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ORIGINAL CONTRIBUTION

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Morphology and crystallization of blends of linear low density polyethylene with a semiflexible liquid crystalline polymer

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Abstract The morphology and the crystallization behavior of blends of linear low density polyethylene (LLDPE) with an experimental sample of a semiflexible liquid crystalline polymer (SBH 1:1:2 by Eniricerche, Italy) have been studied by differential scanning calorimetry (DSC), polarized optical microscopy (POM) and scanning electron microscopy (SEM). The blends possess a two-phase morphology, due to immiscibility of the two components. SEM observations show that dispersion of the minor SBH phase is favored at low (< ca. 15%) SBH concentration. At higher concentrations, the dimensions of the dispersed particles increase strongly. Non-isothermal and isothermal DSC measurements have shown that the LLDPE crystallization rate is strongly enhanced by the addition of SBH. The maximum effect has been found for an SBH concentration of ca. 10% w/w. POM observation shows that the LLDPE spherulite size decreases by ca 50% in the presence of SBH. These results have been interpreted on the basis of a heterogeneous nucleation played by the crystallized SBH particles on the molten LLDPE matrix. The interpretation of the non-isothermal and isothermal data in terms of the Avrami exponents indicates that the nucleation mechanism is not altered by the presence of a dispersed SBH phase. The relationships between blends morphology and nucleation phenomena have been discussed.

Key words Linear low density polyethylene – semiflexible liquid crystalline polymer – polyethylene/LCP blends – morphology – crystallization kinetics

Introduction

During the last decade, it has been shown by several authors that the addition of 5–30% w/w of liquid crystalline polymers (LCPs) into commercial thermoplastics may lead to beneficial effects with respect to either the processing operations and the performance of the products. In fact, a fairly strong reduction of the melt viscosity of the matrix is granted by the dispersed LCP particles, and the latter can give rise to fibrillation, under processing conditions involving elongational flow, thus leading to substantial reinforcing of the host resin [1,2]. A great number of **in situ** composites [3], prepared by the addition of LCPs (generally of the wholly aromatic type) into a variety of flexible resins, such as polyamides, polyesters, polycarbonates, polysulfones, etc., have been investigated [1,2]. On the contrary, the literature data on blends of LCPs with polyolefins are comparatively scarce. In particular, polyethylene (PE) has been used as the blends matrix in very few studies [4–8]. One major reason for this may be that most LCPs available commercially require processing temperatures which are considerably higher than those used for PE. Moreover, very poor interphase adhesion is expected for this type of blends.

In a previous paper [8], we used a semiflexible LCP having a melting point of ca. 230 °C for an investigation of PE/LCP blends. This low melting LCP, indicated here as SBH, was recently developed by Eniricerche S.p.A., together with other semiflexible LCPs, by the melt polycondensation of sebacic acid (S), 4,4′-dihydroxybiphenyl (B) and 4-hydroxybenzoic acid (H) in the 1:1:2 molar ratio [9–11]. We found that the addition of SBH leads to a pronounced reduction of the melt viscosity of both high density PE (HDPE) and linear low density PE (LLDPE). However, some differences between the two types of blends were demonstrated with respect to both the morphology of extruded threads and the mechanical properties of compression molded bars. In fact, whereas with a HDPE matrix poor LCP dispersion and interphase adhesion, and, consequently, no reinforcing effects were observed, more favorable phase interactions were demonstrated for blends based on LLDPE. With the latter matrix, the dispersion of the SBH droplets was fairly good and, as a result, the tensile modulus of LLDPE was found to increase by 50% upon addition of 20% SBH. Moreover, contrary to HDPE, the thermal properties of LLDPE were also influenced by the SBH addition. In particular, the crystallization temperature of LLDPE was found to increase in the presence of SBH.

Based on the latter finding, we thought that the investigation of the crystallization behavior of LLDPE/SBH blends could be interesting. It is known that the LCP dispersed phase may sometimes act as a nucleating agent, thereby enhancing the rate and/or the extent of crystallization of crystallizable matrices such as poly(ethylene terephthalate) (PET) [12–15, poly(butylene terephthalate) [16, 17], aliphatic polyamides [18], poly(phenylene sulfide) [19, 20], etc. In other systems, a depression of the crystallization rate induced by the added LCP was found [21]. Since these effects depend critically on the interactions between the blends components in the molten state, a study of the crystallization behavior of the LLDPE/SBH system was thought to shed more light on the phase interactions in these blends.

In this work, the crystallization kinetics of LLDPE/SBH blends has been investigated under non-isothermal and isothermal conditions, and the results have been discussed with reference to the blends morphology.

Experimental

LLDPE (Riblene LX 2211, by Enichem Polimeri) was an ethylene/1-butene copolymer having a MFI of 1.0 dg/min. SBH was a laboratory sample (LCP1B/024) kindly supplied by Eniricerche S.p.A., and synthesized as described elsewhere [9–11]. The inherent viscosity of SBH, measured in a 50/50 v/v 4-chlorophenol/1,2-dichloroethane solution ($T = 25$ °C, $c = 0.1$ g/dL), was 0.88 dL/g. The melting and crystallization temperatures of SBH, measured by differential scanning calorimetry (DSC) with a rate of 10 deg/min, were 229.6 and 213.4 °C, respectively.

