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Polycarbonate–linear low density polyethylene blends: thermal and dynamic-mechanical properties

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Blends of polycarbonate (PC) and linear low density polyethylene (LLDPE) of different compositions, in the form of slabs obtained by melt extrusion, have been examined by differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA).

DSC measurements show that the melting, crystallization and glass transition temperatures of the two polymeric components in the blends are slightly affected by the composition. On the contrary, large differences are observed in the melting behaviour of layers cut at various depths, parallel to the slab surfaces of samples. This supports the occurrence of different crystal morphologies and distribution of the two components within the samples. The study of the crystallization kinetics from the melt blends shows that the crystallization processes of LLDPE are affected by the presence of PC.

The dynamic mechanical analysis indicates that modulus, transitions and relaxational behaviour of the polymer components are scarcely affected by the composition. Some variations of the damping factor have been interpreted as due to the phase heterogeneity of the system, arising from the processing conditions and rheological behaviour of the blends.

1. Introduction

In recent years the study of the structure–property relationships of multicomponent polymer systems has gained a great deal of attention as a consequence of their wide technological applications. Most of these systems are constituted by scarcely miscible polymers forming multiphase materials whose properties can be greatly affected by the mode of dispersion, size and orientation of the phases [1]. Moreover, interface interactions between the components can often arise during the mixing of polymer melts and influence the nucleation and growth of the crystalline phases [2, 3].

In this present work we have focused our attention on the properties of polycarbonate–linear low density polyethylene (PC–LLDPE) blends which appear to be of potential technological importance because of the peculiar properties of the two polymer components. This study has been developed within the framework of the international VAMAS Project (Versailles Project on Advanced Materials and Standards), Technical Working Area on Polymer Blends.

We examined the thermal and dynamic mechanical behaviour of PC–LLDPE blend samples, obtained by melt extrusion under conditions fixed by VAMAS, in order to analyse the dependence of thermodynamic and mechanical parameters of these materials on the composition and then correlate them with phase morphology, processing conditions and thermal history.

2. Experimental details

2.1. Materials

The starting polymers were polycarbonate (PC) Lexan from General Electric Co. (MI = 9.5 g/10′; density = 1.20 g ml^{-1}) and linear low density polyethylene (LLDPE) Escorene from ESSO Chemicals Canada (MI = 0.5 g/10′; density = 0.918 g ml^{-1}; comonomer content: 15.8 mol % of butene-1, random copolymer).

PC–LLDPE blends, containing 25, 50, 75 wt % of PC respectively, were prepared (at the National Research Council Canada, IMRI) by dry-blending the polymers in a Patterson mixer and drying for 17 h at 100° C under a continuous purging by air. The blends were then extruded in a single screw Extruder Flag Machinery Ltd (D = 6.35 mm; L/D = 30) operating at 60 r.p.m. and 255° C (die temperature), granulated and reextruded. The pure polymers and the blends were supplied by VAMAS in the form of 2 and 6 mm thick slabs.

2.2. Calorimetric measurements

The thermal analysis of the samples was performed using a Perkin-Elmer DSC 4 differential scanning calorimeter equipped with Data Station 3600 and Intracooler I. Test specimens (3 to 6 mg, 0.1 to 0.5 mm thick) were cut, after conditioning at 23 °C and 50% r.h. for 24 h, both perpendicular and parallel to the slab surfaces in the extrusion direction (Fig. 1). All

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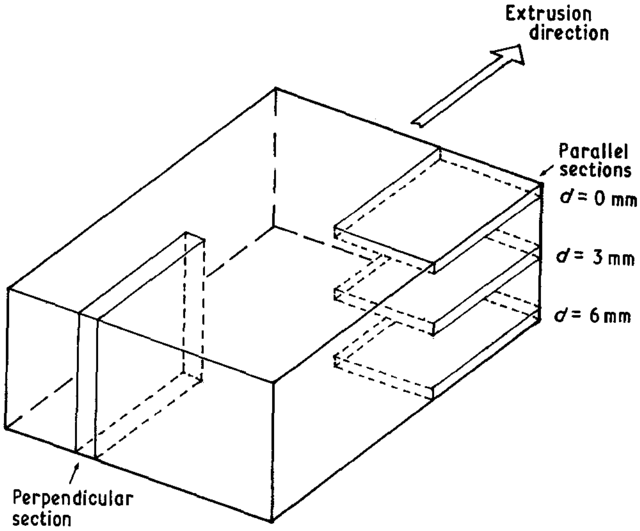

Figure 1 Scheme of a PC–LLDPE extruded slab (thickness: 6 mm) with the different types of examined sections, cut both perpendicular and parallel at various depths (d = 0, 3, 6 mm) to the slab surface.

measurements were made following the International Standard ISO No. 3146.

As received specimens were heated in DSC from −40 to 250° C at 10° C min^{-1} (run I), then left at 250° C for 10 min and cooled to the starting temperature at a rate of −10° C min^{-1}. A second heating run (run II) was performed from −40 to 250° C at 10° C min^{-1}. Melting or crystallization temperatures and relevant enthalpies of LLDPE in the various samples were determined from the maxima and the areas of DSC peaks respectively. Glass transition temperatures of PC were measured both at the onset and the midpoint of the transition by the DSC computer program. The temperature calibration of the apparatus was performed by using standard reference materials (benzyl, indium, tin).

