Structure–property relationships in annealed blends of linear low density polyethylene with isotactic polypropylene

Xiao-Qi Zhou and J. N. Hay*
The School of Chemistry, The University of Birmingham, Edgbaston, PO Box 363, Birmingham B15 2TT, UK
(Received 4 January 1993; revised 19 March 1993)

Blends of isotactic polypropylene (PP) and linear low density polyethylene (LLDPE) have been analysed by thermal analysis and wide-angle X-ray scattering to determine the effect of thermal history on morphology and mechanical behaviour. The blends were quenched directly from the melt, slow cooled and annealed at 130°C. In all cases it was observed that the two components were insoluble and the crystallization behaviour was determined by the blend morphology, particularly in dispersed PP domains in which heterogeneous nucleation was the rate determining step. Slow cooled specimens with the higher degree of crystallinity had the highest yield stresses, and the lowest elongation to break was achieved in the vicinity of 50% blends, characteristic of the effect of blend morphology on properties.

(Keywords: LLDPE; polypropylene; blend)

INTRODUCTION

Polyolefins are commercially important because of their relatively low cost and recently blending of polypropylene (PP) and polyethylene (PE) has become of increasing interest as a way of increasing impact strength[1] and improving low temperature toughness[2]. Another important reason is that PP and PE are major constituents of household plastic waste and recycling as a blend is of considerable value.

The physical properties of crystalline polymers and their blends are strongly influenced by their thermal history. Rapid quenching should not produce a well defined morphology in that the structures produced are not in thermodynamic equilibrium and should readily change during annealing. Schotland[3] has studied the post-crystallization annealing of PP in different temperature ranges and reported that annealing above 130°C increased the tensile modulus and yield stress. Similar changes have also been noted on annealing PE[4]. Although annealing in blends has not been so extensively studied, Varin and Djokovic[5] have studied the effect of annealing on PP/high density polyethylene (HDPE) blends at 130°C. They reported an increase in the elastic modulus and tensile yield stress and considered that the annealing treatment improved the bonding between the phase separated domains.

The present paper investigates the variation of crystalline structure, the degree of crystallinity, morphology and mechanical properties of blends of isotactic PP with linear low density polyethylene (LLDPE) and the effect of annealing at 130°C. The aim of this work is to study the annealing mechanism and the influence of annealing on blend structure and crystalline morphology as well as tensile properties.

EXPERIMENTAL

The samples of PE and PP used were commercial grades supplied by BP Chemical Co. Ltd. The isotactic PP was characterized by g.p.c. and had a M_w of 308 000, a M_n of 24 200 and a polydispersity of 12.7. Isobutyl branched LLDPE was used with a short chain branch concentration of 3.17 mol%, as measured by ^{13}C n.m.r. spectroscopy. It had a M_w of 145 000, a M_n of 25 800 and a polydispersity of 5.6 as measured by g.p.c. in dichlorobenzene at 130°C[6].

Blends with various compositions were prepared on an APV 2000 twin screw compounder. Each zone of the compounder — die, die-head and barrel zones — was set to 250°C. Sheets (1 mm thick) were obtained by pressing pellets of the blends between aluminium sheets in a hydraulic press at 240°C for 5 min. Immediately after pressing, the samples were quenched into cool water.

The annealing of blends was carried out either in the sample holder of the differential scanning calorimeter or in a thermostatically controlled forced air oven. Three types of samples having different thermal histories were used:

1. quenched samples subsequently annealed at 130°C for 24 h and then cooled to ambient temperature over 3 h, or cooled at 0.62 K min^{-1} in the differential scanning calorimeter after annealing. These samples will be referred to as 'slow cooled';
2. quenched samples annealed at 130°C for 24 h and subsequently requenched to room temperature, by plunging into water. These samples will be referred to as 'requenched';
3. the original quenched samples. These will be referred to as 'quenched' samples.

Melting and crystallization behaviour was studied using a Perkin–Elmer differential scanning calorimeter

---

[*] To whom correspondence should be addressed

0032-3861/93/224710-07

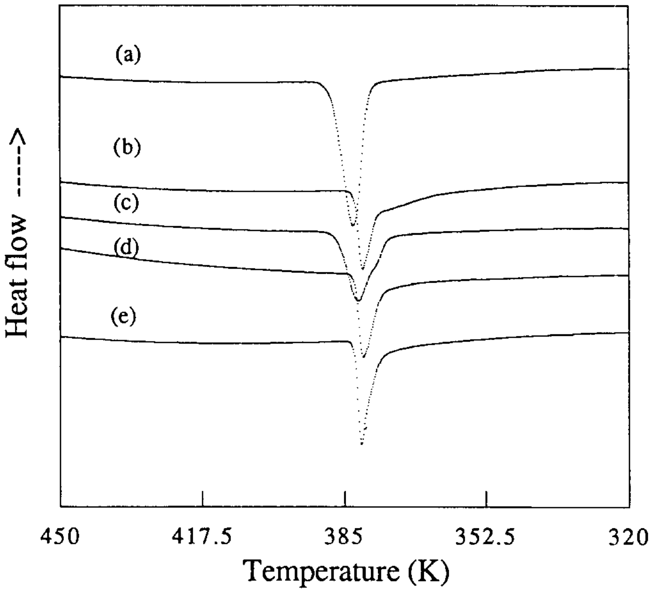

Figure 1 Crystallization exotherms of LLDPE/PP blends: (a) 0/100; (b) 30/70; (c) 70/30; (d) 90/10; (e) 100/0