The polymers were dried in a vacuum oven at 100 °C for at least 24 h, before blending. The blends were prepared by extrusion in a Brabender Compounder attached to a Brabender plasticorder mod. 651. The thermal profile was 175 °, 220°, 240 °C, and the rotational speed was 40 rpm. The neat polymers were subjected to the same treatment. Blends with 0, 5, 10, and 20% SBH (w/w) were prepared.

Optical microscopic observations were made with a Reichert Zetopan polarizing microscope equipped with a hot stage. Blend films were heated to 190 °C with a rate of 10 deg/min, held at this temperature for 5 min, and cooled down to room temperature with a rate of 10 °C/min. The photomicrographs were taken at room temperature. The Hv diffraction patterns of low-angle light scattering were obtained by insertion of a Bertrand lens and using the microscope in the diffraction mode. The average dimensions of the spherulites were determined from the Hv patterns, using the Stein equation [22].

Scanning electron microscopic (SEM) analysis was made with a Philips T550 apparatus, on polymer specimens fractured under liquid nitrogen and coated with gold.

Calorimetric measurements were made with a Perkin Elmer DSC-7 equipment, calibrated with indium and tin standards, under an argon atmosphere. The specimens were heated to 190 °C and held at this temperature for 5 min, in order to destroy the LLDPE crystal nuclei. The DSC cooling traces were recorded with the rates of 5 °, 10°, 15°, and 20 °C/min. The degree of crystallinity was calculated from the crystallization enthalpy, normalized to the LLDPE content. The enthalpy of crystallization of 100% crystalline LLDPE was taken as 276.7 J/g [23]. The crystallization rate coefficient (CRC) was determined with the method proposed by Khanna [24]. For an accurate determination of the non-isothermal kinetic characteristics, the apparatus was calibrated at various scanning rates. The thermal lag between sample and pan holder temperatures was estimated according to the procedure of Eder and Wlochowicz [25]. The equation of Harnisch and Muschik was used for the determination of the Avrami exponents [26].

The DSC experiments of isothermal crystallization were carried out as follows: the specimens were heated to 190 °C with a rate of 10 deg/min, held at this temperature for 5 min, and cooled to the appropriate crystallization temperature T_c (in the range 108–122 °C) with a rate of 200 deg/min. The heat evolved upon isothermal crystallization was recorded and the fraction X_t of the polymer crystallized at time t was evaluated as the ratio of the area under the curve at time t to that of the whole exotherm. The starting time of crystallization ($t = 0$) was taken as that at which thermal equilibrium was reached at T_c. The area of the exotherm was measured by back extrapolation of the baseline after complete crystallization.

The melting temperature T_m of the isothermally crystallized samples was determined by heating them, directly from T_c, with a rate of 10 deg/min.

Results and discussion

The SEM micrographs of 90/10 and 80/20 LLDPE/SBH extrudates of ca. 3 mm diameter, fractured under liquid nitrogen, are shown in Fig. 1. A two-phase morphology with scarce adhesion was always observed for these blends. The LCP forms the dispersed phase with droplets dimensions depending on the blend composition. At 5 and 10% concentration of SBH, the droplets are rather small (0.5–3 μm) and uniformly dispersed. At 20% SBH, the dispersion of the LCP particles appears much poorer: the smaller droplets (0.5–3 μm) have a spherical shape, whereas the larger ones appear as elongated ellipsoids or flat domains having the shortest dimension of 5–20 μm. The interphase adhesion appears definitely worse in the latter blends, and this may be probably attributed to the fact that, when the LCP concentration grows, the dispersed droplets show an enhanced tendency to coalesce and to give rise to larger particles which, in turn, are pulled out more easily from the matrix when the blend specimen is fractured.

LLDPE crystallizes from the melt as fairly large spherulites exhibiting typical spherulitic Hv-diffraction pattern (Fig. 2a). On the contrary, the crystallization of molten films of the blends leads to much smaller spherulites, whose dimensions seem to be practically independent of the blend composition (Figs. 2b and 2c). The

