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Morphology of linear PE blends crystallized at the transition temperature between regime I and regime II growth

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SUMMARY

Binary blends of linear PE sharp fractions [M_w=2 500 (L2.5) and 66 000 (L66)], all crystallized at the temperature of the transition between regime I and regime II growth, have been studied by TEM after Kanig treatment. It is shown that the dominant lamellae are always long and straight and form stacks. The number of lamellae in these stacks decreases with increasing content of L2.5. The lamellar width perpendicular to [010] is 1-3 μm for L66 and the 50/50 blend, but anomalously high for the 80/20 (L2.5/L66) blend. Thin subsidiary lamellae are observed only in the 50/50 and 80/20 blends. A significant fraction of these samples contains domains of segregated L2.5 showing no lamellar contrast.

INTRODUCTION

In previous work (1,2), the morphology and crystallization kinetics of binary linear PE blends of several compositions based on sharp fractions of M_w = 2 500 (L2.5) and 66 000 (L66) have been extensively studied. It was shown (2) that at crystallization temperatures higher than 393 K only the high molecular weight component (L66) crystallizes. The surface free energy of the fold surface was not found to be affected by the presence of the L2.5 component. The transition from the regime I to regime II crystallization occurred at 16.5 K supercooling (with respect to the equilibrium melting point of the pure crystallizable component L66) for both L66 and L2.5/L66 (0.5/0.5 w/w) and at 17.5 K supercooling for L2.5/L66 (0.8/0.2). This 1 degree K difference was interpreted as a 50% reduction in crystal substrate length based in the Z test of Lauritzen (3). At intermediate temperatures both components crystallize, but in separate crystal lamellae (2). The crystallization of L2.5 was however found to be promoted by the presence of L66. At low temperatures of crystallization (383 K), partial co-crystallization of the components in the blend occurred.

In this paper, transmission electron microscopy data are presented for three different blends of L2.5 and L66 (0/1, 0.5/0.5 and 0.8/0.2), all three crystallized at the temperature of the transition from regime I to regime II kinetics. Morphological features, data for the thickness and width of the crystal lamellae and the thickness

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EXPERIMENTAL

The linear PE fractions, L2.5 (M_w=2 500; M_w/M_n = 1.15) and L66 (M_w=66 000; M_w/M_n = 1.1), previously described in ref. (2) were used in this study. Binary blends (0.5/0.5 and 0.8/0.2 by weight in L2.5/L66) were prepared by a solution mixing technique earlier described in ref. (1). Both the blends and L66 were melted in a Perkin-Elmer DSC-2 at 450 K, cooled at a rate of 80 K/min down to the crystallization temperature T_c, held at T_c for a time t_c (L66:T_c=401 K, t_c=1380 min; L2.5/L66 (0.5/0.5): 398 K, 1380 min; L2.5/L66 (0.8/0.2): 396 K, 1440 min) and finally cooled to room temperature at a rate of 80 K/min. The selected crystallization temperatures were the same as the temperatures (denoted $T_{I\text{-}II}$) of the transition between regime I and regime II crystallization (2).

The samples were subsequently treated according to the Kanig method (4): small pieces were treated in chlorosulphonic acid at 306 K for 2 days, stained with a 0.7% aqueous solution of uranyl acetate, embedded in epoxy and finally sectioned with a glass-knife-equipped LKB microtome at room temperature. Sections of 50-100 nm thickness were examined in a JEOL JEM 100B electron microscope.

The micrographs were analysed using magnified images of the negatives. Characteristic dimensions (thickness, apex angles, etc.) of crystal lamellae and amorphous layers were measured from selected areas showing the best contrast. This can only be achieved when the crystal lamellae lie in a plane nearly parallel to the electron beam (5). The crystal lamellae appear white and the amorphous layers black. Approximately 400 crystals and 400 amorphous layers were measured for each sample. The accuracy of the measurement is estimated to be 1 nm. Shrinkage of the thin sections may take place when exposed to the electron beam even at low intensities (5). However, as far as we know, no quantitative study has been performed to correct for this shrinkage and in this work no attempt was made to correct the thickness data.

The melting endotherm and the mass crystallinity (heat of fusion for 100% crystalline polymer = 293 kJ/kg (6)) of the samples were obtained in a temperature and energy calibrated Perkin-Elmer DSC-2 at 10 K/min.