(model DSC-2) interfaced to a BBC Master computer. The temperature scale of the calorimeter was calibrated from the melting points of indium, tin and stearic acid, and the thermal response from the enthalpy of fusion of indium. Corrections were made for thermal lag, as described previously[7].

X-ray diffraction measurements were made on a Picker automated power diffractometer using CuKα radiation at a scanning speed of 1° min^{-1} over a 2θ range from 7 to 65°, and data collection was made using a Phillips PW1710 diffractometer, programmed remotely by a Brother PC AT microcomputer. The data were then transferred to an IBM mainframe computer for further analysis. Flat samples ($20 \times 30 \times 10$ mm) were mounted directly into the diffractometer. The apparatus and sample position as well as curvature were calibrated using the sample coated with a thin layer (0.01 mm thick) of $Pd(NO_3)_2$ powder. The powder was removed and the sample rescanned without repositioning. The influence of X-ray transparency of the sample on peak positions was corrected as outlined by Langford and Wilson[8].

A Jeol model J5200 scanning electron microscope was used to examine the morphology of the blends. Fractured surfaces were prepared by breaking the samples at liquid nitrogen temperature and sputter coating with gold.

Dumb-bell shaped specimens were cut from moulded sheets and tensile properties measured on an Instron testing machine (model TM-BM) at 25°C. The gauge was 21 mm long and 4 mm wide. The yield stress, and elongations at yield and break were averaged over five determinations.

RESULTS

General crystallization characteristics

The crystallization behaviour of LLDPE, PP and the blend with various compositions was investigated as a function of temperature. On cooling at 10 K min^{-1}, the temperature ranges in which the crystallization occurred decreased in the order PP, the blends and LLDPE but there was considerable overlap (*Figure 1*) and there was evidence in the 70/30 LLDPE/PP blend of LLDPE crystallizing by the presence of a shoulder on the crystallization curve at lower temperature.

The crystallization rates of the polymers and the blends were studied isothermally and analysed by the Avrami equation:

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

where X_t is the crystallinity at time t, Z is a composite rate constant including nucleation and growth rates, and n is a constant which varies according to the crystallization mechanism. The half-lives of the crystallization of PP and LLDPE have different temperature dependences (*Figure 2*) but extrapolate to similar values in the temperature range 380–390 K which corresponds to the maximum in the non-isothermal experiments. The LLDPE-rich blends crystallized at similar rates to those of LLDPE, while the PP-rich blends, including the 50/50 blend, crystallized at similar rates to those of PP. It is apparent that provided the PP forms a continuous phase, the crystallization rate is essentially that of the PP component and those blends exhibited a similar crystallization rate to that of PP. However, when LLDPE forms the continuous phase the crystallization rate approaches that of the bulk LLDPE. The crystallization rate studies are clearly consistent with the LLDPE/PP system exhibiting no solubility of the components in one another and the crystallization behaviour being dominated by the rate characteristics of the components alone.

The Avrami exponent, n, for the homopolymers varied between 2.0 and 2.5 for PP, and 2.4 and 3.4 for LLDPE, both increasing with increasing temperature. The values of n for the blends lay between these limits (*Figure 3*) and approximated to the relative proportions of PP and LLDPE present. This range of values of n has been interpreted as being associated with the growth of open textured spherulites produced by branching lamellae and segregation of molecular fractions. The blend morphology clearly has an effect on the crystallization mechanism.

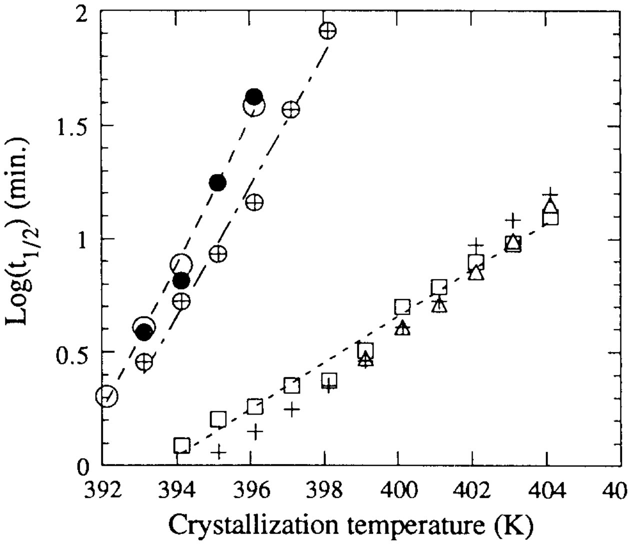

Figure 2 Variation of the half-lives with crystallization temperature of LLDPE/PP blends: (○) 100/0; (●) 90/10; (⊕) 70/30; (△) 50/50; (+) 30/70; (□) 0/100