The isothermal crystallization behaviour of LLDPE and PC–LLDPE blends was also analysed by DSC. Samples were heated at 10° C min^{-1} up to 200° C, kept 5 min at this temperature and then rapidly cooled at a nominal rate of −320° C min^{-1} to a fixed crystallization temperature T_c in the range 105 to 118° C. After thermal equilibrium was reached, the heat of isothermal crystallization was recorded as a function of time and the fraction X_t of the polymer crystallized at the time t, was determined by the ratio of the crystallization area up to the time t over the total area corresponding to the completion of the crystallization.

2.3. Dynamic mechanical measurements

The dynamic mechanical analysis of the blends was carried out under vacuum at acoustic frequencies by using a resonance electrostatic apparatus [4] on circular specimens (2 mm thickness, 36 mm diameter) vibrating on their lowest flexural symmetrical modes. Samples were previously cooled from room to liquid nitrogen temperature, at a cooling rate of about −10° C min^{-1}, and subsequently heated up to the softening point at 10° C min^{-1}. Measurements were performed in the frequency range 1 to 10 kHz.

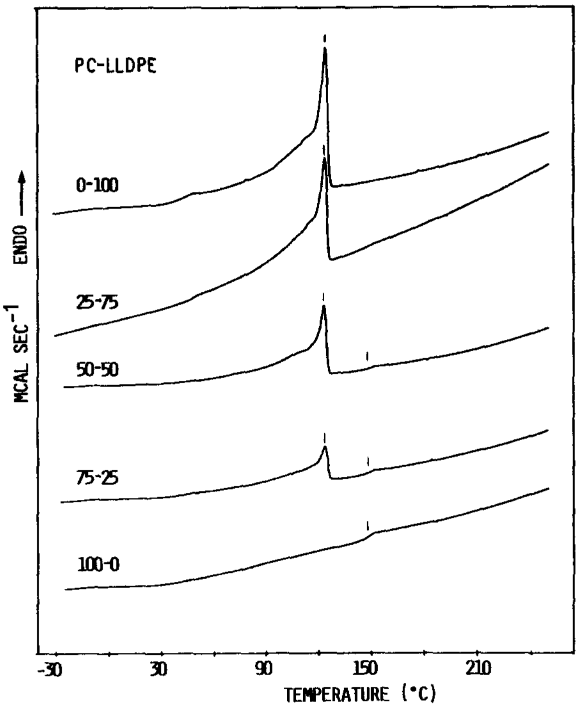

Figure 2 DSC thermograms (run I) of sections perpendicular to the slab surface of PC–LLDPE blends at various compositions (heating rate: 10° C min^{-1}). All curves are normalized to 1 mg sample weight.

3. Results

3.1. Thermal behaviour

3.1.1. Sections perpendicular to the slab surface

DSC thermograms of sections perpendicular to the slab surface (run I) are reported in Fig. 2. The endotherms of PC–LLDPE 25–75, 50–50, 75–25 blends show both the large melting region characteristic of

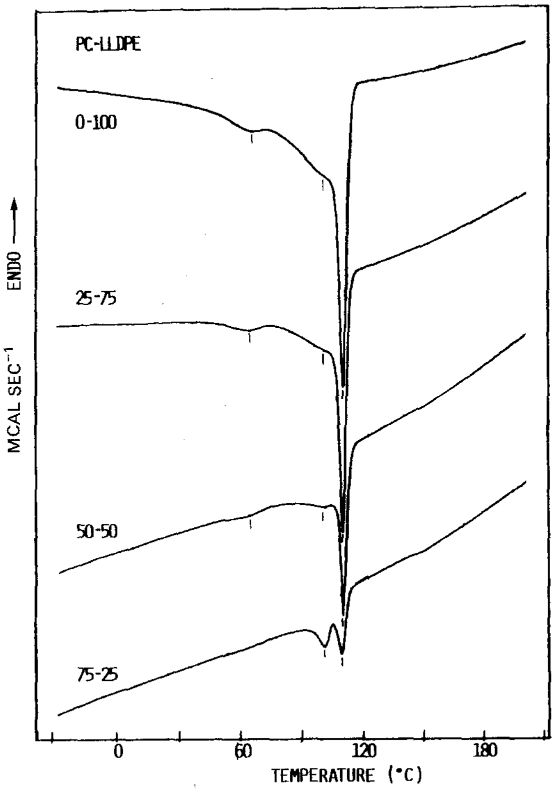

Figure 3 DSC thermograms of sections perpendicular to the slab surface of PC–LLDPE blends, on cooling from the melt at 250° C (cooling rate: 10° C min^{-1}). All curves are normalized to 1 mg sample weight.

LLDPE, with a maximum around 124° C, and the glass transition of PC at about 150° C. It can be observed that the melting and the glass transition temperatures of the two polymers in the various blends are scarcely affected by the blend composition, in agreement with the results obtained by other research groups [5].

As shown in Fig. 3, on cooling from the melt, multiple crystallization exotherms have been recorded for pure LLDPE and PC–LLDPE 25–75 and 50–50 blends, with sharp peaks around 110° C and large shoulders at about 100 and 65° C. In the case of the blend with the lowest LLDPE content (PC–LLDPE 75–25) two distinct crystallization peaks are present at 109.5 and 111° C, respectively. A similar crystallization behaviour, characterized by multiple peaks in the same temperature range, has also been reported by other authors [6, 7] for different commercial LLDPE samples cooled from the melt into DSC.

