

Properties of polyethylene–propylene blends

Part 3 *Mechanical characterization of ultradrawn fibres*

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High density polyethylene–isotactic polypropylene blends have been analysed using mechanical tensile tests at temperatures (T) ranging from 25 up to 150°C and at cross-head speeds ranging from 0.01 to 500 mm min⁻¹. The data have been tentatively interpreted in terms of cold and hot drawing mechanisms, depending on the values of T and v . Such interpretation is quite different from that previously suggested in the literature. Using the results of this analysis it has been possible, by a suitable choice of the operating variables T and v to yield ultradrawn blend fibres. Their mechanical properties, obtained at room temperature and at a cross-head speed of 10 mm min⁻¹ have been analysed and discussed.

1. Introduction

Polyolefin–polyolefin blends have been generally considered very poor materials from a mechanical point of view in the literature. Particularly, their elongation-at-break at room temperature is much lower than the ones relative to the blend constituents [1–3]. Such behaviour, in the case of high density polyethylene (PE)–isotactic polypropylene (PP), has been confirmed in the first paper of this series concerning the properties of unoriented extruded samples [4]. The elongation-at-break values were, however, in that case, the highest among those found in the literature [1–3]. These results were related to the different molecular characteristics of the polymers used, as well as to the various processing conditions used for obtaining the specimens [4, 5].

In the second paper of this series [5] the thermal, swelling and mechanical properties of blend fibres elongated at room temperature up to their “natural draw ratio” [6] were analysed, and also discussed in terms of possible interactions existing between PE and PP during the cold drawing of the fibres. Furthermore an important observation was made, namely that increasing the temperature of drawing at 60°C caused the elongation-at-break to increase so much that

blend fibres could be obtained very easily, as in the case of pure polyolefins. Their mechanical properties, moreover, were very similar to those of the two PE and PP homopolymers at the same testing conditions. In the present paper a more systematic analysis of stretching parameters, such as temperature and rate of drawing, has been performed, for a better understanding of the possible drawing mechanisms. From this study various stretching conditions, depending on blend composition, have been found suitable for obtaining ultradrawn blend fibres.

2. Experimental procedure

2.1. Homopolymers

High density polyethylene (PE) weight average molar mass, ($\bar{M}_w = 9.2 \times 10^4$ and number average molar mass, $\bar{M}_n = 8 \times 10^3$) and isotactic polypropylene (PP) ($\bar{M}_w = 3.1 \times 10^5$ and $\bar{M}_n = 1.6 \times 10^4$) kindly provided by RAPRA were used as-received without any further purification.

2.2. Blend preparation

The PE and PP polyolefins were pre-mixed in a Brabender-like apparatus (Rheocord EC of HAAKE Inc.) at 200°C and at 32 rpm for 10 min. At these operating conditions no degradation

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phenomena were effective. The following PE/PP ratios were explored: PE/PP = 100/0, 75/25; 50/50; 25/75 and 0/100.

2.3. Unoriented specimen preparation

The pre-mixed material was compression-moulded in a heated press at a temperature of 200°C and at a pressure of 240 atm, obtaining 1 mm thick flat sheets. Dumb-bell-shaped specimens were then cut from the sheets by means of a suitable hollow punch.

2.4. Tensile properties of unoriented specimens

Tensile stress-strain curves were obtained at either a constant cross-head speed of 50 mm min⁻¹ with various temperatures, or by maintaining the temperature constant (room temperature) and changing the speed, by an Instron machine. The tests were performed in order to analyse the possible drawing mechanisms acting at low and at high temperatures and speeds.

2.5. Ultradrawn fibre preparation

As a result of the previous analysis, PE and the blend at prevailing PE content (PE/PP = 75/25) were stretched in the Instron machine at 80°C and at a cross-head speed of 200 mm min⁻¹ to obtain ultradrawn fibres.

PP and the other two blends (PE/PP = 50/50 and 25/75) were stretched at 130°C and a cross-head speed of 200 mm min⁻¹. Furthermore, a second step was necessary in the latter case: the fibres obtained by the first step were further stretched at the same temperature (130°C) but at a very low cross-head speed of 1 mm min⁻¹ in order to obtain the final ultradrawn fibres.

2.6. Ultradrawn fibre characterization

Tensile mechanical tests at room temperature and at a cross-head speed of 10 mm min⁻¹ were performed on the ultradrawn fibres, obtained as described above, to obtain their moduli and ultimate properties. Some qualitative wide angle X-ray scattering (WAXS) tests were also performed on these fibres to determine the relative crystalline orientation of the two components PE and PP.