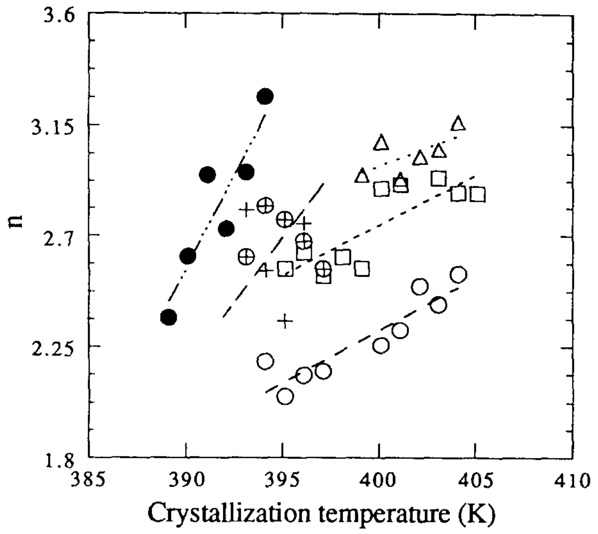

Figure 3 Dependence of n on crystallization temperature of LLDPE/PP blends: (●) 100/0; (+) 90/10; (⊕) 70/30; (△) 50/50; (□) 30/70; (○) 0/100

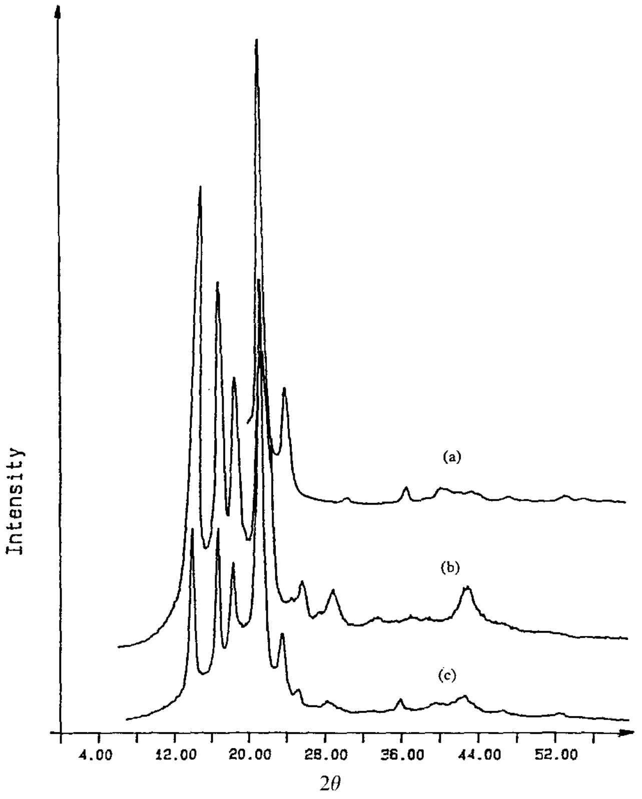

Figure 4 WAXD spectra of (a) LLDPE, (b) PP and (c) 50/50 LLDPE/PP

Crystalline structure

The crystallographic unit cell dimensions of the LLDPE/PP blends were measured by wide-angle X-ray scattering (WAXS) and *Figure 4* shows the diffraction patterns of quenched PP, LLDPE and the 50/50 blend, as a plot of the scattering intensity *versus* the diffraction angle 2θ. The PP scattering pattern (*Figure 4b*) has a broad amorphous background superimposed upon five sharp diffraction lines ascribed to reflections from the 110, 040, 130, 111 and 131, as well as 041 planes in the crystal, while that of LLDPE (*Figure 4a*), as reported previously[9], is dominated by the 110 and 200 reflections. The diffraction pattern of the blend (*Figure 4c*) is a simple addition of the two previous ones without any new peaks, consistent with discrete PP and PE domains and an incompatible system. There are no measurable shifts in the positions of the lines which could be ascribed to distorted unit cells, which ought to accompany the incorporation of a different comonomer unit into a homopolymer unit cell.

Two well separated melting peaks, corresponding exactly to the melting ranges of PP and LLDPE were observed in the d.s.c. melting endotherm of the 50/50 blend and this is consistent with the two polymers being insoluble in one another. The breadth of the melting range varied with crystallization temperature but was widest in quenched samples (*Figure 5*) and annealing decreased the width. Cormia *et al.*[10] explained that heterogeneous and homogeneous nucleation could take place together when PP was subjected to quenching, with the heterogeneous nucleation occurring at lower supercooling, giving thicker lamellae, whereas homogeneous nucleation appeared at lower crystallization temperature and resulted in the development of thinner lamellae.

