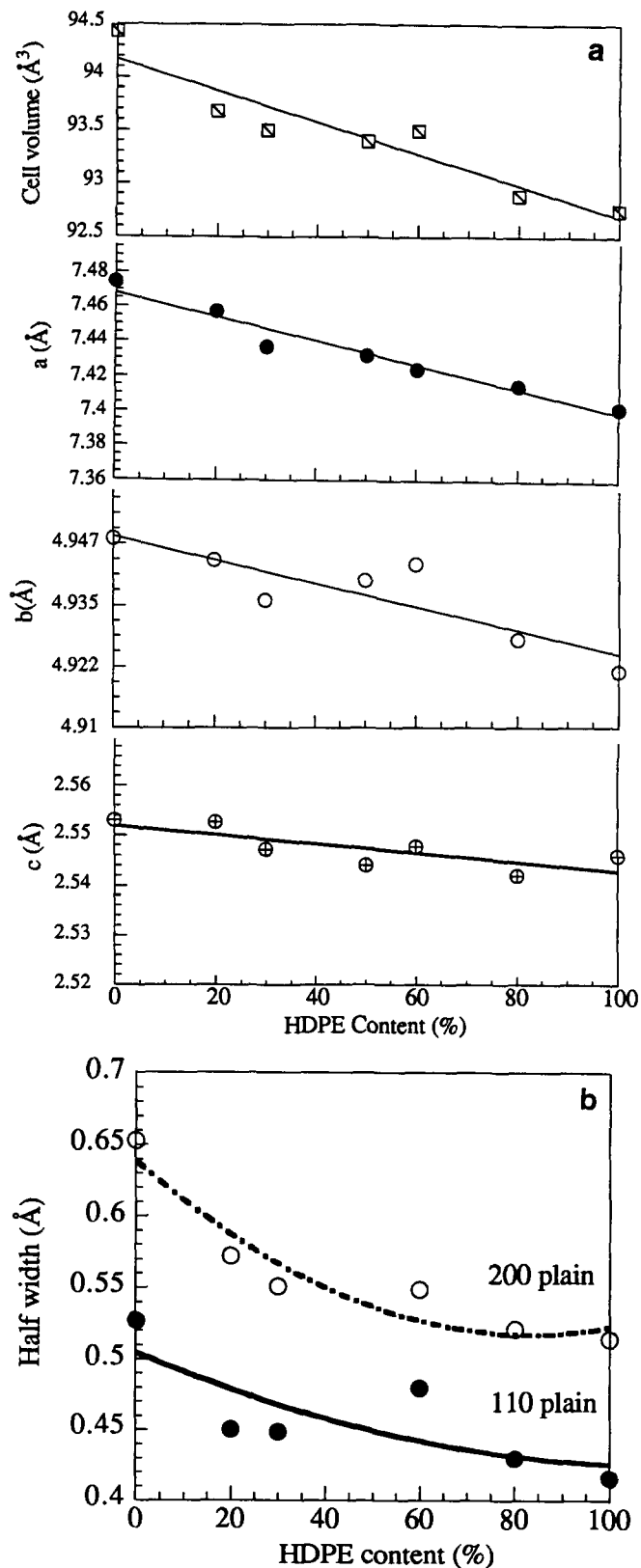


Figure 3 The variation of cell parameters with blend content: (a) the *a*, *b* and *c* axes of the unit cell and cell volume; (b) the half-widths of 200 and 110 absorption bands