RESULTS AND DISCUSSION

A few typical electron micrographs of the studied samples are presented in Fig. 1. A significant proportion of the sections contain areas of low contrast. As the crystal lamellae grow in all directions, a substantial fraction of the lamellae will be tilted with respect to the electron beam and hence give rise to areas of low lamellar contrast. Another reason for the lack of contrast, particularly relevant for this study, is the presence of isolated domains of low molecular weight material (2,7). It is known that low molecular weight species form extended-chain crystals with almost no amorphous interphase (7,8) and that the chlorosulphonic acid does not penetrate the interlamellar phase (2,7).

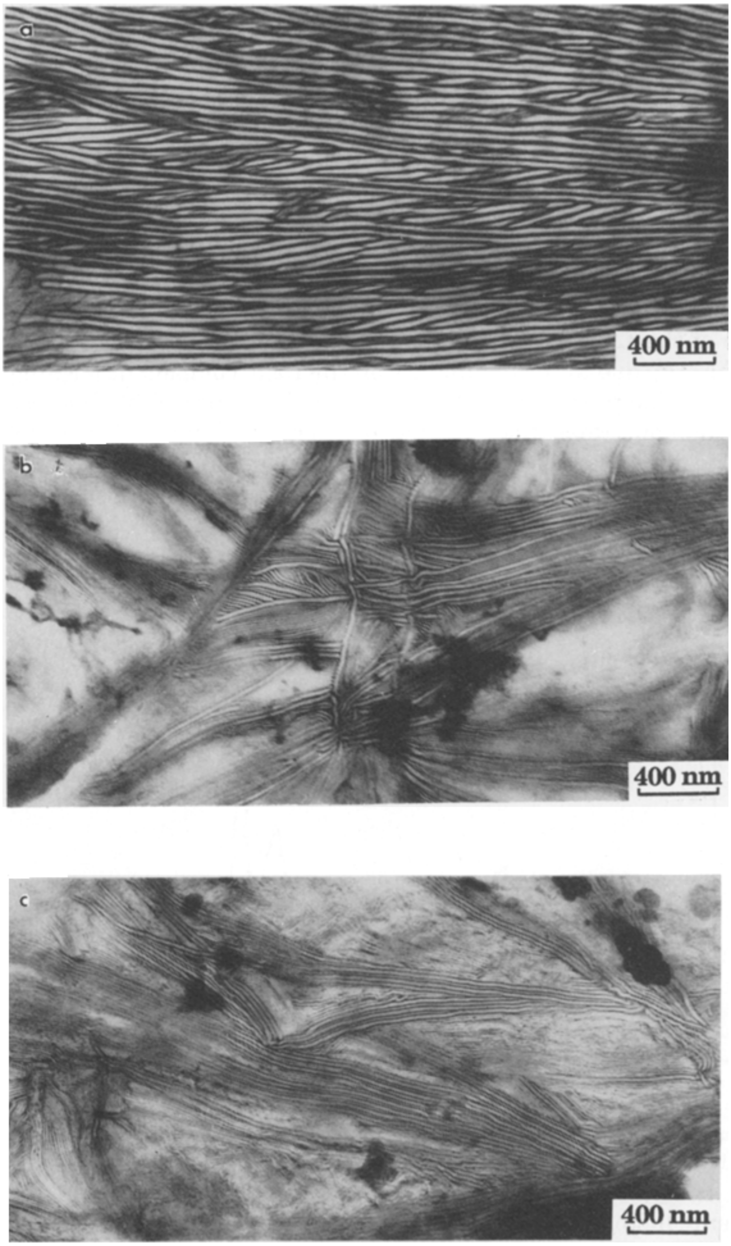

Fig. 1. Transmission electron micrographs of samples treated according to the Kanig method: (a) L66 (b) L2.5/L66 (0.5/0.5) (c) L2.5/L66 (0.8/0.2).The samples have been crystallized under the conditions shown in the Experimental section.

Lamellar structures of good contrast are a general feature of L66 (Fig. 1a). The lamellae are long, straight and arranged in large stacks of parallel lamellae. The uniformity in lamellar thickness is another characteristic of this sample. The DSC trace shown in Fig. 2 reveals a sharp, unimodal melting peak and is consonant with electron microscopy data.