Figure 6 shows the degree of crystallinity, as measured by d.s.c., which develops within the blends with composition assuming a two-phase morphology, of PP and LLDPE domains only, and also that the enthalpy of fusion of PP and PE are 209 and 293 J g^{-1}, respectively. The crystallinity of the LLDPE phase in the blends decreases with increasing PP content, either indicating that PP is present in the phase and altering the degree of perfection of the LLDPE crystals, or that the dispersed droplets of LLDPE have problems in nucleating, and so only crystallize at very low degrees of supercooling[11]. The slow cooled samples exhibited the highest degree of crystallinity both in the PE and PP domains and this was essentially constant at the value for the bulk polymers when that phase was present in excess (*Figure 6*).

Blend morphology

Fracture surfaces are shown in *Figure 7*. The blend microstructure depends on composition in that at lower LLDPE content (*Figure 7a*) domains of LLDPE can be

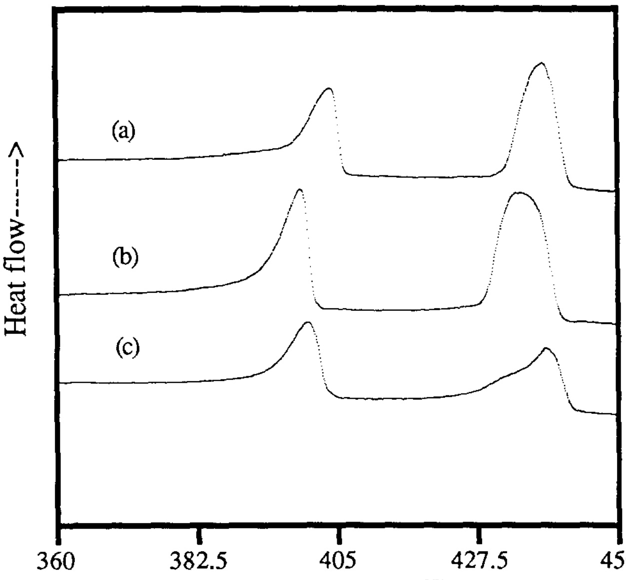

Figure 5 Melting endotherms of (a) slow cooled, (b) requenched and (c) quenched 50/50 LLDPE/PP blends

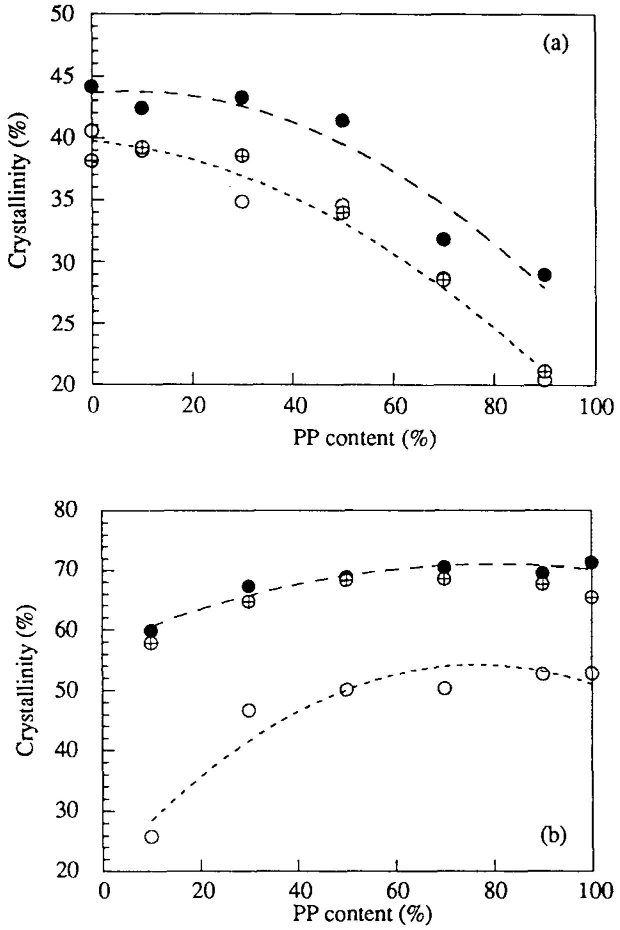

Figure 6 Variation of the crystallinity of LLDPE (a) and PP crystallites (b) in LLDPE/PP blends: (○) quenched; (●) slow cooled; (⊕) requenched samples

seen as unevenly distributed spherical particles of varying sizes dispersed within a continuous PP matrix. When LLDPE content is increased to 50% (*Figure 7b*), the morphology is less well defined with a miscellaneous distribution of the two components but PP still seems to act as the continuous phase. At higher LLDPE content, 70% LLDPE, spherical PP domains are present in the PE matrix (*Figure 7c*). The system is clearly incompatible and the two polymers are insoluble. At higher magnification it can be seen (*Figure 8a*) that the cavities occupied by the dispersed phase are smooth and featureless and during fracture the droplet has fallen out with no deformation of the surrounding matrix. The boundary between the two domains must be sharp with little or no interaction between them. This interface must be relatively weak. Some of the LLDPE domains have deformed in extension (*Figure 8b*) during fracture and this is characteristic of the fracture surface of the quenched specimens, implying more interactions between the domains.