3. Results and discussion

3.1. Stress-strain analysis

3.1.1. Homopolymers

Stress-strain curves, obtained at a cross-head

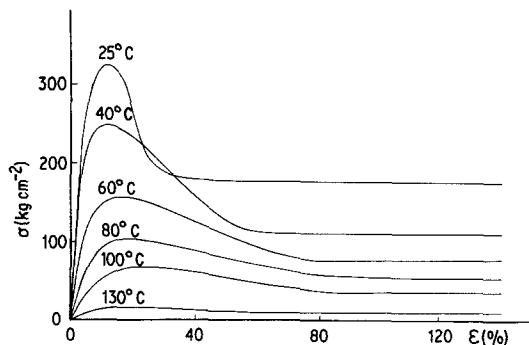


Figure 1 Stress-strain curves for PE obtained with $v = 50 \text{ mm min}^{-1}$ and the temperatures shown.

speed of 50 mm min⁻¹ and at temperatures of 25, 40, 60, 80, 100 and 130°C for the PE specimens; at the same temperature and also at 150°C for the PP specimens, are shown, respectively, in Figs. 1 and 2. Their relative moduli, E , and yield stresses, σ_y , are plotted as a function of the oven temperature, T , in Fig. 3. The trend of E and σ_y for both the polyolefins is a linear decrease with a change in slope at an interpolated temperature, T_B , lying between 60 and 80°C. Figs. 4 and 5, respectively, show the corresponding PE and PP necked specimens after an almost complete elongation at the temperatures stated above. In both cases the fibrous portions of the samples, obtained at temperatures lower than 60°C, appear to be very opaque. This effect can be attributed mainly to craze formation during the neck propagation. Beyond 60°C the necked specimen-regions become more and more transparent with a strong decreasing evidence of craze formation. This change in the final appearance of the fibres seems to be in a direct relationship with the occurrence of the break point, T_B ,

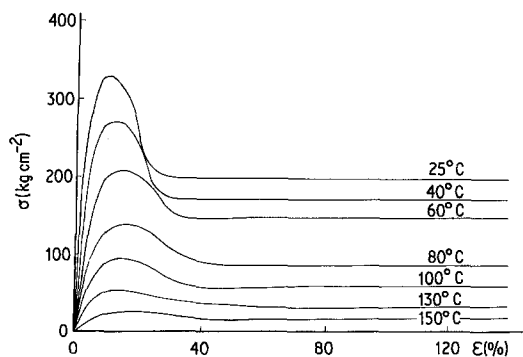


Figure 2 Stress-strain curves for PP obtained with $v = 50 \text{ mm min}^{-1}$ and the temperatures shown.

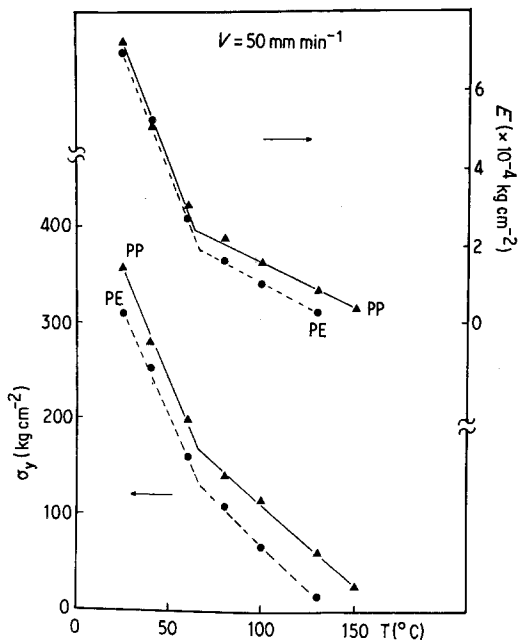


Figure 3 Yield stress σ_y and apparent moduli, E , for PE and PP homopolymers as a function of the operating temperature T .

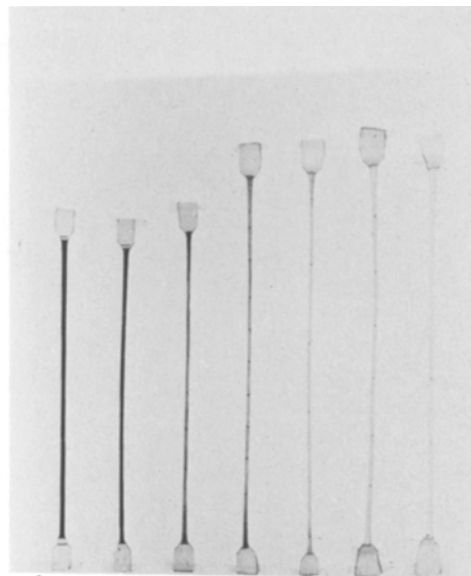


Figure 5 Transparency photographs of PP samples elongated at the temperatures shown.