Table 3 Crystallization rate parameters

(a) 50:50 blends

Type	Crystallization temperature (K)	<i>n</i> value	$\ln[Z \text{ (min}^{-n}\text{)}]$	$t_{1/2}$ (min)
SM	391.9	2.6 ± 0.1	1.73	1.68
	392.9	2.7	2.99	2.61
	393.9	3.1	5.45	5.00
	394.9	2.9	7.12	10.59
	395.9	2.7	9.33	24.58
	396.9	2.5	10.71	59.13
	397.9	2.5	13.18	160.7
RMM	393.9	2.8 ± 0.1	2.09	2.43
	394.9	2.9	2.47	4.71
	395.9	2.9	2.57	10.52
	396.9	2.6	3.89	23.73
	397.4	3.1	10.38	60.61
	397.9	3.1	13.63	75.39
TSEM	393.9	2.4	1.68	1.71
	394.9	2.9	3.51	2.96
	395.9	2.4	4.86	6.31
	396.9	2.4	6.49	12.63
	397.9	2.5	10.83	66.36
	398.9	2.3	11.76	142.70

(b) Effect of blend composition

HDPE:LLDPE	T_c (K)	$t_{1/2}$ (min)
10:90	394.9	58.8
20:80	394.9	28.6
30:70	394.9	12.5
90:10	394.9	1.3

in which Z is a composite rate constant incorporating nucleation and growth rate and n is a constant that depends on the crystallization mechanism. The procedure adopted by Banks *et al.*¹⁴ of separating the primary from the secondary crystallization processes was adopted and n determined from:

$$n = -t(dX'/dt)/[(1-X') \ln(1-X')] \quad (3)$$

where X' refers to the primary process. Z is determined from the half-life of the primary process, $t_{1/2}$:

$$Z = \ln(2)/t_{1/2}^n \quad (4)$$

Values of the exponent, half-life and Z parameter are listed for the 50:50 blends produced by the three mixing methods in Table 3. In all cases the n values were between 2.5 and 3.1, which is consistent with spherulitic crystallization from athermal nuclei, $n=3.0$, but the n value is lower owing to the presence of non-crystallizable groups, such as branches etc. From the half-lives (see Figure 4) it is apparent that the twin-screw blended material has the highest crystallization rate at each crystallization temperature, although the difference between the twin-screw and roll-mill mixed samples is not marked. The solution mixed material, however, crystallizes about 2°C lower than the twin-screw extruded material. This difference could arise from either a reduction in heterogeneous nucleation, as a result of dissolution and filtration, or molecular weight fractionation during precipitation.

Within each series of blends, and at the same temperature, the isothermal crystallization rates varied with blend composition, decreasing with increasing

LLDPE. The half-lives change by over an order of magnitude on going from a blend of 90% of one component to 90% of another (see Table 3b). Accordingly, there could be some separation of the highly branched LLDPE fractions, and co-crystallization of HDPE with less-branched material. This will be addressed in a later publication.

The melting behaviour of the blends

The overall crystallinity of the blends, crystallized under identical conditions, was determined from the heat of fusion of polyethylene, and assuming 293 J g⁻¹ for the totally crystalline material. Mixing had no effect on the degree of crystallinity, which increased progressively with HDPE content (see Figure 5). However, the m.p. as defined by the disappearance of the last trace of crystallinity did change with the method of mixing (see Figure 6). In these melting studies the samples were cooled slowly at 10 K min⁻¹ and allowed to crystallize under non-isothermal conditions. This m.p. dependence reflected crystallization conditions. Samples crystallized under isothermal conditions exhibited a similar trend, in that the twin-screw mixed material had higher melting points. In all cases the m.p. exhibited a linear

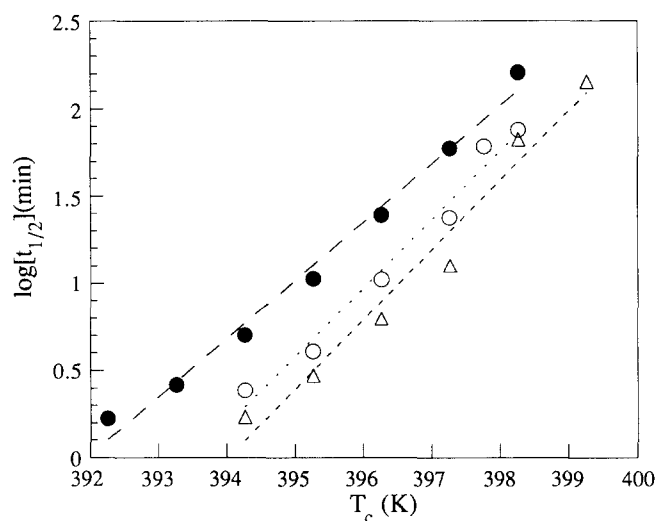


Figure 4 The variation of the half-life of 50:50 blend with crystallization temperature: (Δ) TSEM, (○) RMM and (●) SM blends