Tensile properties of the blends

The variations of the tensile strength and elongation at yield of the blends with composition as well as to break, at a cross-head speed of 5 mm min^{-1} at 25°C, are shown in *Figures 9* and *10*. The yield stress in all cases increased non-linearly with PP content and there were no obvious differences between the yield stresses of quenched and requenched samples, but slow cooling of the samples produced the highest yield stresses. Irrespective of thermal history a minimum was always reached in the vicinity of 50% content in the elongation at break. This was considered to be characteristic of the change in morphology of incompatible blends[12], and annealing dramatically reduced the elongation at break particularly in the case of slow cooled samples, at high PP content. The LLDPE domains act as defects which lead to failure at low extension. The quenched samples cold draw with well defined necks while the annealed blends did not neck but broke in the vicinity of the yield point at maximum stress.

Annealing had no marked influence on the yield strain, and similar values which decreased with PP content were found for quenched and requenched samples. The slow cooled samples exhibited considerably lower values.

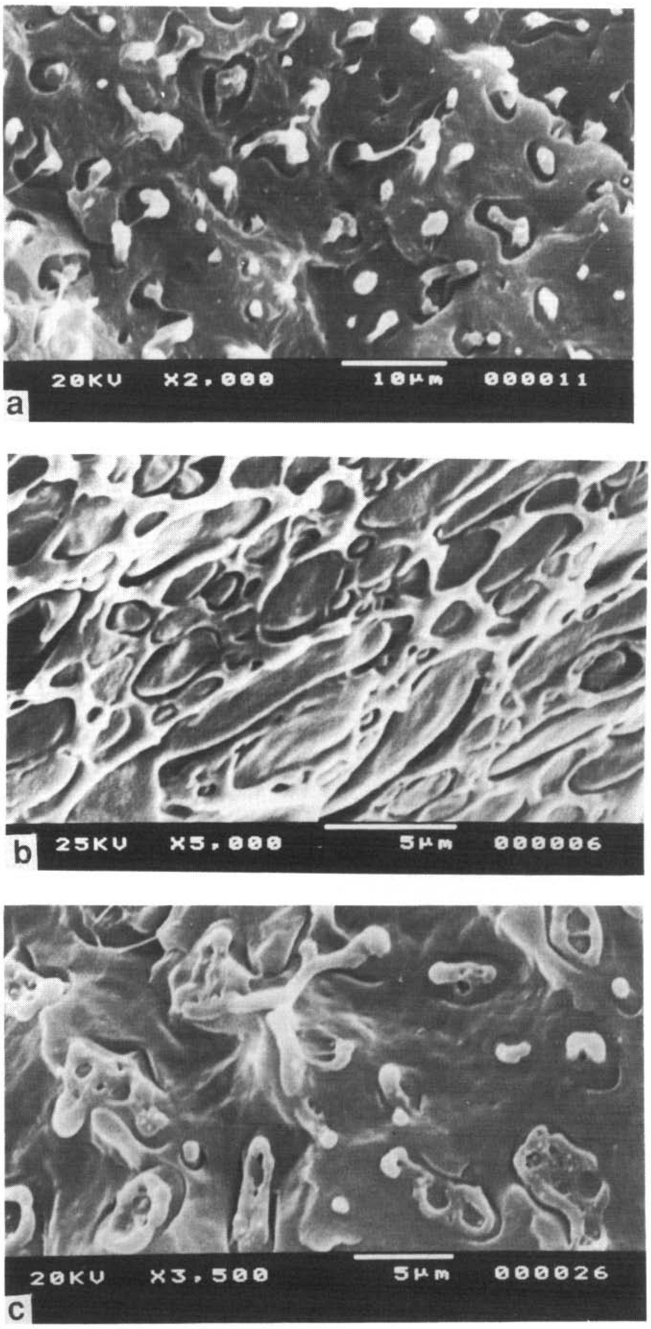

Figure 7 Stereoscan electron micrographs of cryogenically fractured surfaces of LLDPE/PP blends: (a) 30/70; (b) 50/50; (c) 70/30

