

A STUDY OF CRYSTALLISATION BEHAVIOUR AND COMPATIBILITY OF HIGH-DENSITY POLYETHYLENE / LINEAR LOW-DENSITY POLYETHYLENE BLENDS *

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ABSTRACT

Blends of high-density polyethylene (HDPE) with a linear low-density polyethylene (LLDPE) (ethylene-but-1-ene copolymer) at various compositions were examined by optical microscopy and differential scanning calorimetry in order to study their crystallisation processes and compatibility. The thermal behaviour of blend samples cooled from the melt under various conditions pointed to the presence of co-crystallisation phenomena. Microscopic observations of blend films isothermally crystallised from melt did not reveal any phase segregation of LLDPE in the spherulitic regions of HDPE. Analysis of the isothermal crystallisation kinetics (in the range 392–400 K) indicated that the crystallisation rate of HDPE is largely depressed in the blends, suggesting that the nucleation and growth rate of the crystals are affected by the presence of melted LLDPE. The melting behaviour of isothermally crystallised samples can be mainly attributed to morphological effects relevant to crystal size and perfection. No depression of the equilibrium melting temperature of HDPE was observed in the blends.

INTRODUCTION

The crystallisation processes of polymer blends with crystallisable components can be greatly affected by the molecular characteristics of such components, the type of intermolecular interactions, and the composition and thermal history of the system. In many cases, the nucleation and growth rates of polymer crystals in the blends prove to be considerably different

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from those of the single components. In addition, there may be variations in the overall morphology, the degree of crystallinity, and the thermal and mechanical properties [1,2]. The study of the crystallisation behaviour of these systems is thus of general interest as a subject for academic research, and with a view to technological applications.

Our investigation of the relationships between structure and properties of polymer blends, based on commercial polyolefins [3] and polyolefins functionalised with polar groups in the side chain [4,5], began a few years ago. Polyolefin blends are materials with very wide applications owing to their peculiar properties and high performance. In particular, blends based on different types of polyethylene have been the subject of several studies and patents [6].

It has been reported that high-density polyethylene (HDPE) and low-density polyethylene (LDPE), on cooling from the melt blends, give rise to distinct crystalline phases [7–9]. In contrast, for blends of HDPE and linear low-density polyethylenes (LLDPE), a single crystal phase has been observed at all compositions and has been interpreted as evidence of polymer compatibility [9–12]. Blends of LDPE and LLDPE, however, display separate crystalline phases [9,13]. Nevertheless, no data concerning the isothermal crystallisation behaviour and the related melting parameters of these blends have been reported.

This paper describes part of a study on the relationships between structure and properties of HDPE/LLDPE blends, and the corresponding functionalised polymers with diethylmaleate. The kinetics of isothermal crystallisation from the melt, the morphology and the melting behaviour of HDPE/LLDPE samples are analysed in order to study the effect of the crystallisation conditions and composition on the structural, kinetic and thermodynamic parameters of the crystal growth, and therefore on the compatibility of the system.

EXPERIMENTAL

Materials

The polyethylene samples used (ENICHEM, Italy) were an HDPE with average molecular weights $\overline{M}_w = 145\,000$ and $\overline{M}_n = 26\,000$ ($\overline{M}_w/\overline{M}_n = 5.5$; M.F.I. = 1.4) and an LLDPE, obtained by high-pressure catalysis, containing about 7 wt.% of but-1-ene as comonomer ($\overline{M}_w \sim 110\,000$; $\overline{M}_w/\overline{M}_n = 6$; M.F.I. = 1.0, density = 0.922 g cm^{-3} ; ~ 3.5 mol% of ethyl branches).

Blends containing 50 wt.% LLDPE (HDPE/LLDPE, 50/50) and 75 wt.% LLDPE (HDPE/LLDPE, 25/75) were prepared by dissolution of the plain polymers in boiling toluene and precipitation with methanol. The precipitate was first washed with fresh methanol and acetone, then dried under vacuum

for several hours at room temperature. Samples of pure HDPE and LLDPE were prepared by solution precipitation in the same conditions.

Microscopic analysis

The morphology and crystallisation behaviour of films of HDPE, LLDPE and blends were analysed with a Reichart optical polarising microscope equipped with a Mettler FP52 hot stage. Small amounts of samples were melted between glass slides at 450 K, then isothermally crystallised into the hot stage in a temperature (T_c) range from 381 to 403 K. Photomicrographs of films were taken at various times both during crystallisation at T_c and after cooling to room temperature. The crystallised films were then reheated under the microscope at 10 K min^{-1} and melting temperatures were recorded on the disappearance of spherulite birefringence.