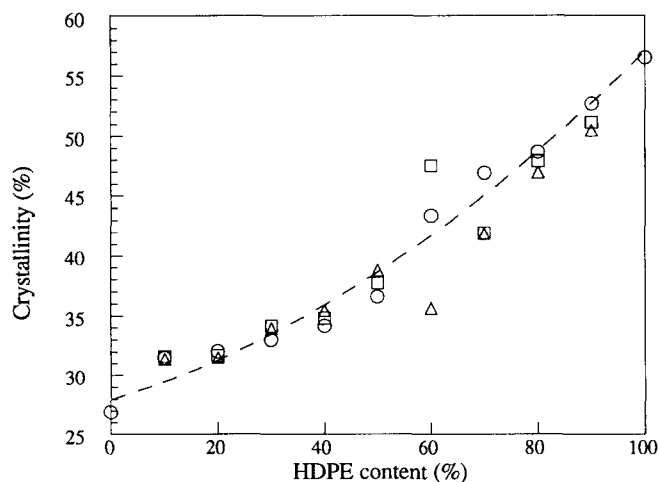


Figure 5 The variation of crystallinity with composition: (○) TSEM, (Δ) RMM and (□) SM blends

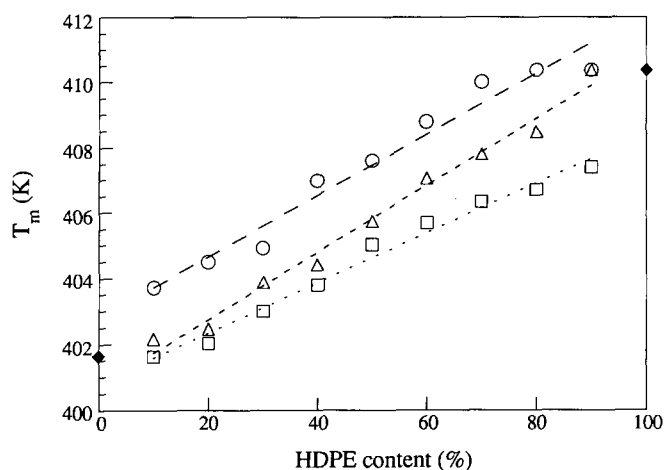


Figure 6 The variation of the observed melting point of the blends with composition: (○) TSEM, (△) RMM and (□) SM blends

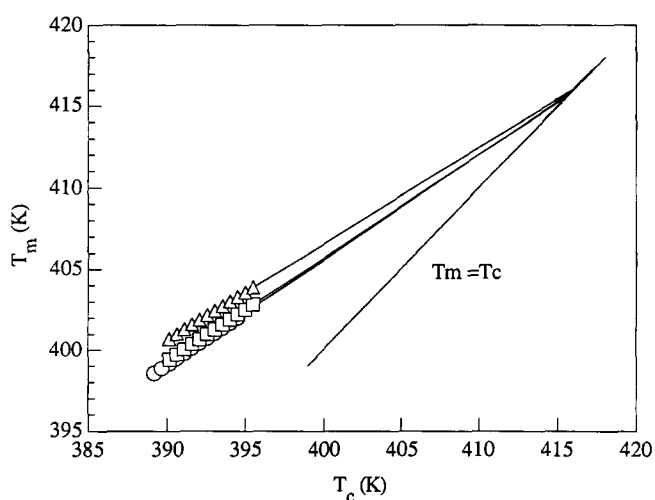


Figure 7 Hoffman-Weeks plots for the 50:50 blend: (△) TSEM, (□) RMM and (○) SM blends