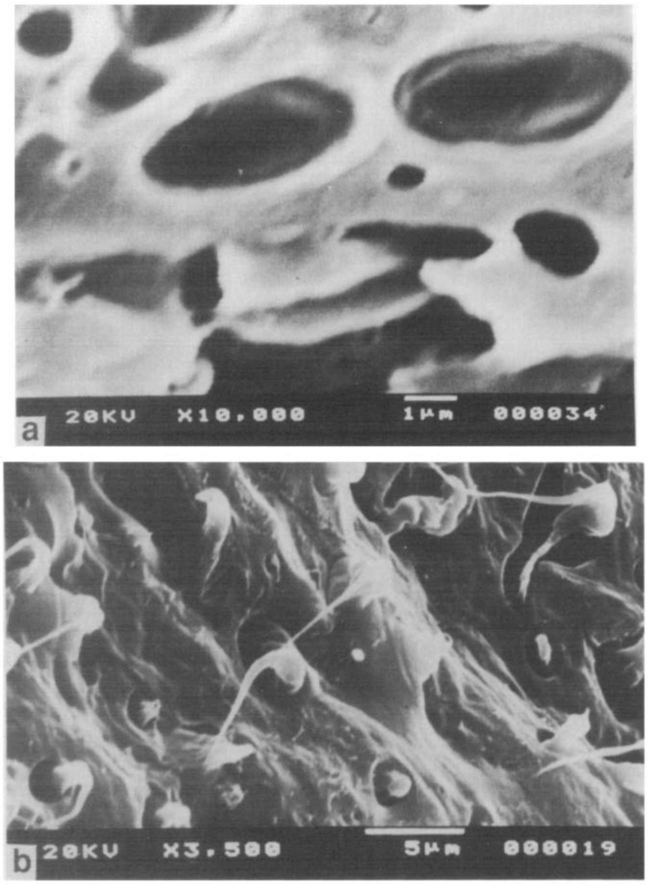

Figure 8 SEM micrographs of the interface between LLDPE and PP: (a) requenched 70/30 LLDPE/PP blend; (b) quenched 50/50 blend

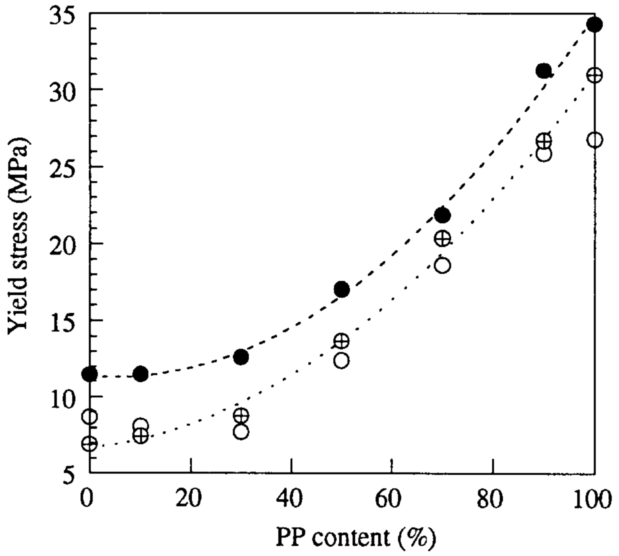

Figure 9 Yield stress of LLDPE/PP blends: (○) quenched; (●) slow cooled; (⊕) requenched samples

DISCUSSION

PP has a complex phase diagram. The α form with a monoclinic unit cell is the most commonly encountered occasionally co-existing with the β form with a hexagonal unit cell. Triclinic γ and δ forms have also been reported[13]. The crystal structure of LLDPE is much simpler than PP in that only the orthorhombic crystal has been identified[9]. The WAXS patterns of PP and PE were independent of time and annealing temperature when measured at room temperature, in that there was no increase in crystallinity, or changes in crystallographic form.

The annealing of the blends is complicated by the blend morphology and the separation of the domains of the homopolymer. Annealing of the PP alone occurs since 130°C is higher than the melting point of LLDPE, and the annealing occurs with the LLDPE in the molten state and the LLDPE crystals subsequently recrystallize during cooling.

The WAXS pattern of quenched PP is characteristic of the α form only since the line at 16.1°, reported as being characteristic of the β form[14], is not present. The same form is present after annealing, and there is clearly no crystallographic rearrangement. However, the crystallization behaviour was very sensitive to blend morphology. The results shown in *Figures 2, 3* and *7* and the microstructure viewed directly by polarizing microscope indicated that in the blends with PP contents from 90 to 50%, the LLDPE was always present as a disperse phase. The crystallization behaviour was then dominated by the PP component, with lower *n* values and shorter half-lives, characteristic of bulk PP. With LLDPE content above 50%, the blend morphology changes to that of the PP droplets dispersed in LLDPE. The extent of crystallization which can occur in these PP droplets becomes seriously hindered by the low nucleation density of PP. This explanation is consistent with the experimental evidence shown in *Figure 11*, where the crystallinity of the PP component reached within 10 min is plotted against the crystallization temperature