On subsequent heating of the slow cooled PC–LLDPE samples (run II), melting endotherms with a broad peak at about 114° C, followed by another sharp and intense peak at 124° C, have been recorded both for pure LLDPE and blends. On the contrary, a single melting peak at about 120° C was observed for samples quenched from the melt to $-150°$ C directly into DSC, in agreement with a similar finding for other LLDPE samples [8].

Melting and glass transition temperatures of PC–LLDPE blends recorded on run II remain practically constant, independent of LLDPE content as observed for run I. These facts support the incompatibility of the two polymer components.

In Fig. 4 the values of the melting enthalpy ΔH_m of the various blends are plotted against the LLDPE content (in wt %) for runs I and II, respectively. In both cases an almost linear variation of ΔH_m with the composition can be observed. However, the corresponding values of the melting enthalpy and entropy per gram of LLDPE in the blends decrease with decreasing LLDPE content, suggesting existence of major imperfections in the crystalline phase of the samples with higher PC content. This fact indicates that the crystallization processes of the LLDPE crystals in the blends are affected to a certain extent by the composition of the system.

3.1.2. *Sections parallel to the slab surface*

In order to investigate more extensively the role of extrusion process on the thermal properties and morphology of the various PC–LLDPE blends, we analysed in DSC the melting behaviour of sections cut parallel to the surface of 6 mm thick slabs, at various depths (see Fig. 1).

In Fig. 5 DSC thermograms are shown of the top, middle and bottom layers of an as-received LLDPE slab, on heating from 40 to 180° C at 10° C min^{-1}. It appears that melting curves of the various layers of the slab (curves a to c) are different with respect to the thermogram of the perpendicular section of the same sample shown in Fig. 2. The thermograms of the top and bottom layers are characterized by the presence of three distinct melting peaks: the first, broad and shallow, between 95 and 101° C, the second ranging from 109 to 117° C, and the third, narrow and sharp, at 121° C. The thermogram of the middle layer shows

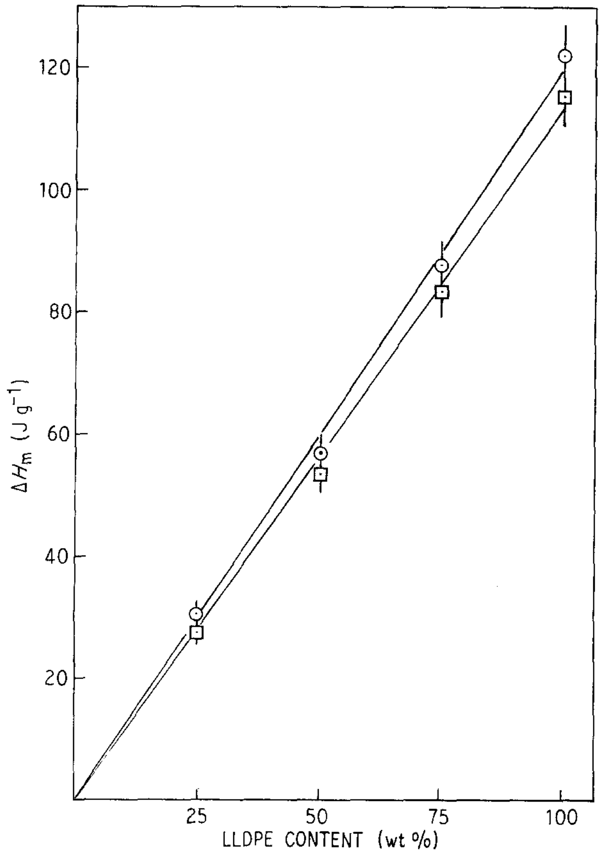

Figure 4 Melting enthalpy ΔH_m per gram of PC–LLDPE blend as a function of the blend composition. Run I: (○); run II: (□).

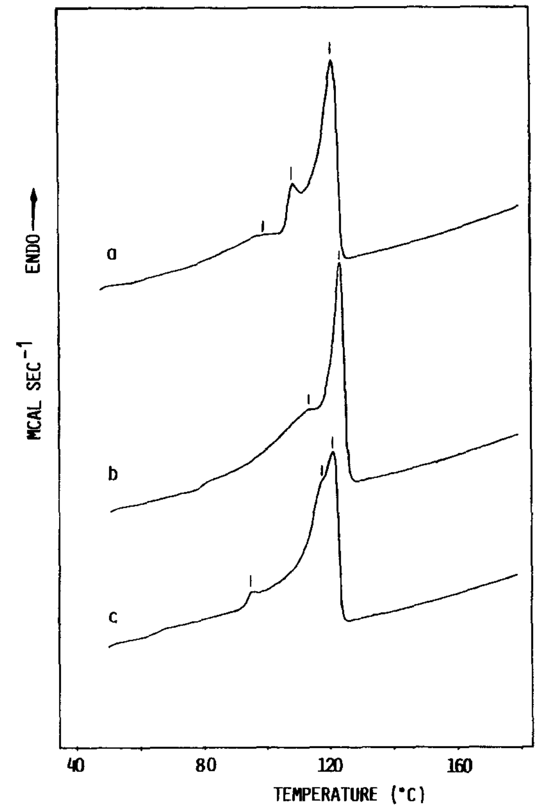

Figure 5 DSC melting thermograms of sections parallel to the slab surface of LLDPE extruded sample (heating rate: 10° C min^{-1}). (a) Top layer (d = 0 mm), (b) middle layer (d = 3 mm); (c) bottom layer (d = 6 mm).