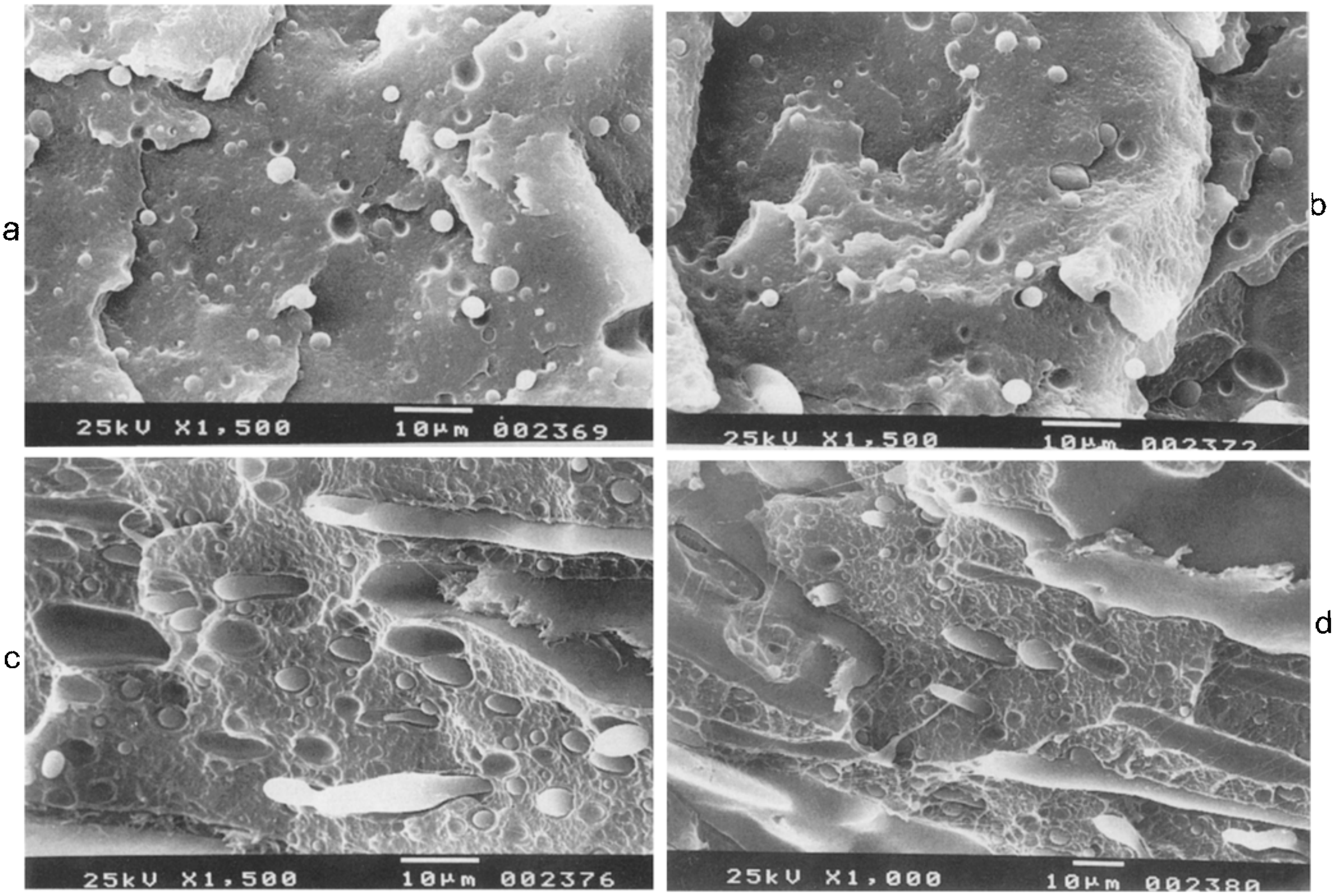

Fig. 1 SEM micrographs of the fractured surfaces of: a, b) LLDPE/SBH 90/10; c, d) LLDPE/SBH 80/20