Further morphological observations of the blends were performed in a Jeol T300 scanning electron microscope using isothermally crystallised samples.

Calorimetric measurements

The thermal behaviour of the crystallised HDPE/LLDPE samples was analysed with a Perkin-Elmer DSC-2C differential scanning calorimeter interfaced with a Data Station 3600 and operating under nitrogen flow. In an initial set of experiments, as-prepared specimens (5–8 mg) were heated in DSC from 310 K to 450 K, then cooled to the starting temperature at various rates ($2.5\text{--}20 \text{ K min}^{-1}$), and reheated at 20 K min^{-1} above the melting region. Temperatures and heats of fusion were determined from the thermogram maxima and areas respectively.

The overall crystallisation kinetics of the samples from the melt were analysed as follows. Weighed specimens were first heated in DSC at 20 K min^{-1} up to 450 K, held for 5 min at this temperature, and then rapidly cooled to a fixed T_c (in the range 381.8–399.8 K) at a nominal rate of -320 K min^{-1} . The heat developed during the isothermal crystallisation was recorded as a function of time and the fraction X_t of the polymer converted at time t was evaluated from the ratio between the crystallisation area at time t and the total area. The starting time of crystallisation ($t = 0$) was taken as the time at which the DSC cell reached thermal equilibrium at T_c . The total crystallisation area was determined by the baseline extrapolated from the isothermal curve after completion of crystallisation. The effect of the melt annealing temperature (and time) on the crystallisation kinetics was also checked.

The melting temperature (T_m) of the isothermally crystallised samples was determined by heating them directly in the DSC from T_c up to 450 K at 20

K min⁻¹. The DSC temperature-scale was calibrated by using standard materials according to the ASTM D3417-83 procedure. Indium was used to calibrate the heats of transitions.

RESULTS AND DISCUSSION

Non-isothermally crystallised samples

Blend and single polymer thermograms obtained on cooling from the melt and on subsequent heating (from RT) are shown in Figs. 1 and 2 respectively.

A sharp crystallisation peak (Fig. 1) was always observed between 390 K (HDPE) and about 373 K (LLDPE). The temperature and intensity of these peaks decrease with decreasing HDPE content in the samples. LLDPE and the 25/75 blend also displayed a broad exothermic shoulder below 380 K. On heating from RT (Fig. 2), a single melting peak was recorded for HDPE, whereas the 25/75 blend and LLDPE displayed broad, shallow peaks at around 380 K and narrow, intense peaks between 390 K (LLDPE) and 409 K (HDPE). The main peak temperature values for both runs are plotted in Fig. 3 as a function of LLDPE wt.% in the blends.

Multiple LLDPE melting patterns have already been ascribed to the existence of two crystal species with different degrees of order and thermal stability [9,10]. For blends with LLDPE > 50 wt.%, multiple melting persists, but the presence of the higher melting peak, at temperatures intermediate between those of HDPE and LLDPE, suggests the occurrence of co-crystal-

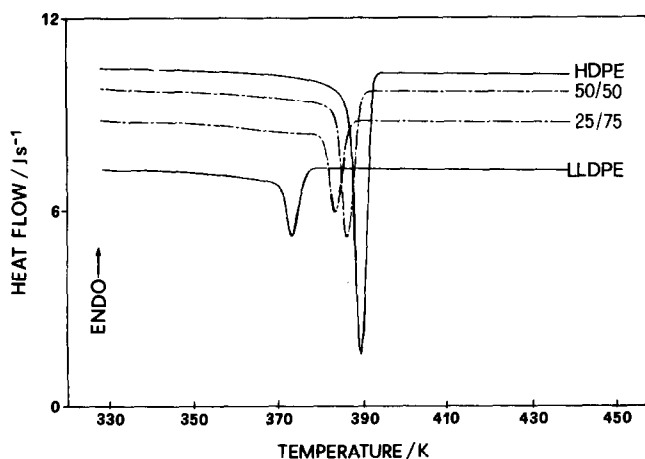


Fig. 1. DSC thermograms of HDPE, LLDPE and HDPE/LLDPE blends on cooling from the melt (450 K) at -10 K min⁻¹.