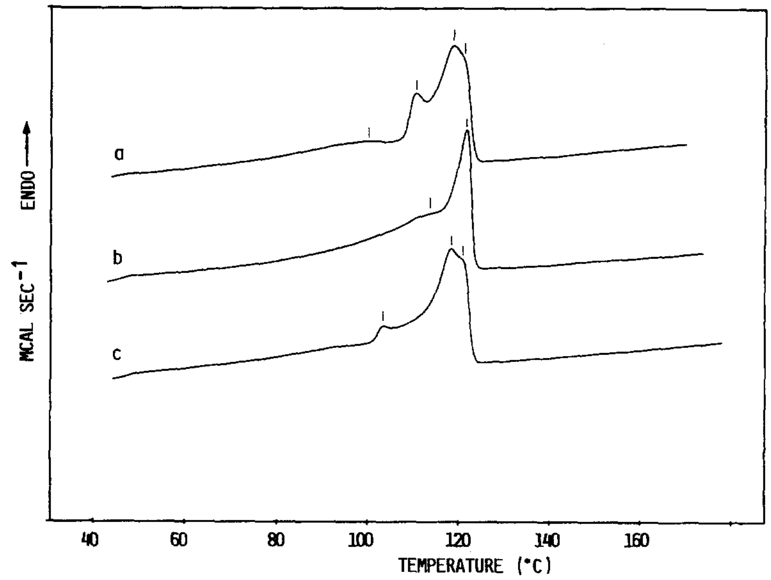

Figure 6 DSC melting thermograms of sections parallel to the slab surface of PC–LLDPE 25–75 blend (heating rate: 10° C min^{-1}). (a) Top layer (d = 0 mm); (b) middle layer (d = 3 mm); (c) bottom layer (d = 6 mm).

a very broad melting transition at 114° C followed by a sharp peak at a temperature near 124° C.

The differences observed in the melting behaviour of the various layers may be accounted for by the presence in these samples of different crystal types, with distinct morphological characteristics (structure, lamellar thickness, orientation) and thermal stability. Moreover, an important role can be played by differences in the cooling conditions of the surface and internal layer of the slabs during the post-extrusion processes.

A multiple melting behaviour has also been described by Datta and Birley [6, 7] for some LLDPE samples. For samples fast cooled from the melt they found three melting peaks between 107 and 124.5° C, whereas only two melting peaks in the same range were observed for slow cooled ones. This behaviour was ascribed to the existence of two crystalline species, one responsible for the low temperature melting peak and the other for the high temperature melting peak. The intermediate peak, appearing in the case of fast cooled samples, was interpreted as due to the cocrystal formation of the two crystal species. However no structural evidence has been supplied to support these conclusions.

As far as our samples are concerned, it is reasonable to assume that, owing to the higher cooling rate of the surface layers with respect to that of the inner layers, the presence of lower melting peaks at temperatures around 100° C in the thermograms of the top and bottom layers, is probably due to polymer fractions which crystallized separately in a different and less ordered way as compared with higher melting crystals. The peaks at higher temperatures, in the range 114 to 124° C, can conversely be associated with the occurrence of reorganization (or melt recrystallization) phenomena of the crystals during the heating run in DSC. According to previous suggestions, Edward [8] related the melting behaviour of LLDPE samples to the lamellar thickness of the crystals and found a bimodal distribution of the thicknesses also in the case of samples slow cooled from the melt.

The melting thermograms of the surface and middle layers of PC–LLDPE 25–75, 50–50 and 75–25 blends are reported in Figs 6, 7 and 8, respectively. In all cases distinct melting behaviours of the various layers (similar to that found for plain LLDPE) have been observed. However for PC–LLDPE 25–75 blend (Fig. 6) an additional peak (as compared with the corresponding curve of LLDPE) at about 118° C