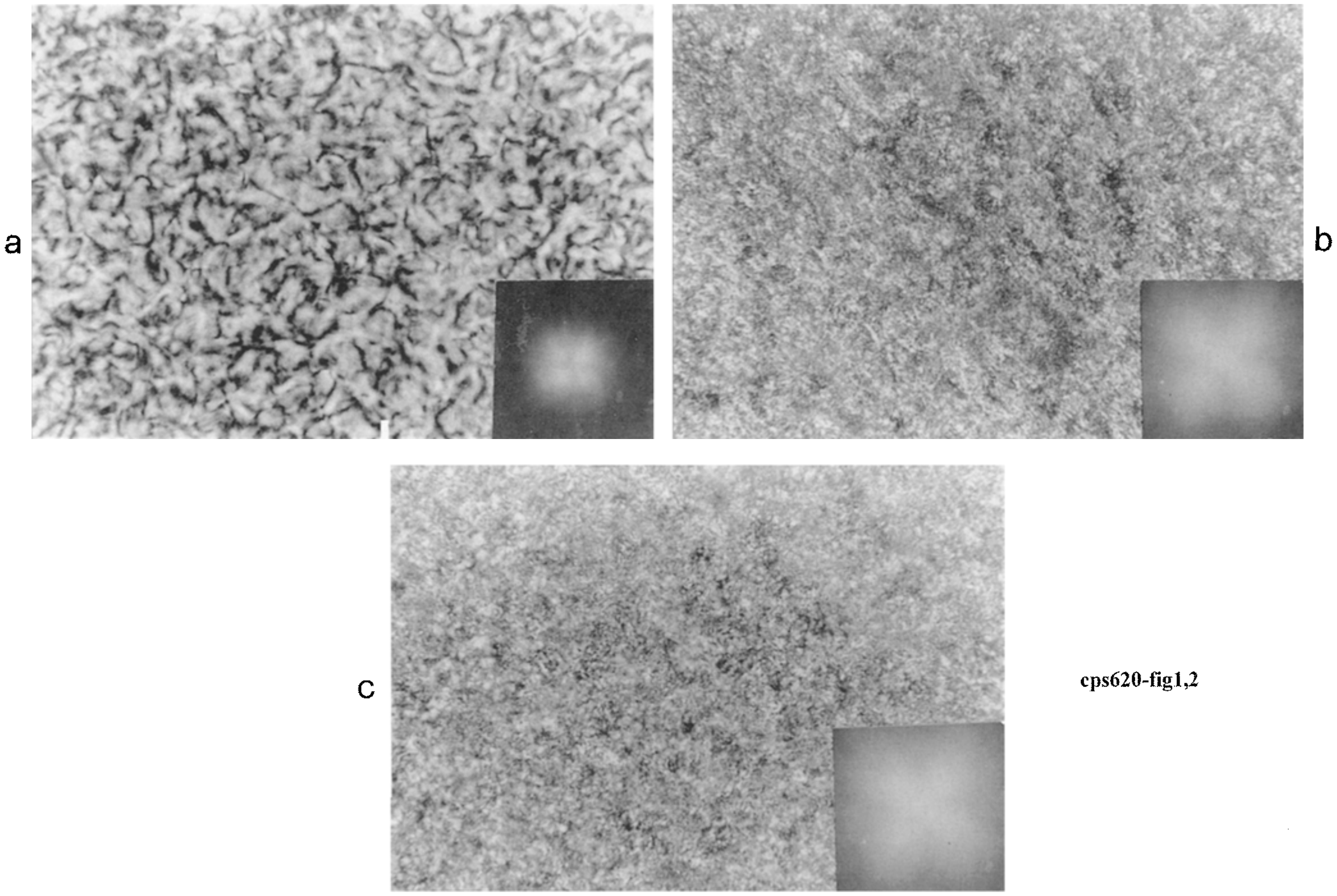

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Fig. 2 Optical micrographs and corresponding Hv patterns of: a) LLDPE, b) LLDPE/SBH 95/5, c) LLDPE/SBH 90/10

average dimensions of the spherulites were determined from the Hv-patterns by means of the equation [22]:

$$R_{sph} = c \cdot \lambda/(n \cdot \pi \cdot \sin Q_m) ,$$

where R_{sph} is the spherulite radius, c is a constant. ($c = 2.05$ for spheres), λ/n is the wavelength of the light in a medium of refractive index n, and Q_m is the angle of the incident and scattered beams corresponding to the maximum pattern intensity. The determination of R_{sph} was made from 4–5 Hv-diffraction patterns. Inspite of the LCP birefringence itself, it is still possible to obtain, spherulitic Hv diffractogram from LLDPE/SBH blends when the SBH concentration is low (5–20 wt%) (Fig. 2b, c). The average radius of the LLDPE spherulites decreases from ca. 8 μm to ca. 4 μm when the LCP is added into the matrix polymer. This demonstrates that SBH acts as a nucleating agent for LLDPE crystallization [27].

The crystallization of LLDPE, either pure or blended with SBH, was investigated under non-isothermal conditions, using different cooling rates, as described in the experimental section. It must be pointed out that, during the whole thermal treatment used for the measurements, including the preliminary 5 min heating at 190 °C, the SBH particles remained in the crystalline state [8]. The results of the measurements are collected in Table 1.

The dependence of the crystallization temperature (T_{cr}) of LLDPE, measured under non isothermal conditions with different cooling rates, on the SBH concentration is shown in Fig. 3. It is apparent that, at every cooling rate, the crystallization temperature increases steadily upon increasing the SBH concentration up to 10%, and then decreases for higher SBH contents. The maximum T_{cr} increase, which is found for blends with 10% SBH, is of ca. 13 °C and is practically independent of the cooling rate. It is known that the nucleating effect played by many inorganic fillers on the crystallization of the polymer matrix of different kinds of composites tends to fade at high cooling rates. This is not so for the LLDPE/SBH system investigated here, as well as for a poly(phenylene sulfide)/LCP blend [28], for which the nucleating ability of the LCP was found unaltered even at a cooling rate of − 30 °C/min.