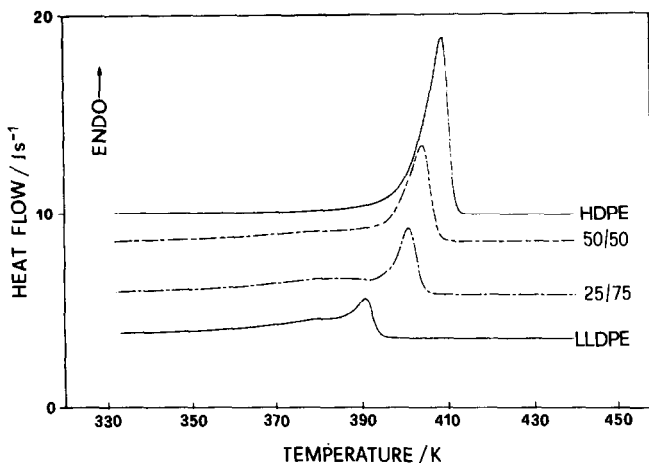


Fig. 2. DSC melting thermograms of HDPE, LLDPE and HDPE/LLDPE blends crystallised from the melt (heating rate, 20 K min^{-1}).

lisation. This should only concern the high-melting crystal form of LLDPE, whereas the low-melting form crystallises separately and gives rise to the broad melting peak at around 380 K.

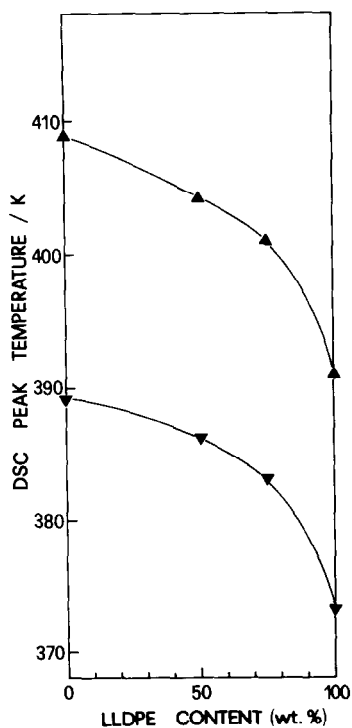


Fig. 3. Crystallisation (▼) and melting (▲) temperatures of HDPE/LLDPE blends as a function of the LLDPE content.

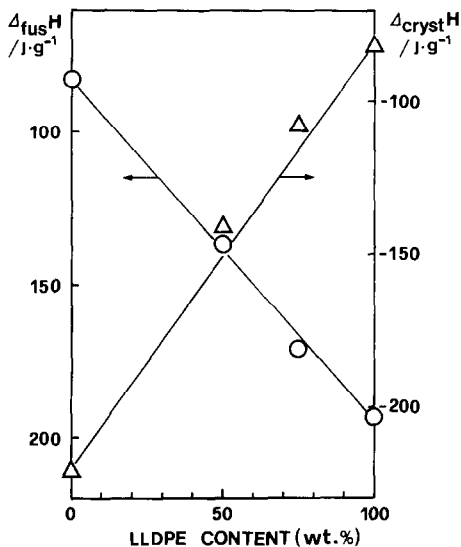


Fig. 4. Variation of the overall enthalpy of fusion $\Delta_{\text{fus}}H$ and enthalpy of crystallisation $\Delta_{\text{cryst}}H$ of HDPE/LLDPE blends with the composition.

Similar findings have been interpreted as evidence of partial compatibility of HDPE and LLDPE [9]. However during the crystallisation of polydispersed polymers, fractionation has been known to occur, depending on several factors such as molecular weight distribution and chemical structure [14].

The occurrence of co-crystallisation in these blends was analysed by Edward [10] who showed by X-ray measurements of lattice parameters that side branches of the LLDPE component could be included to some extent in the crystal lattice of HDPE.

The values of the overall enthalpy of fusion, $\Delta_{\text{fus}}H$, and enthalpy of crystallisation, $\Delta_{\text{cryst}}H$, of HDPE/LLDPE blends are linearly related to the LLDPE concentration (Fig. 4), clearly indicating the additivity of the two polymer contributions, as determined from the DSC thermograms.

Isothermally crystallised samples

Morphological observations

The isothermal crystallisation behaviour of HDPE/LLDPE blends and starting polymers from the melt was examined by both optical microscopy and DSC between 381 and 403 K. Pure LLDPE was crystallised in isothermal conditions at T_c temperatures (381–387 K) lower than those for pure HDPE (394–403 K); in the blends, isothermal crystallisation was observed at $T_c > 390$ K where only the crystallisation of the HDPE component can occur.