dependence on crystallization temperature, following the Hoffman-Weeks relationship¹⁵:

$$T_m = T_m^{\circ}(1 - 2/\beta) + (1/2\beta)T_c \quad (5)$$

with $\beta = \sigma_e l / \sigma_e l_e$ where σ and σ_e are the lateral surface free energies, l and l_e the lamellae thicknesses for the crystallization, and subscript 'e' refers to the equilibrium values. Accordingly, under equilibrium conditions the plot of T_m against T_c will be linear with slope of 0.5 (see Figure 7). Extrapolation of the plot to the line $T_m = T_c$ enabled the equilibrium m.p., T_m° , to be determined. These are listed in Table 4. All the β values were close to the equilibrium value, i.e. $\beta = 1.0$, and the equilibrium m.p. values were similar within experimental error, at 416 ± 1.0 K, and comparable with those determined by others, 416 K¹⁶ and 416 ± 1 K¹⁷.

Figure 4 shows a plot of the half-life against crystallization temperature for the various blends, and it can be seen that the TSEM material always exhibited the fastest crystallization rates. The blends have virtually identical equilibrium melting temperatures, and so crystallization occurs over the same degree of supercooling, $T_m^{\circ} - T_c$. The temperature dependence of the half-lives for crystallization were analysed by the Turnbull and Fisher equation¹⁸, assuming the same temperature dependence

for nucleation and growth:

$$A - \ln(t_{1/2}) = 4\sigma\sigma_e(T_m^{\circ})^a / R\Delta H(\Delta T)^a T_c \quad (6)$$

where A is a constant, σ and σ_e are the lateral and fold surface energies, ΔH is the heat of fusion, and a is a constant such that $a = 1$ or 2 for primary or secondary nucleation. Plots of $\ln(t_{1/2})$ against the r.h.s. of equation (6) with $a = 1$ and 2 were linear with the same least-squares correlation coefficient, 0.99 (see Figure 8). It was not possible to distinguish between either type of nucleation, and within experimental error there was no significant difference in the σ_e values determined (see Table 4). The data for the TSEM and RMM blends appeared to be identical within experimental error, and only the SM blends were significantly different, the difference clearly being in the value of the constant A .

Table 4 The influence of mixing on melting behaviour

Mixing method	T_m° (K)	β	σ_e (kJ mol ⁻¹)
TSEM	416.0 ± 1.0	0.91	25.0 ± 2.0
RMM	415.6 ± 1.0	0.79	25.9
SM	415.8 ± 1.0	0.77	26.7

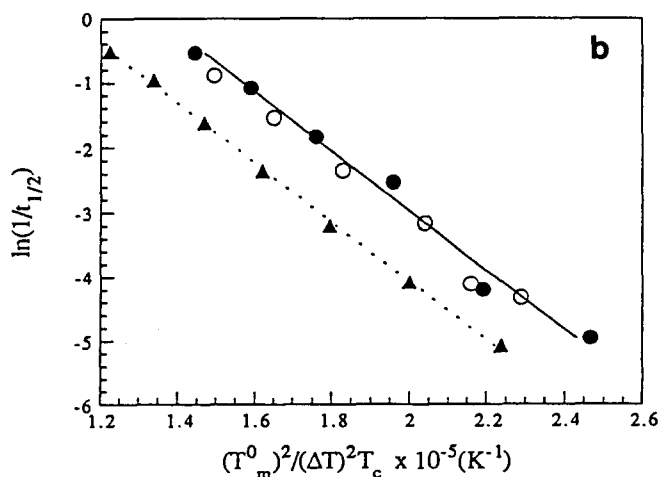
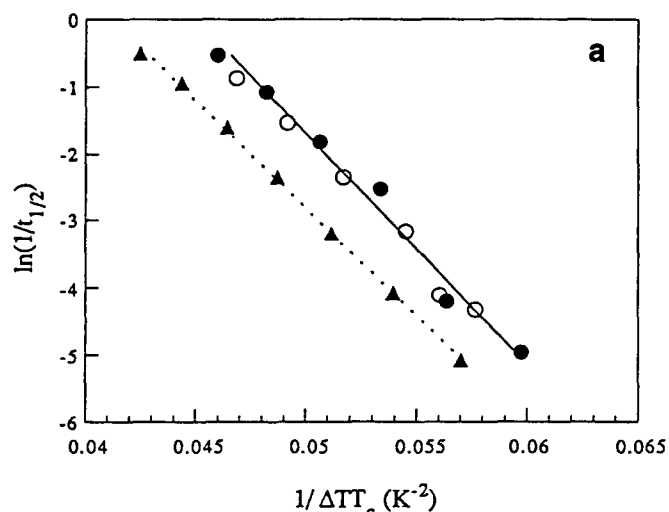