The degree of crystallinity α, determined from the enthalpy of crystallization, is of ca. 0.4 for both neat LLDPE

Table 1 Calorimetric data of LLDPE/SBH blends

LLDPE/ SBH	5 °C/min			10 °C/min			15 °C/min			20 °C/min			CRC	n
	T_{cr} (°C)	H_{cr} (J/gPE)	α	T_{cr} (°C)	H_{cr} (J/gPE)	α	T_{cr} (°C)	H_{cr} (J/gPE)	α	T_{cr} (°C)	H_{cr} (J/gPE)	α	h^{-1}	
100/0	102.9	115.3	0.42	98.2	111.7	0.40	94.9	114.1	0.41	92.7	116.9	0.42	87	2.6
95/5	109.6	112	0.40	106.0	111	0.40	102.5	110..6	0.40	99.9	109.1	0.395	110	2.5
90/10	115.3	131.7	0.475	110.8	128.5	0.47	108.6	135.2	0.49	106.3	126.3	0.46	110	2.5
80/20	109.5	106.5	0.39	106.2	112.7	0.41	103.1	111.1	0.40	101	110.6	0.40	110	–

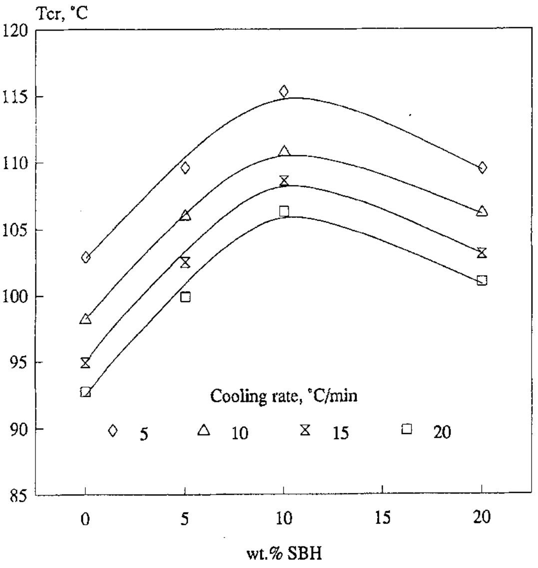

Fig. 3 Crystallization temperatures versus SBH concentration

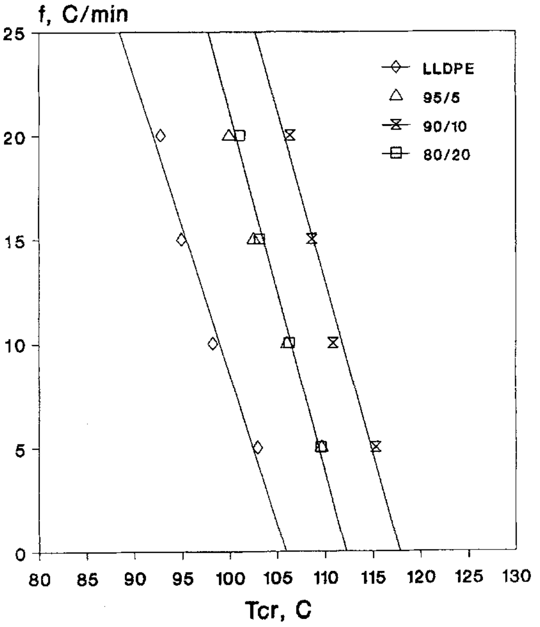

Fig. 4 Dependence of the cooling rate on the crystallization temperature of the samples

and the blends with 5 and 20% SBH (cf. Table 1). The blend with 10% SBH, on the contrary, shows a much higher α (0.47 is the average of the figures measured for this blend using different cooling rates), which corresponds to an increase of ca. 15%.

If the cooling rate is plotted against the crystallization temperature, the slopes of the straight lines drawn through the experimental points, according to Khanna [24], can be taken as the crystallization rate coefficients (CRC). It may be observed from these plots, shown in Fig. 4, and from the CRC values (error ±3%) shown in Table 1, that the CRC of neat LLDPE ($87\,h^{-1}$) is at the same range of values as that found by Khanna for HDPE ($98\,h^{-1}$), but slightly lower as could be expected. Interestingly, the CRC of the blends are all of ca. $110\,h^{-1}$, independent of the LCP concentration. These data confirm that the nucleating role of SBH is revealed at all investigated cooling rates.

The overall non-isothermal crystallization kinetics of LLDPE has been studied by DSC, with the Harnisch and Muschik's method [26]. The Avrami exponents n were determined according to the following equation, which is valid at $T = T_c$:

$$n = 1 + \{\ln[\dot{x}_1/(1 - x_1)] - \ln[\dot{x}_2/(1 - x_2)]\}/\ln(f_2/f_1)\,,$$

where x_i is the crystalline fraction calculated by integration of the DSC endotherm; $\dot{x}_i$ is the derivative of x_i and f_i is the cooling rate used in the experiment. The Avrami exponents n for neat LLDPE and its blends with 5 and 10% SBH were measured from the plots of ln $[\dot{x}/(1 - x)]$ vs. T shown in Fig. 5, and are collected in Table 1. The values of the Avrami exponents suggest a spherulitic three-dimensional growth process controlled by heterogeneous nucleation. It is interesting that SBH does not seem to alter the mechanism of non-isothermal crystallization of LLDPE.