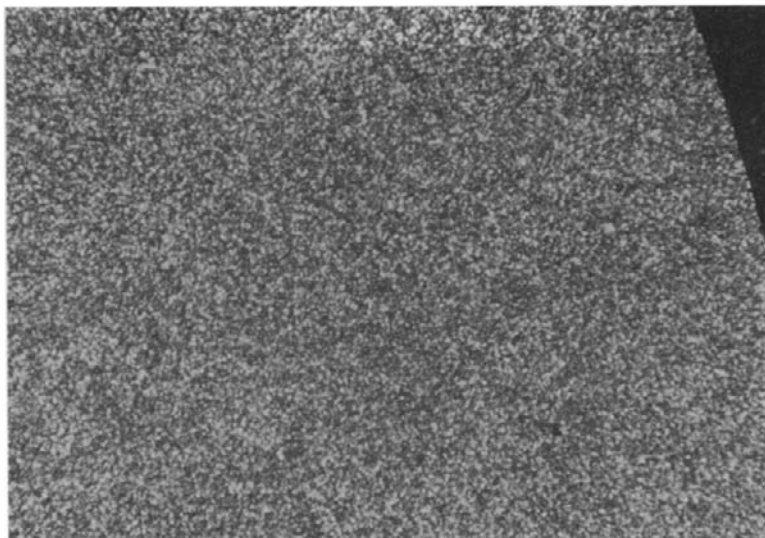


Fig. 5. Optical micrographs of the HDPE/LLDPE, 50/50 blend crystallised at $T_c = 395$ K (crossed polarisers, $130\times$).

Polarising microscopy of HDPE/LLDPE-blend films revealed that the overall morphology of the samples did not significantly change with the composition and melt annealing conditions. Optical micrographs of thin films of the two blends, isothermally crystallised at $T_c = 395$ K, are shown in Figs. 5 and 6, respectively. All samples are composed of small spherulites, a

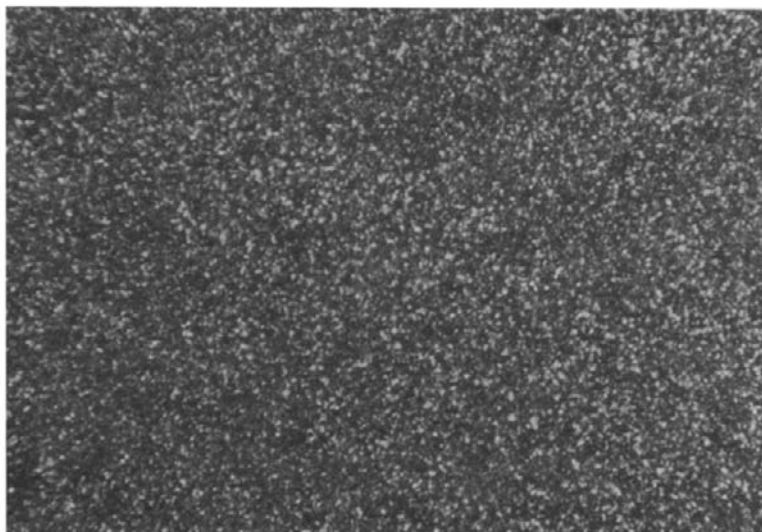


Fig. 6. Optical micrographs of the HDPE/LLDPE, 25/75 blend crystallised at $T_c = 395$ K (crossed polarisers, $130\times$).

few μm large, which do not show any apparent difference in superstructure on varying the composition, as also confirmed by analysis with the scanning electron microscope. Moreover, no macrophase separation between the components was observed at the T_c examined; the blend films appear to be completely filled with HDPE spherulites, even at lower concentrations of the crystallising component. This should mean that at least a fraction of melt LLDPE, which does not crystallise at those T_c , is occluded into the intraspherulitic regions of HDPE, depending on both thermodynamic and kinetic factors [11,12]. Electron microscopy and X-ray diffractometry are currently being used for a closer examination of these features.

Crystallisation kinetics

The DSC thermograms of the two blends for crystallisation from the melt at $T_c = 395.8\text{ K}$, are shown against the crystallisation time in Fig. 7. The overall transformation process is drastically slowed down as the content of the crystallisable component decreases. Plots of the crystallinity fraction X_t , determined from the areas of the isothermal DSC curves, are shown in Fig. 8 as a function of log time, for various T_c in the range 392.8–398.8 K. When the LLDPE content increases, the crystallisation isotherms are shifted parallel to each other to higher crystallisation times; a difference of more than one order of magnitude has been observed for the HDPE/LLDPE 25/75 blend compared with pure HDPE at the same temperature. This trend is more clearly indicated in Fig. 9, where crystallisation half-time values, $t_{0.5}$ (determined from Fig. 7) are plotted as a function of T_c . It will be seen that $t_{0.5}$ always increases exponentially with T_c . Below 395.8 K, isothermal crystallisation of HDPE may only be observed in the blends, owing to the rapid decrease of the crystallisation rate when the LLDPE concentration