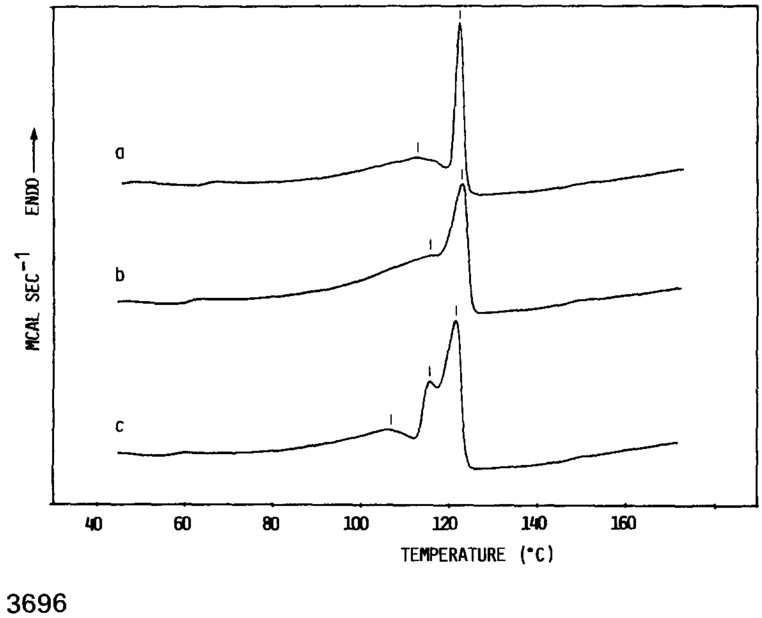

Figure 7 DSC melting thermograms of sections parallel to the slab surface of PC–LLDPE 50–50 blend (heating rate: 10° C min^{-1}). (a) Top layer (d = 0 mm); (b) middle layer (d = 3 mm); (c) bottom layer (d = 6 mm).

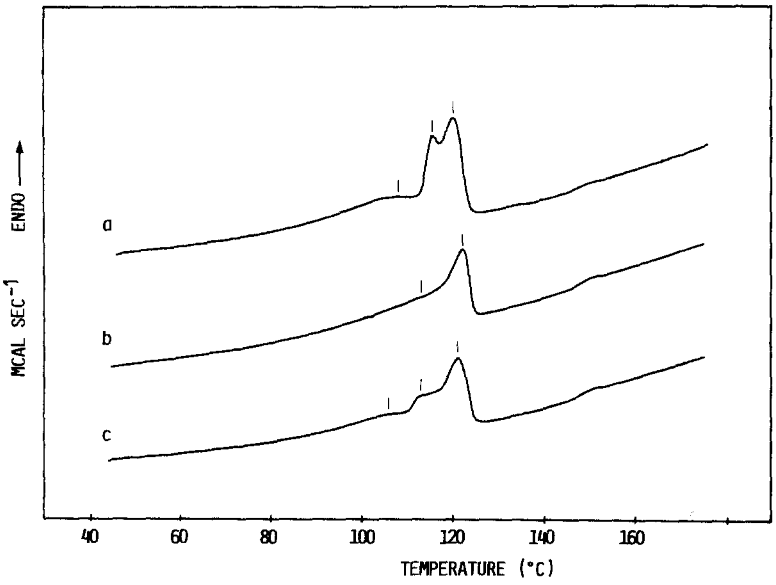

Figure 8 DSC melting thermograms of sections parallel to the slab surface of a PC–LLDPE 75–25 blend (heating rate: 10° C min^{-1}). (a) Top layer (d = 0 mm); (b) middle layer (d = 3 mm); (c) bottom layer (d = 6 mm).

in the DSC curve of the top layer should be noted. In the case of the 50–50 blend (Fig. 7) the thermogram of the top layer shows only two peaks at about 115 and 122° C, respectively, rather similar to those recorded for the middle layer.

The peak temperatures of LLDPE and PC–LLDPE blends are reported in Table I. With varying composition, the largest differences of melting temperatures were observed for the lower and intermediate melting peaks of the surface layers, whereas the temperatures of the higher melting peaks were similar throughout. Some variations of the melting temperatures and intensity of the peaks have been also found with varying the layer thickness. Moreover it is important to stress that no significant differences were observed in the melting thermograms of the same layers after they were cooled from the melt in DSC. This fact supports the hypothesis that the different melting behaviour observed for the various layers of the as-received samples can only be ascribed to the effects of the extrusion process.

In Table II, values of the melting enthalpies ΔH_m per gram of blend, are compared for all the examined blends and for different layer thickness. It is possible to see, within the limits of reproducibility of the measurements, that some differences exist between ΔH_m values of the surface layers with varying the thickness. Particularly, in the case of PC–LLDPE 75–25 blend for thinner surface layers (~0.1 mm) values of ΔH_m about twice larger than those found for thicker layers (0.5 mm), are observed. Such differences can be related mainly to the composition of the surface layers in the blends. In fact, the higher values of ΔH_m observed for the sample with the lowest LLDPE content may suggest the presence of thin regions, both at the top and the bottom of the extruded slabs, richer in LLDPE (Figs 9a and b). This probably arises from the migration of LLDPE toward the slab surfaces, due to the viscosity differences between the two components in the melt and owing to the forces acting on the system during the extrusion.

These results are confirmed by electron microscopy investigations and IR analysis which clearly evinced the presence of distinct morphological features and variations of distribution of the two components through the thickness [9]. It is noteworthy that for the 75–25 blend all the results confirm the presence of a surface monophase layer of LLDPE in the slabs.

TABLE I Melting temperatures T_m of sections cut parallel to the slab surface of extruded PC–LLDPE blends

PC–LLDPE (w/w %)	T_m (° C)		
	Top Layer* (d = 0 mm)	Middle Layer* (d = 3 mm)	Bottom Layer* (d = 6 mm)
0–100	101		95
	108.8	114	117
	121.5	123.6	121.2
25–75	100.3		96
	110.4		103.8
	119	113	118.6
	121.3	123.2	121.3
50–50			107
	114	116.4	115.9
	123.2	123.1	121.7
75–25	109.5		106
	118	113	113.5
	123.3	122.2	121.2

*Average thickness: 0.5 mm

3.2. Crystallization kinetics

In order to investigate the effect of the blend composition on the crystallization behaviour of LLDPE from the melt we examined in DSC the crystallization kinetics of the PC–LLDPE blends at various temperatures in the range 105 to 118° C.