In the 50/50 blend (Fig. 1b) smaller stacks of long and straight dominant crystal lamellae surrounded by areas of thinner subsidiary lamellae are observed. Roof-ridge-shaped lamellae are occasionally observed. This sample displays bimodal melting (Fig. 2). The low temperature melting peak relates to about 50% of the sample and is associated with the subsidiary lamellae formed during the cooling phase. About 15% of the total sample consists of areas without lamellar contrast associated with extended-chain crystals essentially composed of L2.5.

In the case of the L2.5/L66 0.8/0.2 sample, most of the sections have no lamellar contrast (Fig. 1c), due to the dominance of the L2.5 component forming extended-chain crystals. The presence of holes in the sections, most probably created by the sectioning, demonstrates the extreme brittleness of the low molecular weight material. The minor portion consisting of stacks of dominant lamellae contains long and straight lamellae. The number of lamellae in these stacks is low.

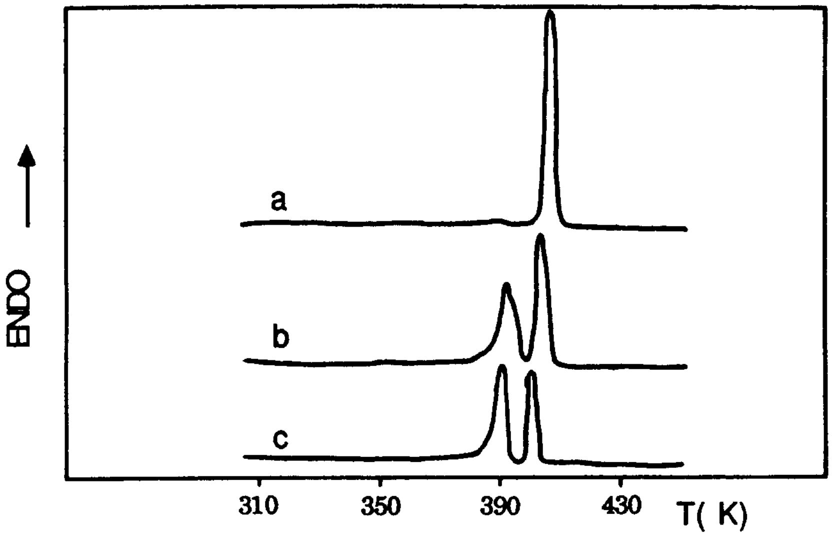

Fig. 2. Melting thermograms of (a) L66; (b) L2.5/L66 (0.5/0.5), (c) L2.5/L66 (0.8/0.2); The samples have been crystallized under the conditions shown in the Experimental section.

Fig. 3 presents histograms for the distributions in thickness of crystal lamellae (L_c) and amorphous interlayer (L_a). It is generally found that the L_a distributions are unimodal and significantly sharper than the L_c distributions. The L_c distributions differ greatly between the different samples. L66 exhibits a unimodal distribution in L_c which is in agreement with its sharp and unimodal melting shown in Fig. 2. The 50/50 blend has an almost symmetrical distribution with two pronounced maxima centering at 10.5 nm (subsidiary lamellae) and 17.5 nm (dominant lamellae). It is probable that the subsidiary lamellae contain a mixture of low molecular weight species from L66 and high molecular weight species from L2.5. The L_c distribution of L2.5/L66 0.8/0.2 also has a bimodal character for similar reasons as the 50/50 blend. Table 1 presents data for L_c and L_a together with a comparison of mass crystallinity obtained by TEM and DSC respectively. The agreement between the two sets of crystallinity data is excellent. The crystal thickness values here reported are however low in comparison with estimates based on other techniques for similar samples (cf. data presented in ref. (9)). This discrepancy has been noticed before (10) and may be due to shrinkage of the section by the action of the electron beam (5).