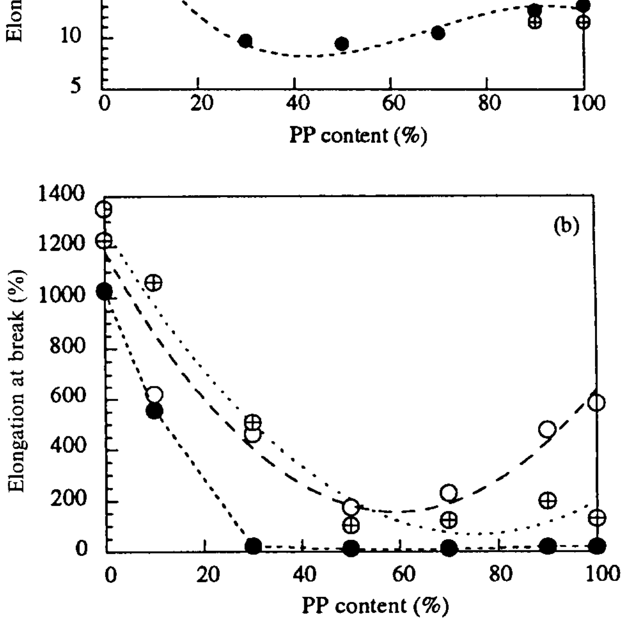

Figure 10 Elongation at yield (a) and break (b) of LLDPE/PP blends: (○) quenched; (●) slow cooled; (⊕) requenched samples

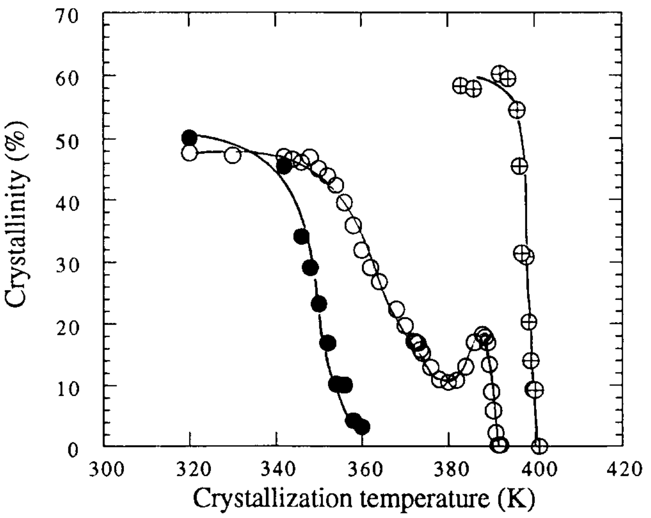

Figure 11 Variation of the crystallinity of the PP phase with temperature within 10 min of crystallization: (●) 90/10; (○) 70/30; (⊕) 0/100 LLDPE/PP blends

for the 10 and 30% PP blends. A comparison is also made with bulk PP and this is characteristic of the conventional dependence of the rate of crystallization on temperature and time. The degree of PP crystallinity in the low content blends did not change with time but was limited by the crystallization temperature. This is characteristic of nucleation control in that each droplet will not crystallize unless the correct heterogeneous nuclei are present for crystal growth to occur. The droplets are so small that growth occurs within a short time period, and the degree of nucleation which develops is a measure of the fraction of droplets which have been nucleated. PP does not have a high nucleation density, and as such crystallizes with larger spherulites than observed in LLDPE. These limitations imposed by the low heterogeneous nucleation density in PP ensure that the blends can only crystallize at high degrees of supercooling, depending on the size and number of dispersed PP droplets. The 30% PP appears to behave anomalously in that there is a bimodal distribution of nuclei present. A possible explanation of this anomaly is that there is a change in crystallographic form from the α form at high temperature to the β form at lower temperatures. Lovinger *et al.*[14] have reported that the β form is nucleated at a lower rate than the α form, and that at ~403 K there is a change in the phase of the PP which crystallizes from the melt. Wide-angle X-ray diffraction (WAXD) studies on the blends confirmed this (*Figure 12*) in that the quenched 30/70 blend and the slow crystallized 10/90 blend display the minor diffraction peak at 16.1° which is characteristic of the β phase. None of the higher PP content blends exhibit it. According to Ryu *et al.*[15] and Jacoby *et al.*[16] the β crystallographic form is characterized by the presence of this minor peak at 16.1°. An enlargement of this region of the diffraction pattern is shown in *Figure 12* for the various blends.

Under the annealing conditions chosen, the LLDPE domains are in the melt and do not anneal so that the differences observed in the change in properties reflect only the influence of the crystallization conditions, i.e. rapid or slow cooling. No crystallinity changes were found between quenched and requenched samples.