Figure 8 The temperature dependence of the crystallization half-lives of the 50:50 blends for (a) $a = 1$ and (b) $a = 2$: (▲) TSEM, (○) RMM and (●) SM blends

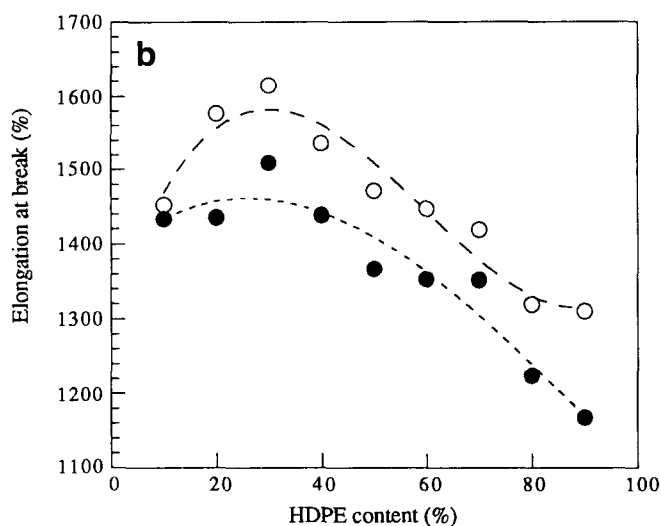
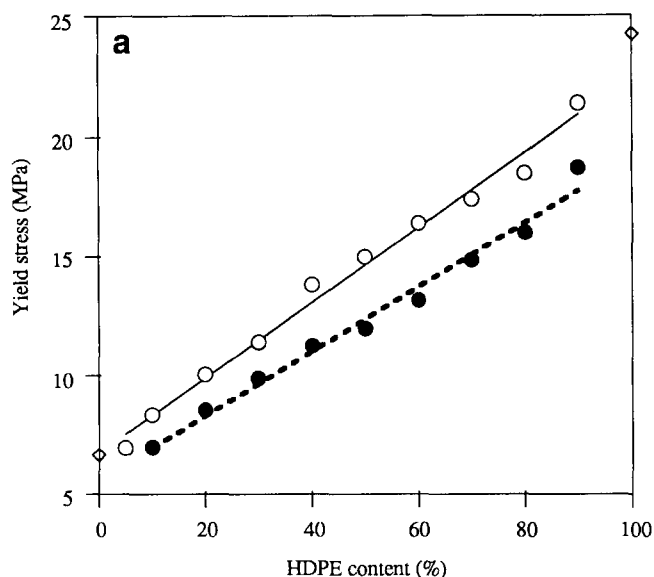


Figure 9 The variation of tensile properties with composition, showing (a) yield stress and (b) elongation at break, for strain rate 0.038 s^{-1} ; (○) TSEM and (●) RMM blends

In the bulk crystallization the n values are close to 3.0 for spherulitic growth and in PE nucleation is normally observed to be heterogeneous¹⁹. The A parameter is considered to incorporate a term for primary nucleation. It would appear that the difference in crystallization rate reflects differences in nucleation density between the blends, solution mixing and filtering removing active nuclei.