All the results described so far indicate that the dispersed SBH particles play a nucleating role in the crystallization of the LLDPE matrix, and that this effect is maximum

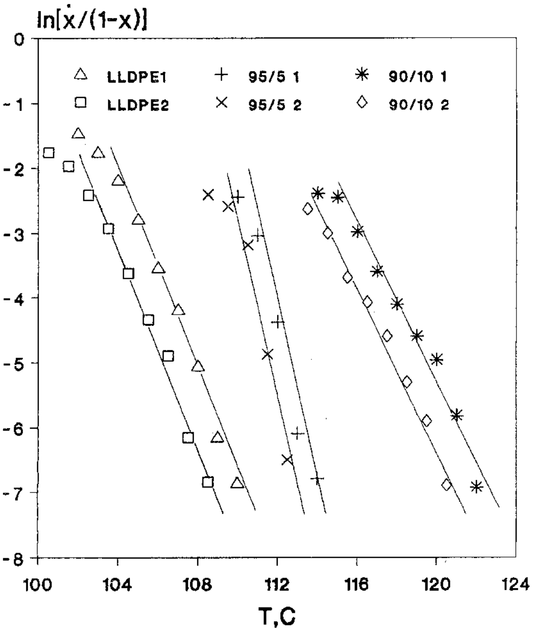

Fig. 5 Ln $\dot{x}/(1-x)$ values versus T for LLDPE, LLDPE/SBH 95/5 and LLDPE/SBH 90/10 : curve 1–cooling rate 5 °C/min, curve 2–cooling rate 10 °C/min

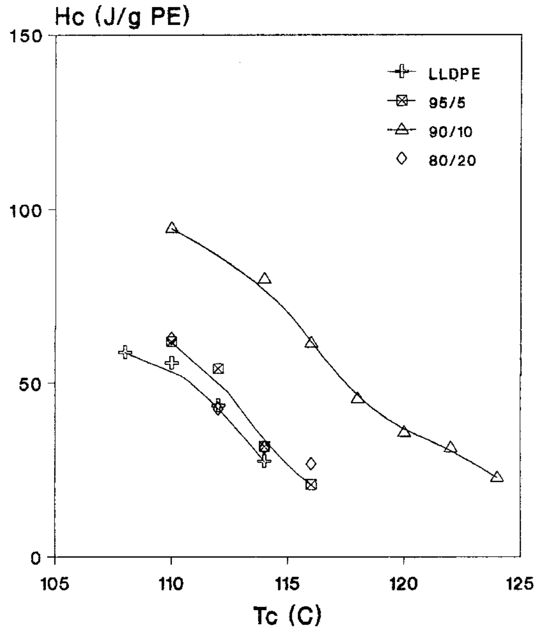

Fig. 6 Dependence of the enthalpy of isothermal crystallization on the temperature of isothermal crystallization for the samples

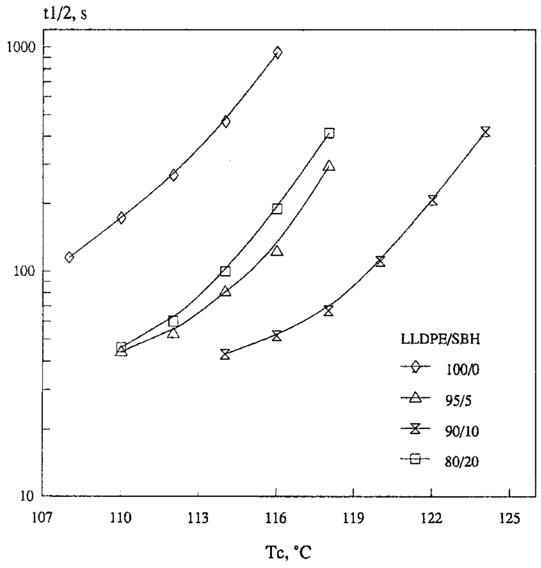

Fig. 7 Variation of the half-time of crystallization $t_{0.5}$ as a function of T_c

for a concentration of SBH of ca. 10%. At higher concentrations the effect appears to become of lesser importance. This apparent discrepancy may be tentatively attributed to a reduction of the interphase area, taking place at SBH concentrations exceeding 10%, which results from coalescence of the dispersed droplets as demonstrated by the SEM investigation.

The crystallization of LLDPE, either neat and blended with SBH, was also studied by isothermal DCS analysis in the range of crystallization temperatures between 108° and 124 °C. As already stated, the LCP remained in the solid crystalline state in the whole temperature interval covered during the measurements. Thus, the recorded isothermal DSC traces consist of single exothermic peaks whose area provides a measure of the extent to which LLDPE crystallization occurs. As it is shown in Fig. 6, the enthalpy of the isothermal crystallization decreases strongly on increasing T_c in the investigated range, either for neat and for blended LLDPE. It has been suggested [29] that, upon isothermal crystallization, the macromolecules of LLDPE of lower structural order are rejected into the amorphous zones between the crystalline lamellae. The higher the T_c, the larger is the fraction of polymer segregated during crystallization. Obviously, the presence of a dispersed SBH phase does not change this qualitative picture. However, the results of the isothermal crystallization experiments confirm that the crystallization of the blend with 10% SBH can be made to occur at considerably higher temperatures, with respect to, e.g., neat LLDPE, and, at any selected T_c, it takes place with an appreciably higher conversion (cf. Fig. 6).