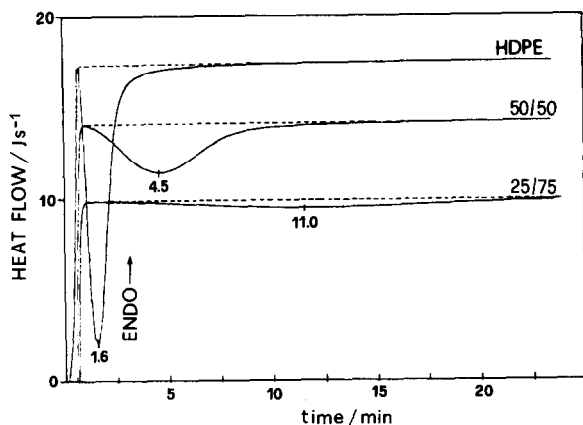


Fig. 7. DSC thermograms of isothermal crystallisation of HDPE and HDPE/LLDPE blends at $T_c = 395.8\text{ K}$.

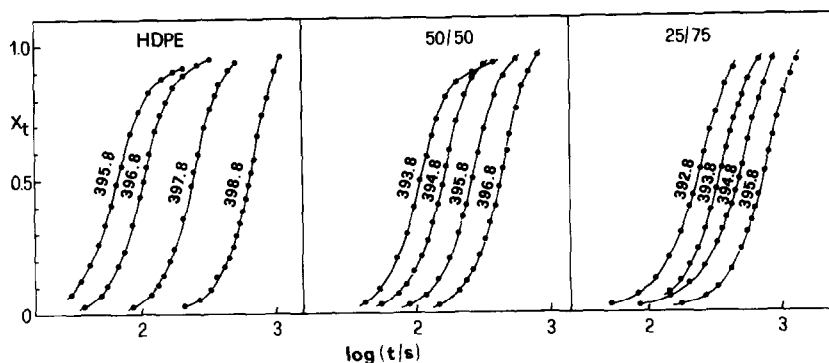


Fig. 8. Isotherms of crystallisation from melt, at various T_c , for HDPE and HDPE/LLDPE blends. X_t is the fraction of polymer crystallised after time t .

increases. Moreover, at the lowest T_c investigated for the blends, the LLDPE component does not crystallise over the time interval experimentally available for these samples, even though its melting temperature is higher than these T_c .

The crystallisation kinetics of the samples were analysed at each T_c by means of the Avrami equation

$$X_t = 1 - \exp(-K_n t^n) \quad (1)$$

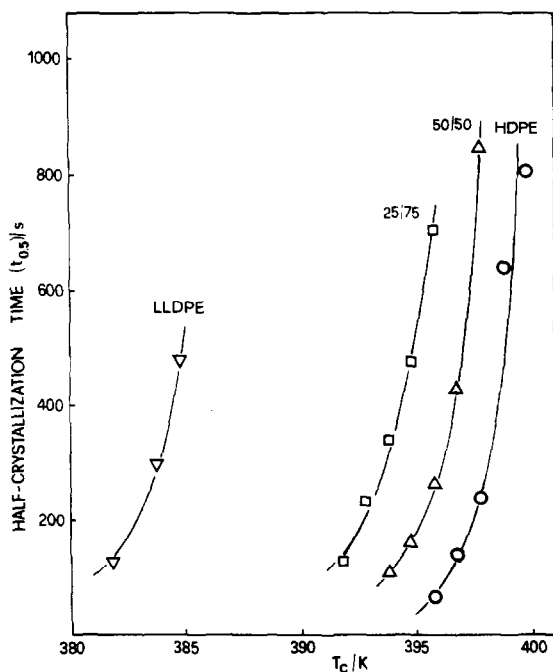


Fig. 9. Variation of the half-time of crystallisation, $t_{0.5}$, as a function of T_c for HDPE, LLDPE and HDPE/LLDPE blends.

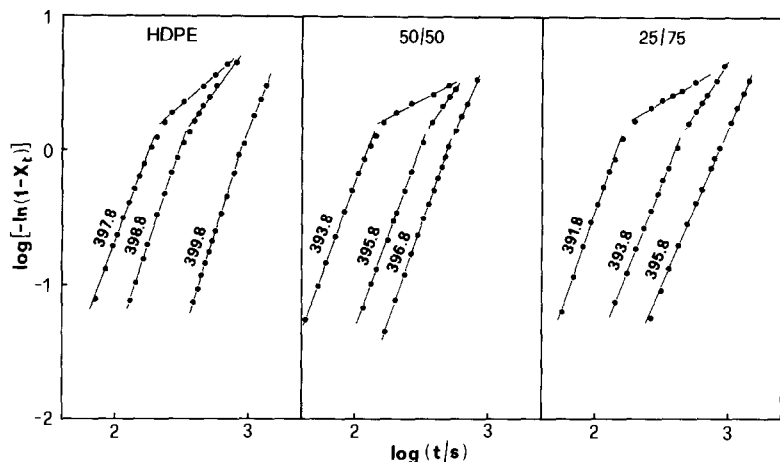


Fig. 10. Avrami plots for HDPE and HDPE/LLDPE blends crystallised at various T_c (see eqn. (1)).