Mechanical properties

The effect of composition on the yield stress and elongation at break of the TSEM and RMM blends were examined (see Figure 9) in tension. The TSEM blends exhibited the higher yield stresses and elongation at break. According to Paul and Robertson²⁰ the yield stress is more sensitive to blend morphology than is the tensile modulus owing to interfacial interactions. However, the yield stress of both of the blends, irrespective of method of preparation, exhibited the same linear increase with degree of crystallinity (see Figure 10). This has also been observed²¹ with polyethylene grades with densities in the range $910\text{--}990 \text{ kg m}^{-3}$. Molar mass and structural abnormalities had no marked effect on yield. Blend

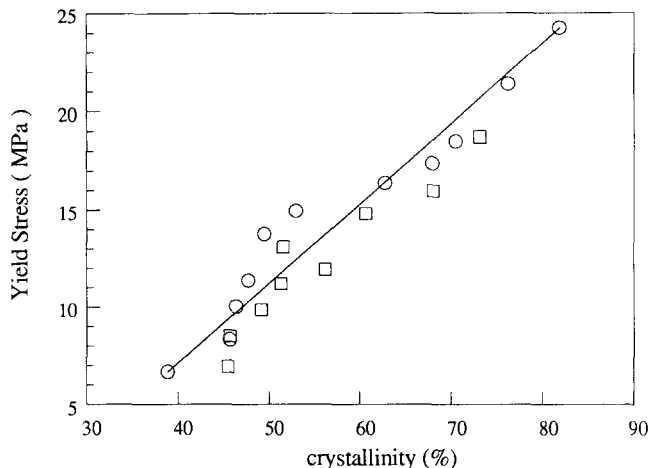


Figure 10 The variation of yield stress with sample crystallinity: (○) TSEM and (□) RMM blends

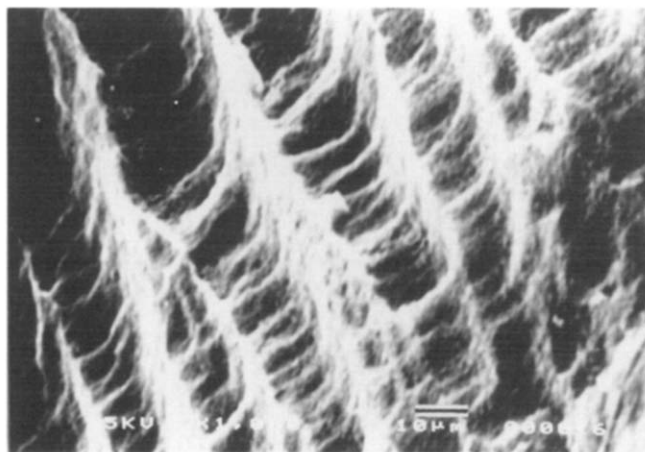


Figure 11 Stereoscan electron micrograph of fracture surface of 50:50 composition for the TSEM blend (scale bar = $10 \mu\text{m}$)

samples with the same crystallinity have the same yield stress, irrespective of method of production. It must be concluded from this that the blend systems are analogous to polyethylene homopolymers and are homogeneous in composition, although two-phase, being partially crystalline.

Scanning electron micrographs were taken of fracture surfaces that had been etched with permanganic acid to remove amorphous content (see Figure 11). No texture of the order of $1\text{--}10 \mu\text{m}$ could be detected in the TSEM blends, inconsistent with bulk phase separation of the LLDPE and HDPE.

CONCLUSION

Evidence is given that on mixing LLDPE with HDPE with a twin-screw extruder the two polymers are compatible. Mixing either with a roll mill or using a solvent does not appear to be so effective, and the products exhibit lower crystallinity, melting points, yield stress and elongation at break. The increased crystallization rates associated with the TSEM blends are attributed to a greater nucleation density in these specimens.

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