In Fig. 7, the half-crystallization times, i.e., the times at which crystallization has occurred to 50% of the final conversion, are plotted against T_c. It is apparent that the addition of SBH into LLDPE decreases the half-crystallization times dramatically. The reduction is particularly

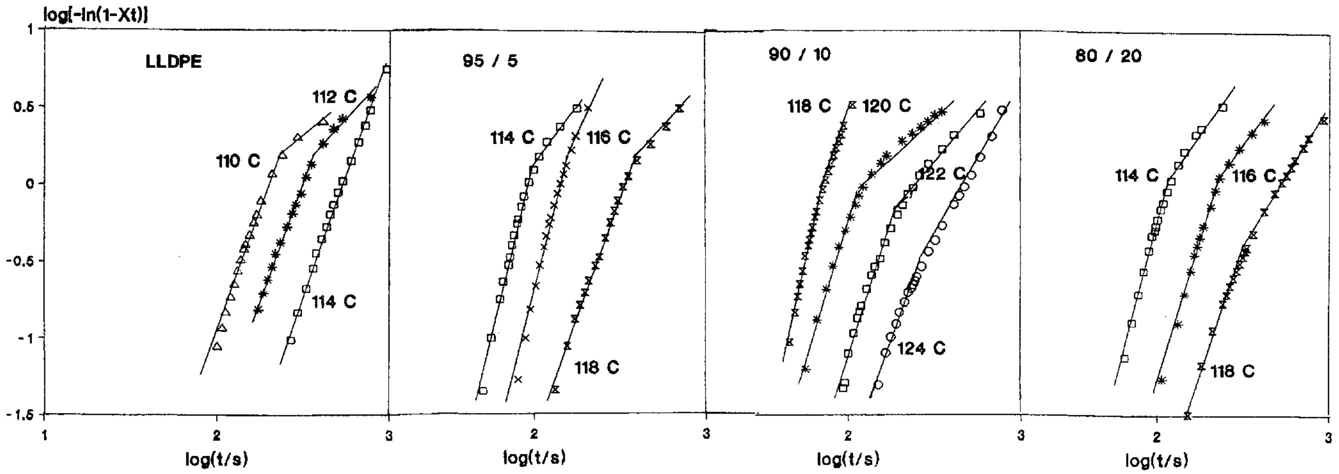

Fig. 8 Avrami plots for LLDPE and LLDPE/SBH blends crystallised at various T_c: a) LLDPE; b) LLDPE/SBH 95/5; c) LLDPE/SBH 90/10; d) LLDPE/SBH 80/20

Table 2 Isothermal Crystallization Parameters for LLDPE and LLDPE/SBH Blends

Blend	T_c (°C)	$t_{1/2}$ (sec)	n	K_n s^{-n}
100/0	116	950	–	–
	114	467	2.8	2.3×10^{-8}
	112	269	2.8	1×10^{-7}
	110	173	3	1.3×10^{-7}
	108	115	–	–
95/5	118	296	2.8	8.3×10^{-8}
	116	123	3.3	8.8×10^{-8}
	114	81	3.3	3.5×10^{-7}
	112	53	–	–
	110	44	–	–
90/10	124	420	2.8	3.1×10^{-8}
	122	208	3	7.7×10^{-8}
	120	111	3	5×10^{-7}
	118	67	3.3	6.5×10^{-7}
	116	52	–	–
	114	43	–	–
80/20	118	415	2.9	1.7×10^{-8}
	116	206	3	7.9×10^{-8}
	114	107	3.1	3.5×10^{-7}
	112	60	–	–
	110	46	–	–

important for the 10% SBH blend (more than an order of magnitude), in good agreement with the results of the non-isothermal analysis.

The isothermal crystallization kinetics was analyzed by means of the Avrami equation:

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

where X_t is the fractional crystallization occurred at time t, K_n is the kinetic constant and n is the Avrami exponent, which depends on the type of nucleation and on the crystal growth geometry. The values of K_n were determined with the equation:

$$K_n = \ln(2/t_{0.5}^n) ,$$

where $t_{0.5}$ is the time of half-crystallization. The Avrami exponents n were calculated from the slopes of the linear plots of $\log[-\ln(1 - X_t)]$ versus $\log(t)$ shown in Fig. 8. It is clearly observed that the slope of the plots tends to become smaller at high X_t, thus showing that secondary crystallization processes take place.