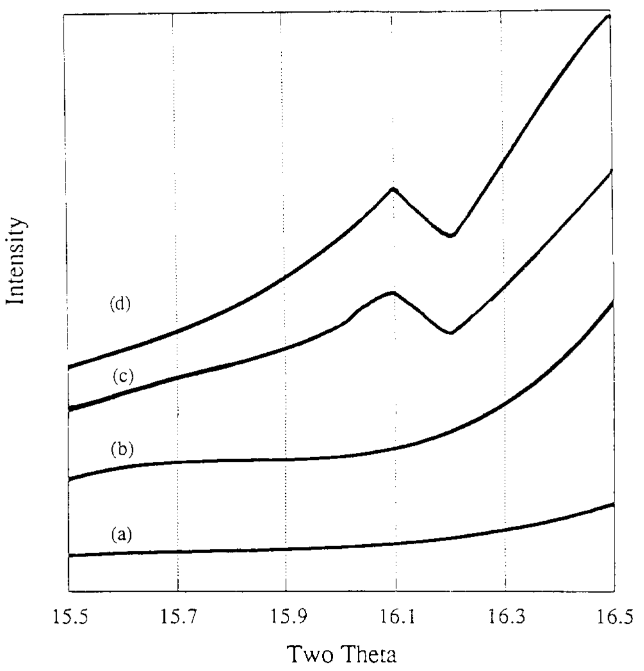

Figure 12 WAXS spectra of (a) quenched PP, (b) quenched 50/50 LLDPE/PP blend, (c) 90/10 LLDPE/PP blend crystallized at 353 K and (d) quenched 70/30 LLDPE/PP blend

The yield in a partially crystalline polymer is associated with interlamellar deformation and slip, such that in a homopolymer the yield stress increases with crystallinity[17]. The situation becomes much more complex in a multiphase system. As can be seen in *Figure 6*, requenched samples have a higher crystallinity than quenched ones, but there is no obvious difference in the yield stress as shown in *Figure 9*. This demonstrates that the interfacial energy between the domains dominates the failure behaviour. Electron microscopy suggests that the boundary between the PP and PE domains in the annealed specimens is quite weak. The very low elongation at break which leads to brittle behaviour of the annealed samples must be a result of the change in the number of trapped tie molecules[18]. For quenched samples, crystallization takes place locally since molecular chains were 'frozen' very quickly and the system is interconnected by many tie molecules which can act effectively as load transducers and the blend has a ductile mechanical behaviour. On annealing, a considerable amount of molecular rearrangement can take place and some disentanglement of tie molecules can occur. In this case only a few tie molecules are left. Once an external force is applied, the spare tie chains are unable to carry the load. Another structural factor which can account for the difference in the elongation is that the quenched samples crystallize at a lower temperature, have thinner lamellae and a lower degree of crystal perfection. This should increase the ductility and lower the yield stress.

REFERENCES

1 Sherman, E. S. *J. Mater. Sci.* 1984, **19**, 4014
2 Wenig, W. *Angew. Makromol. Chem.* 1978, **74**, 147
3 Schotland, R. S. *Polym. Eng. Sci.* 1966, **6**, 244
4 Wunderlich, B. 'Macromolecular Physics', Vol. 2, Academic Press, New York, 1976
5 Varin, R. A. and Djokovic, D. *Polym. Eng. Sci.* 1986, **28**, 1477
6 Haddon, M. R. and Hay, J. N. 'Size Exclusion Chromatography' (Eds B. J. Hunt and S. R. Holding), Blackie, London, 1989
7 Hay, J. N. and Mills, P. J. *Polymer* 1982, **23**, 1380
8 Langford, J. I. and Wilson, A. J. C. *J. Sci. Instr.* 1962, **29**, 581

9 Hay, J. N. and Zhou, X. Q. *Polymer* 1993, **34**, 2282

10 Cormia, R. L., Price, F. P. and Turnbull, D. J. *J. Chem. Phys.* 1962, **37**, 1333

11 Aref-Azar, A. A., Hay, J. N., Marsden, B. and Walker, N. *J. Polym. Sci., Polym. Phys. Edn* 1980, **18**, 637

12 Paul, D. R. and Robertson, K. E. *J. Appl. Polym. Sci.* 1973, **17**, 2579

13 Turner-Jones, A., Aizlewood, J. M. and Becktt, D. R. *Makromol. Chem.* 1964, **75**, 134

14 Lovinger, A. J., Chua, J. O. and Gryte, C. C. *J. Polym. Sci., Polym. Phys. Edn* 1977, **15**, 641

15 Ryu, S. H., George, C. G. and Xanthos, M. *Polymer* 1991, **32**, 2449

16 Jacoby, P., Bersted, B. H., Kissel, W. J. and Smith, C. E. *J. Polym. Sci., Polym. Phys. Edn* 1986, **24**, 461

17 Popli, R. and Mandelkern, L. *J. Polym. Sci., Polym. Phys. Edn* 1987, **25**, 441

18 Brown, N. and Ward, I. M. *J. Mater. Sci.* 1983, **18**, 1405