For crystallization temperatures T_c lower than

TABLE II Melting enthalpies ΔH_m of sections cut parallel to the slab surface of extruded PC–LLDPE blends

PC–LLDPE (w/w %)	ΔH_m (J/g blend)		
	Top Layer* (d = 0 mm)	Middle Layer* (d = 3 mm)	Bottom Layer* (d = 6 mm)
0–100	96.2	99.8	96.2
25–75	76.1–70.6†	78.3	79.8–68.8†
50–50	47.8–45.8†	47.6	47.9–52.1†
75–25	20.5–42.8†	20.6	21.8–39.0†

*Average thickness: 0.5 mm.

†Values determined for layer thicknesses of ~0.1 mm.

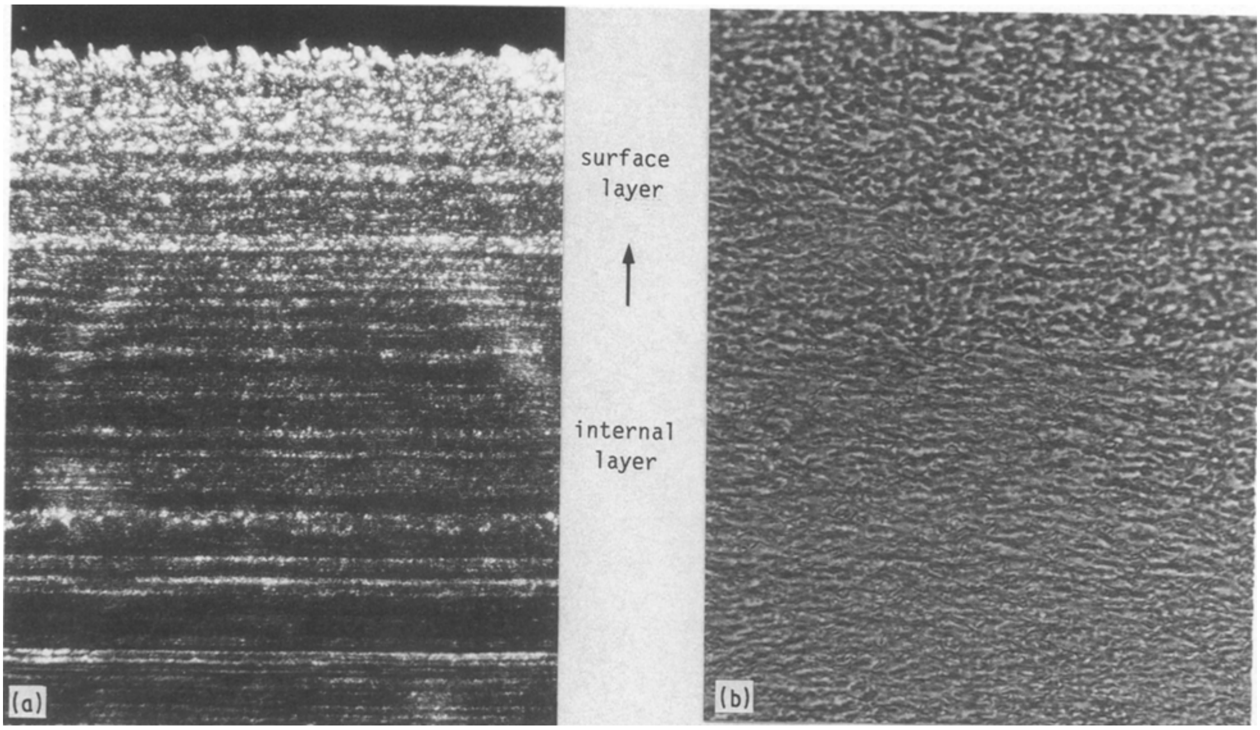

Figure 9 Optical micrographs of a microtomed perpendicular section (thickness = 10 μm) cut from a 2 mm thick slab of PC–LLDPE 75–25 blend, showing (a) (crossed Nicols, 121 ×) different distributions of the birefringence due to the LLDPE crystals and (b) (parallel Nicols, 777 ×) distinct morphological characteristics of surface and internal layers of the slab, respectively.

112° C the crystallization rate of LLDPE is so high that for all the blends the process generally occurs within a time interval of a few minutes. Under these conditions no differences can be observed for the various samples. On the contrary, for T_c higher than 112° C the crystallization of LLDPE takes place over longer periods of time and it is possible to quantitatively analyse the kinetics under isothermal conditions.

In Fig. 10 plots of the crystallinity fraction X_t as a function of crystallization time at $T_c = 118°\mathrm{C}$ are reported for LLDPE, PC–LLDPE 25–75 and 75–25 blends. It can be noticed that the crystallization isotherms are shifted along the time axis with varying the concentration of the crystallizable component LLDPE. Thus, in the case of PC–LLDPE 75–25 blend the time necessary for the completion of the crystallization at 118° C is about twice as large as that of the PC–LLDPE 25–75 blend. Values of the crystallization half-time $t_{0.5}$ of the various blends are listed in Table III at two different T_c.