The isothermal crystallization parameters are collected in Table 2. The Avrami exponents are close to 3, indicating heterogeneous nucleation with three-dimensional growth, and drop to 1–2 during secondary crystallization. The values of the Avrami exponents found from isothermal measurements (ca. 3) are slightly higher than those determined under non-isothermal conditions. This is a common finding which has been attributed to the formation, during non-isothermal crystallization, of sheaf-like superstructures not fully developed into spherulites, and to spherulites impingement effects [30].

The kinetic parameters found for LLDPE are in good agreement with literature data [31]. The values of the kinetic constants for the blends, especially that with 10% SBH, are appreciably higher than that measured for neat LLDPE. These results are in perfect agreement with the data of the non-isothermal kinetic analysis described before, and confirm that the dispersed SBH particles act as nucleating agents for the crystallization of LLDPE. They also confirm that the nucleating effect is more pronounced when the LCP content is of ca. 10%, probably because the best dispersion of the minor phase and, consequently, the largest interfacial surface obtained for this composition, as proved by SEM.

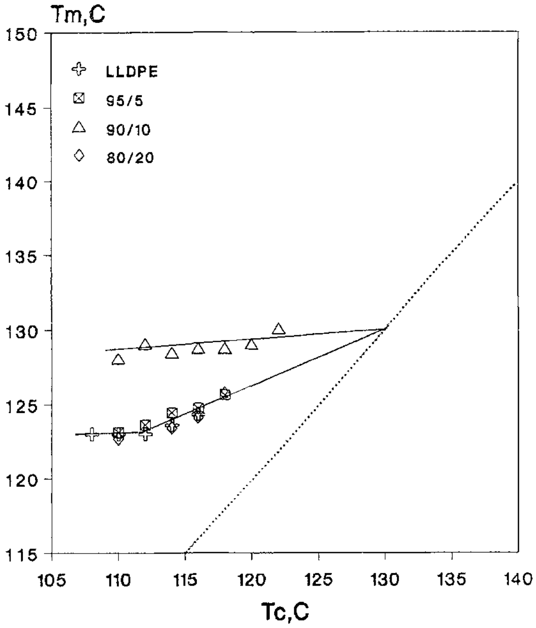

Fig. 9 Melting temperatures of isothermally crystallised LLDPE phase in LLDPE/SBH blends versus crystallization temperature

The melting temperatures of the isothermally crystallized samples are plotted as a function of T_c in Fig. 9. It has been shown [32] that the dependence of T_m on T_c can be described by the relation:

$$T_m = T_m^o \cdot (1 - 1/Y) + T_c/Y ,$$

where T_m^o is the thermodynamic equilibrium melting point of the crystallizable component and Y is a constant relating to crystal size and perfection. It is interesting that, for $T_c > 110\,°C$, the T_m figures measured for neat LLDPE and the blends with 5 and 20% SBH practically fit the same straight line which extrapolates to $T_m^o = 130\,°C$. The T_m values found for the 90/10 LLDPE/SBH blend are appreciably higher and lay on a straight line characterized by a smaller slope. However, this straight line too can be extrapolated to the same T_m^o. The latter is in good agreement with the value (129 °C) reported by Pracella et al. for LLDPE [31]. The values measured for Y are of ca. 2.7 for LLDPE and its blends with 5 and 20% LCP, and ca. 8.1 for the 90/10 blend. On the basis of the Hoffman and Weeks theories [32], Y is determined by the ratio of the mean lamellar thickness of the crystal (1) to the initial thickness of the growing nuclei (1*), at T_c. Values of $Y \approx 2$ have been reported by Wunderlich for polyethylene [33]. Higher Y values may be ascribed to: i) occurrence of crystal thickening effects; ii) superheating of perfect crystals; iii) annealing of imperfect crystals. The almost horizontal line representing the melting temperatures of isothermally crystallized LLDPE in the 90/10 blend, suggests that crystal annealing has taken place during the isothermal crystallization experiments.

Conclusion

The morphological and calorimetric investigation of LLDPE/SBH blends has shown that the two immiscible components give rise to a mutual dispersion which depends on composition. In particular, a very good dispersion of minute SBH droplets has been observed for LCP concentrations up to 10%, whereas, for the 80/20 LLDPE/SBH blend, extensive droplet coalescence with formation of large LCP domains has been found to occur. It has been demonstrated that the morphology of the blends influences their crystallization behavior. In fact, both non-isothermal and isothermal studies have shown that the dispersed LCP phase plays a nucleating role whose efficiency is maximum for the 90/10 blend. Apparently, the nucleating effect depends on the interfacial surface available: this increases with the SBH concentration in the 0–10% range, and then decreases when the droplets coalescence becomes favored. The mechanism of the crystallization of LLDPE does not change in the presence of the LCP. The strong increase of the crystallization temperature (for non-isothermal experiments) and of the crystallization rate (for isothermal experiments), which has been observed for the 90/10 LLDPE/SBH blend, is accompanied by a slight increase of the degree of crystallinity, with respect to that measured under comparable conditions for neat LLDPE.

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