where K_n is the kinetic constant and n is the Avrami exponent, depending on the nucleation type and growth dimensions of the crystals [15]. K and n values were calculated from the intercepts and slopes, respectively, of linear plots of $\log[-\ln(1 - X_t)]$ versus $\log t$. Some examples are shown in Fig. 10 for HDPE and the two blends at various T_c .

In general, linear trends with a slope n of between 2 and 3, were observed for all samples up to a crystallinity fraction X_t of about 0.7; for higher X_t values, and depending on T_c , the slope n drops to 1–2. This marked variation can be ascribed to the occurrence of secondary crystallisation, as observed for many polymers with a logarithmic time dependence of the crystallinity over long periods of time [16].

Kinetic parameter values of the samples are summarised in Table 1. The average n values for HDPE ($\bar{n} = 2.9$) and the HDPE/LLDPE 50/50 blend ($\bar{n} = 2.8$) are in good agreement with the literature data for linear polyethylenes of comparable molecular weight [16,17], and consistent with a spherulitic crystal growth initiated by athermal-like nucleation. The lower values found for the 25/75 blend ($\bar{n} = 2.4$) and for LLDPE ($\bar{n} = 2.5$) suggest a different growth type and geometry. The values of the kinetic constant K_n (and K_3) of the blends are much lower than the values of HDPE at the same T_c . According to the crystallisation theories [15], this behaviour can be accounted for by a decrease in the spherulite growth rate and/or the primary nucleation density of HDPE as the concentration of the non-crystallisable component increases. Similar effects have been observed in the isothermal crystallisation from the melt of other polyolefin blends, such as PP/LDPE [18] and PP/HDPE [19]. In some cases, they have been related to miscibility of the polymers in the molten state [20,21].

TABLE I
Values of the kinetic parameters for the isothermal crystallisation from melt of HDPE/LLDPE blends (according to eqn. (1))

Blend composition HDPE/LLDPE (w/w, %)	T_c (K)	$t_{0.5}$ (s)	n	n_s	K_n (Ω^{-n})	Corre- lation coef- ficient	K_3^a (Ω^{-3})
100/0	399.8	800	3.1	—	6.12×10^{-10}	0.9999	1.21×10^{-9}
	398.8	638	2.9	1.3	7.04×10^{-9}	0.9989	3.69×10^{-9}
	397.8	238	3.0	1.4	4.77×10^{-8}	0.9996	4.77×10^{-8}
	396.8	103	3.0	0.8	8.09×10^{-7}	0.9987	8.09×10^{-7}
	395.8	66	2.6	0.7	1.27×10^{-5}	0.9989	2.24×10^{-6}
$\bar{n} = 2.92$							
50/50	397.8	848	2.7	—	7.07×10^{-9}	0.9990	8.79×10^{-10}
	396.8	429	2.8	2.3	2.96×10^{-8}	0.9994	8.58×10^{-9}
	395.8	265	2.8	1.5	1.14×10^{-7}	0.9997	3.64×10^{-8}
	394.8	159	2.8	1.2	4.64×10^{-7}	0.9995	1.64×10^{-7}
	393.8	107	2.7	0.5	1.99×10^{-6}	0.9989	4.63×10^{-7}
$\bar{n} = 2.76$							
25/75	395.8	710	2.3	—	1.54×10^{-7}	0.9987	1.30×10^{-9}
	394.8	476	2.2	—	1.01×10^{-6}	0.9994	6.67×10^{-9}
	393.8	340	2.5	1.6	2.78×10^{-7}	0.9998	1.36×10^{-8}
	392.8	234	2.2	n.d.	4.02×10^{-6}	0.9999	4.39×10^{-8}
	391.8	128	2.9	0.6	3.72×10^{-7}	0.9990	2.13×10^{-7}
$\bar{n} = 2.42$							
0/100	383.8	298	2.5	1.6	4.23×10^{-7}	0.9990	2.25×10^{-8}
	381.8	126	2.5	1.3	3.49×10^{-6}	0.9991	2.83×10^{-7}
$n = 2.5$							

^a Values of the kinetic constant recalculated for $n = 3$ by using the relation: $K_3 = (K_n)^{3/n}$ (ref. 19).