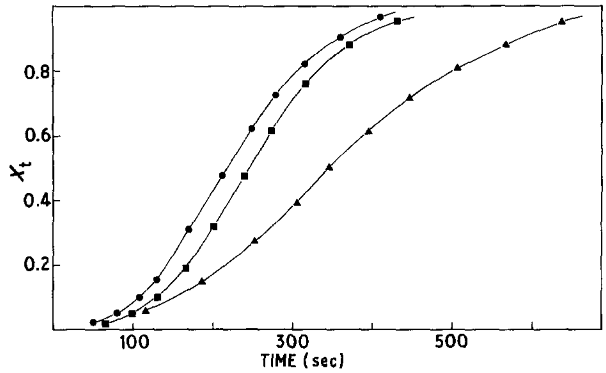

Figure 10 Isotherms of crystallization from the melt of LLDPE (●). PC–LLDPE 25–75 blend (■), and PC–LLDPE 75–25 blend (▲), as a function of the crystallization time t at $T_c = 118°\mathrm{C}$.

The results indicate that the overall crystallization rate of LLDPE in the blends decreases with increase of PC concentration. These findings are in agreement with those found for other heterogeneous systems containing polyolefins [10, 11] where marked reduction of the overall crystallization rate of the crystallizable component in the blends was reported.

The kinetics of isothermal crystallization of all the blends investigated can be described by means of the Avrami equation [12].

$$X_t = 1 - \exp(-k_n t^n) \qquad (1)$$

where n is the Avrami constant which depends on the growth geometry and nucleation type of the crystals, and k_n is the kinetic constant related to the crystal growth rate. The values of n and k_n for all the blends (reported in Table III) have been determined respectively from the slopes and the intercepts of linear plots of $\log[-\ln(1 - X_t)]$ against $\log t$. The Avrami constant has an average value of about 2.6, which is comparable to those reported in the literature for

TABLE III Values of half-time of crystallization $t_{0.5}$, Avrami constant n and kinetic constant k_n for PC–LLDPE blends isothermally crystallized from the melt at different T_c

PC–LLDPE (w/w %)	T_c (° C)	$t_{0.5}$ (sec)	n	k_n (sec^{-n})
0–100	115	84	2.5	1.3×10^{-5}
	118	217	2.6	5.6×10^{-7}
25–75	115	90	2.7	3.5×10^{-6}
	118	244	2.8	8.9×10^{-8}
50–50	115	92	2.6	6.3×10^{-6}
	118	249	2.4	1.0×10^{-6}
75–25	115	107	2.4	1.2×10^{-5}
	118	347	2.4	5.5×10^{-7}

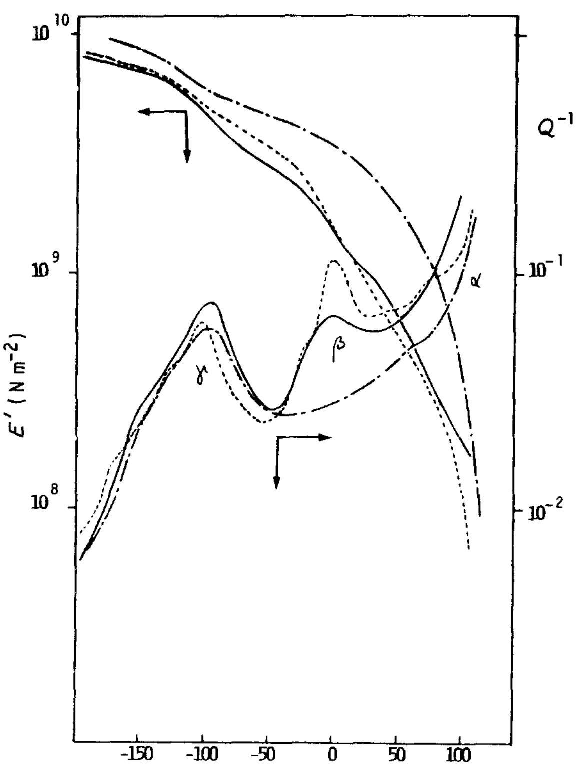

Figure 11 Temperature dependence of the Young's modulus E' and damping factor Q^{-1} for various polyethylene samples: LLDPE (——), HDPE (–·–·–·–) and LDPE (····).

linear polyethylenes [13]. The observed variations of the kinetic parameters for the various blends could be accounted for mainly by an effect of the composition on the crystal nucleation processes from the melt, particularly at lower concentration of the crystallizing polymer [2, 3].

3.3. Dynamic-mechanical behaviour

In Fig. 11 the Young's modulus E' and the damping factor Q^{-1} (the reciprocal of the resonance coefficient) of LLDPE and conventional high and low density polyethylenes (HDPE and LDPE) are plotted as a function of temperature in the range from −180 to 100° C.

It can be observed that, with increasing temperature, the modulus E' of LLDPE steadily decreases over the explored range showing three marked changes of the slope dE'/dT at about −130, −20 and 40° C. Correspondingly, the curve of the damping factor Q^{-1} exhibits two maxima, the first (γ-transition) at about −98° C, the second (β-transition) around 0° C, whereas a continuous increase of mechanical loss is observed with increasing temperature above 50° C (α-transition region).