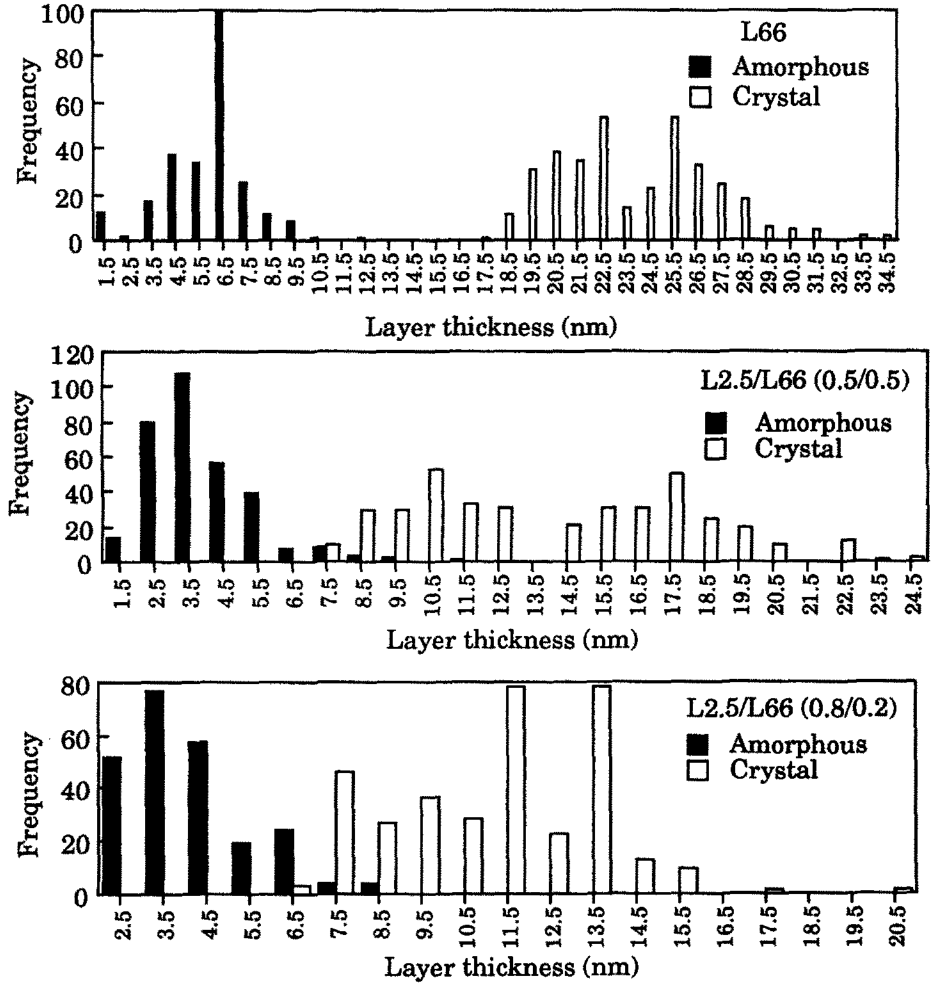

Fig. 3. Histograms showing the distribution in amorphous layer thickness and crystal thickness for the different samples as are shown in the diagrams.

Table 1. Average thickness of crystals ($<L_c>$) and amorphous layer ($<L_a>$), mass crystallinity (w_c), defect content (D_e) and lamellar width (w)

Sample	$<L_a>/<L_c>^a$ (nm)	w_c^b/w_c^c	D_e^d $(\mu m)^{-2}$	w^e (μm)
L66	5.9/24	0.83/0.80	15.3	2.7
L2.5/L66(0.5/0.5)	3.9/14.1	0.81/0.83	58.5	1.2
L2.5/L66(0.8/0.2)	4.1/11.2	0.76/0.77	8.5	10.5

a) Arithmetic mean values

b) By TEM according to the following eqs.:

$$v_c = <L_c>/[<L_c> + <L_a>] \quad ....(1)$$

$$w_c = 1/[1 + \rho_a/\rho_c(1-v_c)/v_c] \quad ....(2)$$

where v_c is the volume crystallinity , w_c is the weight crystallinity , ρ_a and ρ_c are the densities of the amorphous and crystalline phases respectively. Values from the literature (14) for ρ_a and ρ_c are inserted in eq. 2 to calculate w_c.

c) By DSC

d) D_e = edge defects per $(\mu m)^2$ section and is equal to $Dr/(r+1)$,; D is the number of defects per $(\mu m)^2$ section area and r is the ratio of edges to screw dislocations.

e) Mean crystal width; $w = (<L_c>D_e)^{-1}$

The 50/50 blend in particular showed both in stacks of dominant and subsidiary lamellae occasional lamellae shaped as "roof-ridges". These are visible only when the roof gable is perpendicular to the thin section (11), indicating that the roof gable is along [010]. The apex angles result from different combinations of (h0l) crystallographic planes (12). The most common apex angles are 108°, 111°, 119°, 126° and 135°. These are associated respectively with (301)(302), (201)(201), (201)(302) and (101)(302). Chain tilt angles between 18° and 45° are indicated by the data obtained.