Melting behaviour

The DSC melting thermograms of HDPE and the blends immediately after isothermal crystallisation show a single melting endotherm at all compositions and temperatures. In Fig. 11, the melting temperatures, T_m , are plotted as a function of T_c . It can be observed that, for the same T_c , the T_m of HDPE decreases as the content of LLDPE in the blends increases, as was found for non-isothermally crystallised samples.

The linear variation of T_m versus T_c can be described by the relation [22]

$$T_m = T_m^o(1 - 1/\gamma) + T_c/\gamma \quad (2)$$

where T_m^o is the thermodynamic equilibrium melting point of the crystallisable component at each composition, and γ is a constant relating the mean lamellar thickness (l) of the crystals to the initial thickness (l^*) of the growth nuclei at T_c . Values of T_m^o , $1/\gamma$ and γ , as determined from the intercepts and the slopes of the plots of Fig. 11, are reported for all the samples in Table 2.

The T_m^o value observed for HDPE (416 K) is in good agreement with the values reported by Wunderlich [23]. There is an appreciable difference between the values for HDPE and LLDPE ($T_m^o = 402$ K), whereas no significant variations were found for T_m^o values of HDPE in the blends. In contrast, the slope $dT_m/dT_c = 1/\gamma$ is markedly dependent on the blend composition: for the 25/75 blend its value is about twice that for HDPE. However it is important to note that values of γ from 1 to 2 have been reported for polyethylene and other polymers crystallised from melt [22,23]; higher values can be ascribed to the presence of thickening effects of the

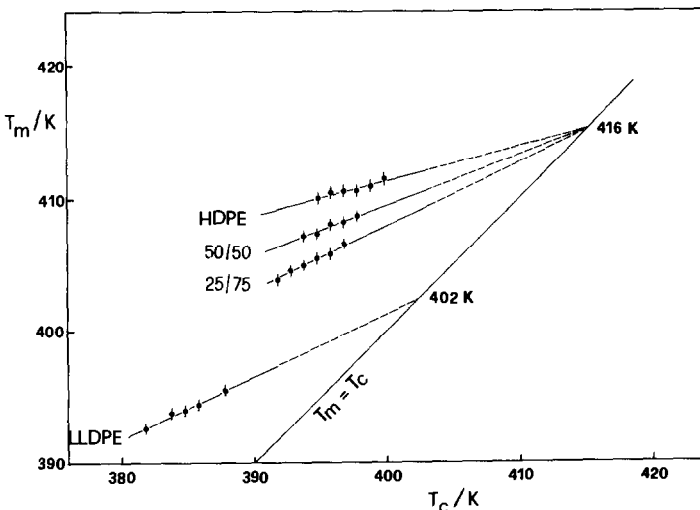


Fig. 11. DSC melting temperatures (T_m) of HDPE, LLDPE and HDPE/LLDPE blends versus T_c .

TABLE 2

Equilibrium melting parameters for HDPE/LLDPE blends (according to eqn. (2))

Blend composition HDPE/LLDPE (w/w, %)	T_m° (K)	l/γ	$\gamma = l/l^*$	Correlation coefficient
100/0	416 ± 1	0.25	4.0	0.9174
50/50	416 ± 1	0.39	2.6	0.9500
25/75	416 ± 1	0.51	2.0	0.9909
0/100	402 ± 1	0.47	2.1	0.9927

crystals at high crystallisation temperatures, generally above 400 K [22]. The observed melting behaviour of the two HDPE/LLDPE blends thus suggests that depression of the HDPE melting point is mainly determined by morphological effects relevant to crystal size and perfection. It has, in fact, been inferred by Rim and Runt [24] that melting points may be significantly lowered when the crystallite size decreases. On the other hand, if the two polymers are mixed in the melt, a decrease in the T_m° of HDPE in the blends could be expected due to a diluent effect of the non-crystallisable component [20].

Temperature dependence of crystallisation rate

According to polymer nucleation theory [22], the temperature dependence of the overall crystallisation rate can be related to the activation energy for the transport of the crystallisable units across the solid-liquid interface, the free energy of formation of critical sized nuclei, which in turn depends on the composition of the melt at the growth front, and the concentration of primary (heterogeneous) nuclei in the melt.