The dynamic-mechanical behaviour of LLDPE is similar to that shown by low density polyethylene [14, 15]. The maxima of the γ- and β-transitions of these polymers are located practically at the same temperatures but the width of the β-relaxation peak is more restricted in the case of LDPE. Analogously to the conventional polyethylenes the γ-transition of LLDPE can be connected with the onset of motions of methylene units both in the amorphous and the crystalline phases of the polymers [16]. The β-transition is attributed to motions of the main chain segments containing branch points.

It has been observed by many authors that the β-peak decreases in height and shifts to higher temperatures as the degree of branching decreases and nearly disappears in high density polyethylene [14]. Thus the width reduction of β-transition region observed for LLDPE, with respect to that of LDPE, can be interpreted as due to different molecular structure of the former as compared with the latter polymer, particularly as the number, length and distribution of the branchings are concerned (for LLDPE these are the origin of a restriction in the relaxation times distribution).

The α-region, characterized by a continuous increase of mechanical loss with increasing temperatures, has been ascribed to vibrational and reorientational motions of $-CH_2-$ sequences within the crystals [16].

In Fig. 12 the temperature dependence of modulus and damping factor for PC–LLDPE blends are compared with those of neat LLDPE and PC.

In the $E' - T$ curve of 100% PC sample two changes of slope can be observed, one of low intensity at about 90° C and another, very strong, at about 145° C. Correspondingly, an extended mechanical relaxation region is noticed in the Q^{-1} curve from about −170 to about 45° C (β-transition), culminating in a small but well defined maximum at −40° C. A rapid increase of mechanical loss, accompanied by a sudden decrease of modulus, is observed at temperatures above 140° C.

The extended loss region of polycarbonate, characterized by various shoulders in the Q^{-1} curve, has been investigated by several authors by means of dynamic-

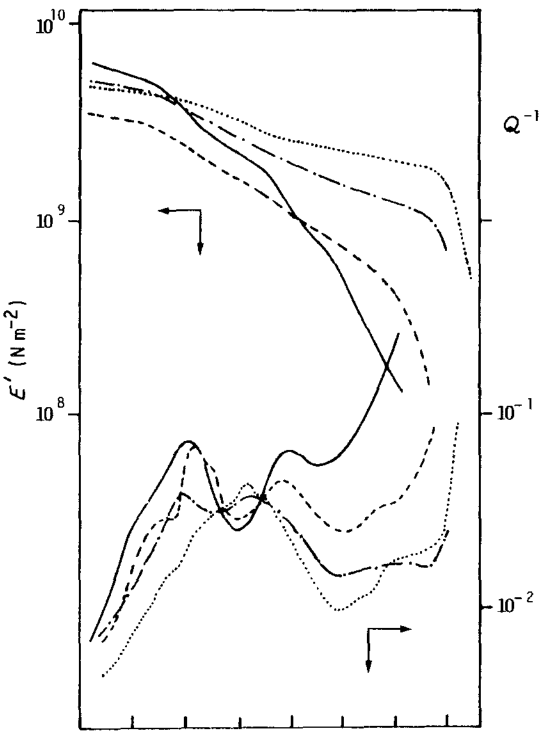

Figure 12 Temperature dependence of the Young's modulus E' and damping factor Q^{-1} for extruded PC–LLDPE blends at various compositions: 0–100 (——), 50–50 (— —), 75–25 (–·–·–·–) and 100–0 (····).

mechanical, dielectric and NMR measurements [14]. Such a behaviour seems to be due to the overlapping of more than one relaxation phenomenon connected with the rotation of methyl groups and coupled motions of phenylene and carbonate groups [17]. Moreover, the α-transition region is clearly associated with the glass transition of the polymer.

In the case of PC–LLDPE blends all the transitions of the component polymers can be recognized. The variation of the damping factor for the 25–75 blend is practically coincident with that observed for neat LLDPE, whereas small shifts of the damping maxima have been found for the other blends as compared with neat components. In particular, a complex behaviour is observed in the γ-transition region of the 50–50 blend with the presence of multiple peaks. However, it must be borne in mind that these effects are strongly dependent on the overall morphology of the samples, i.e. on the phase distribution and type of the polymer components.

4. Concluding remarks

The DSC analysis of PC–LLDPE blend, obtained either by melt extrusion or by cooling from the melt, shows that melting, crystallization and glass transition temperatures of the components are little affected by composition as expected for the incompatible blends.

Sections of blends, cut parallel to the surfaces of the extruded slabs, exhibit different melting behaviours which can be accounted for by the presence of LLDPE crystals with different morphological characteristics and thermal stability. Moreover, the melting enthalpy of the surface layers of the blend with higher PC content is found to vary with the layer thickness. These facts indicate the existence of a non-uniform morphology and distribution of the components within the extruded samples. This is also confirmed by the results of electron microscopy and IR analysis.

The crystallization processes of LLDPE from the melt are affected by the presence of PC kinetic measurements by DSC show that the overall crystallization rate of LLDPE is decreased in samples with high concentrations of PC.

The dynamic mechanical behaviour of the blends is in agreement with previous results. The modulus, transitions and relaxations of the components remain substantially unchanged with composition. However, some anomalies are observed in the γ-transition region for some samples. This can be ascribed to the occurrence of different morphology and phase distribution of LLDPE and PC within the slabs, due to the processing conditions.

Acknowledgement

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