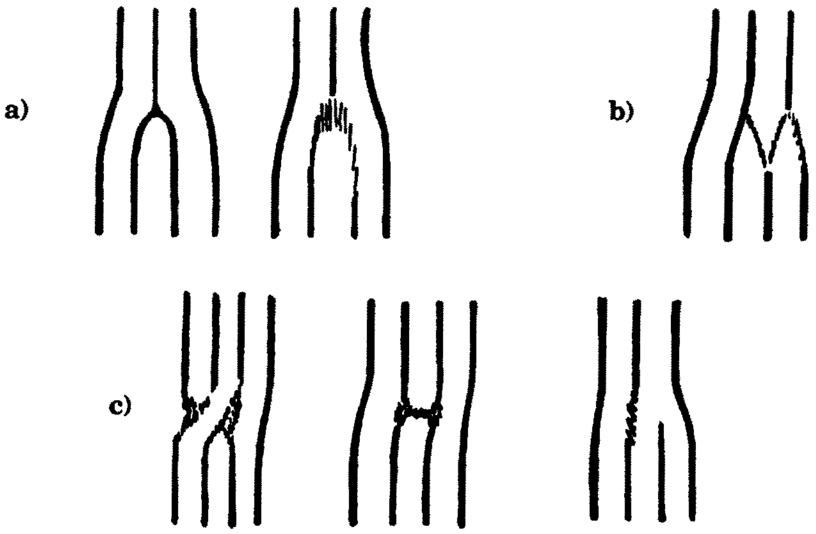

FIGURE 4. Classification of defects in accordance with Grubb and Keller (5); (a) Edge of crystal (b) screw dislocation (c) indeterminate defect

A question which was addressed in the introductory section of this paper is whether there is a decrease in width (perpendicular to [010]) of crystal lamellae (so-called substrate length) with an increasing content of L2.5 in the blends. Our analysis of the electron micrographs has followed the method/classification system earlier used by Grubb and Keller (5). Three classes of defects exist in the lamellae: edges, screw dislocations and indeterminates (Fig. 4). The indeterminate defects were found to be very few, less than 5% of the total number of defects. The data from this analysis are presented in Table 1. The crystal width data obtained for L66 and the 50/50 blend are similar to earlier data reported by Bassett et al (13) who found values between 0.7 and 1 µm for quenched PE samples. Based on crystallization kinetic data, Hoffman (3) calculated a value for the substrate length at $T=T_{I\text{-}II}$ of 0.77 µm. For L2.5/L66 0.8/0.2 there is an unexpected and very significant increase in width of the dominant lamellae, clearly in disagreement with theory.

CONCLUSIONS

Three binary mixtures of two linear PE sharp fractions [M_w= 2 500 (L2.5) and 66 000 (L66)], all three crystallized at $T_{I\text{-}II}$, have been studied and the question here addressed is whether the lamellar morphology is the same in the different samples.

It appears that the dominant lamellae are always long and straight and form stacks. The number of dominant lamellae in a stack decreases strongly with increasing content of L2.5. The lamellar width perpendicular to [010] is 1-3 µm for the pure high molecular weight component and the 50/50 blend, but anomalously higher for the blend containing 80% of L2.5. The lamellar thickness decreases with increasing content of L2.5 and is thus related to the absolute crystallization temperature rather than to the degree of supercooling.

Thin subsidiary lamellae are observed only in the 50/50 and 80/20 blends. These subsidiary lamellae contain a mixture of low molecular weight species from L66 and high molecular weight species from L2.5. Significant portions of the sections of these samples contain "blank" areas showing no lamellar contrast composed of segregated L2.5.

The amorphous interlayers exhibits similar sharp, unimodal distributions in all the samples studied.

ACKNOWLEDGEMENTS

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