Figure 12 shows plots of $\log(1/t_{0.5})$ against $1/T_c \Delta T$, where $\Delta T = T_m^{\circ} - T_c$, for the two blends. Linear trends were found at all temperatures. Following the conventional description of the kinetic equations, and using a single value of T_m° for HDPE and the blends (see Table 2), the slopes in Fig. 12 can be related to the energy of formation $\Delta\Phi^*$ of (secondary) nuclei on the crystal surface [22]

$$\Delta\Phi^* = ab_0\sigma\sigma_c T_m^{\circ} / (\Delta_{\text{fus}} H^{\circ} \Delta T) \quad (3)$$

where a and b_0 are constants depending on the growth regime and geometry, σ and σ_c are the lateral and fold-surface free energies of the crystals, $\Delta_{\text{fus}} H^{\circ}$ is the equilibrium melting enthalpy and ΔT the supercooling.

The calculated slope values decrease from $4.16 \times 10^4 \text{ K}^2$ for pure HDPE to $3.78 \times 10^4 \text{ K}^2$ for the 50/50 blend, and $3.62 \times 10^4 \text{ K}^2$ for the 25/75 blend. Without speculating on the general features of these plots and thus on the mode of nucleation referred to, it is worth stressing that the rate of formation of the crystal nuclei at the growth front is scarcely affected by the presence of the melted LLDPE component. By taking the HDPE values of

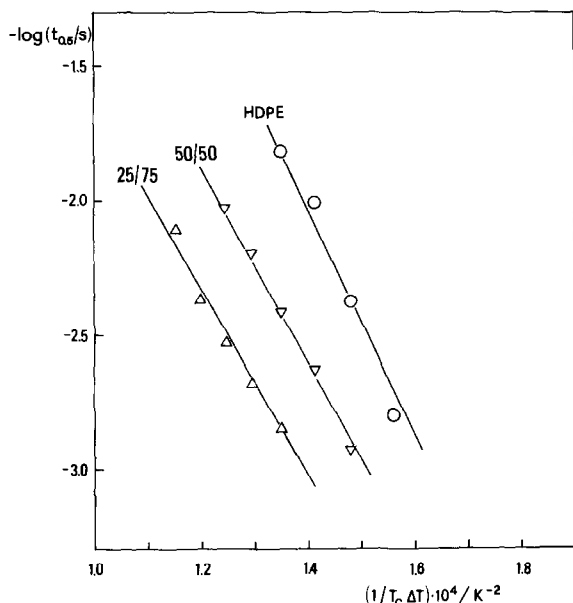


Fig. 12. Plots of $\log(1/t_{0.5})$ vs. $1/(T_c \Delta T)$ for HDPE and HDPE/LLDPE blends.

$a = 2$, $b_0 = 4.15 \times 10^{-8}$ cm, $\sigma = 10$ erg cm^{-2} and $\Delta_{\text{fus}} H^\circ = 2.80 \times 10^9$ erg cm^{-2} from the literature [22], a σ_e of about 107 erg cm^{-2} was calculated for HDPE from eqn. (3), in good agreement with that reported by Hoffmann et al. [22]. Values of 97 and 93 erg cm^{-2} were found for the two blends.

CONCLUDING REMARKS

Thermal analysis of blends of high-density and linear low-density polyethylenes crystallised from melt under various conditions indicates that co-crystallisation between the two components occurs. This is consistent with previous results [9–12] and can be interpreted as evidence of the compatibility of these blends.

It has been shown by optical microscopy that blend films, crystallised in a temperature range where only the crystal phase of HDPE can grow, do not reveal any macrophase separation of the two components in the interspherulitic regions; moreover, no apparent difference in the crystal morphology was found on varying the blend composition. Analysis of the crystallisation kinetics from the melt reveals that the crystallisation rate of HDPE in the blends is markedly reduced when the LLDPE content is increased. This can be ascribed to a decrease in the primary nucleation and/or the spherulite growth rate of HDPE. The temperature dependence of the overall crystallisation rate displays only a small variation in $\Delta\Phi^*$ when the blend composition is changed. On the other hand, the melting behaviour

of the isothermally crystallised samples indicates that the T_m^0 of HDPE does not depend on the LLDPE content, and that the observed decrease in the melting temperature of HDPE in the blends should be mainly ascribed to morphological effects relevant to crystal size and perfection. The presence of LLDPE molecules on the lamellar structure of HDPE crystals can decrease the regularity of the crystal surfaces and limit the thickness, as reported for some miscible crystalline blends [24]. The absence of T_m^0 depression for HDPE in the blends (as expected for a compatible system) does not support the previous suggestions. However it must be pointed out that, according to the Flory–Huggins theory [20], if the interaction parameter χ_{AB} approaches zero for these blends, no T_m^0 depression will be observed.

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