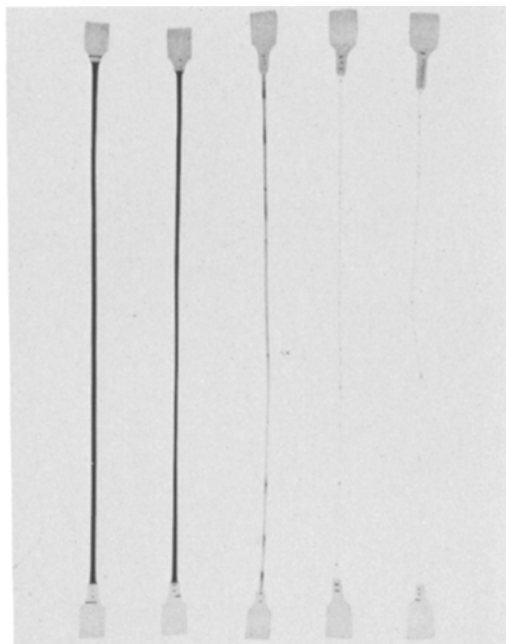


Figure 4 Transparency photographs of PE samples elongated at the temperatures shown.

Figure 4 Transparency photographs of PE samples elongated at the temperatures shown.

Figure 5 Transparency photographs of PP samples elongated at the temperatures shown.

shown in Fig. 3. In other words the two extrapolated straight lines (the real curves give a smoother transition) possibly reflect two types of limiting drawing mechanisms.

The first at $T < T_B$, very similar for both PE and PP, produces, after the neck initiation and propagation along the specimen, opaque fibres. The second at $T > T_B$ yields transparent fibres (the degree of transparency increases with increasing temperature T), but with different elongation features for PE and PP samples, respectively. In fact for PE, after the neck initiation in the weakest section of the specimen, the elongation proceeds only in that restricted region without possibility of propagation of the neck along the rest of the material and therefore it yields locally very high extension ratios (Fig. 4). In contrast, the PP samples always appear to be homogeneously stretched at all temperatures. This is because the neck is able to propagate along the whole sample and hence the local elongation ratios have approximately the same values as the overall extension ratios. All the above mentioned features can be tentatively attributed to the semicrystalline nature of the polyolefins for which crystalline and amorphous interconnected regions are simultaneously present in the sample morphology. This situation creates during stretching high local stress

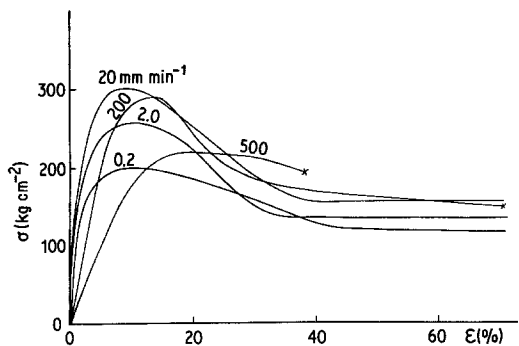


Figure 6 Stress-strain curves for PE obtained at room temperature and at the cross-head speeds shown.

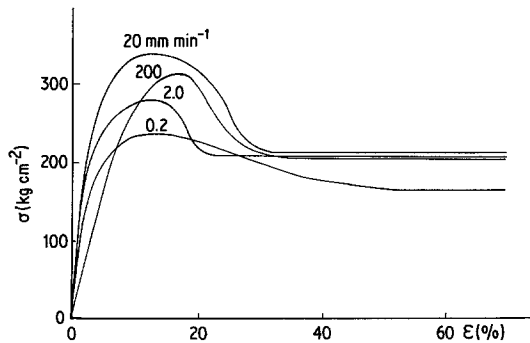


Figure 7 Stress-strain curves for PP obtained at room temperature and at the cross-head speeds shown.

concentrations which cannot be tolerated by the material without a neck formation in the weakest section of the specimen. Since adiabatically (if the speed is high enough) all the work of deformation is concentrated in a small piece of the sample, the local rise in temperature can melt, at least partially, the crystallites or leave them unaffected. This possibility depends on both the temperature of the oven, T , as well as on the cross-head speed, v , of the Instron machine. After neck initiation, if some melting occurs the samples may undergo two different drawing mechanisms which are observed in Figs. 4 and 5 for PE and PP, respectively. In the first case the characteristics of the material (average molecular weight, molecular weight distribution and chemical structure) are of such a nature that the overall viscosity at local temperature is too low to make the neck propagate. Therefore only a tiny piece of the specimen is very highly elongated (such an effect increases, of course, by raising the temperature because this causes viscosity to become more and more lowered). In the second case the viscosity of PP is high enough at all the temperatures so that the neck is able to propagate (even at 150°C) yielding a very homogeneous deformation.

The strong influence of the work of deformation on the drawing mechanisms is confirmed also by data concerning the stretching of a specimen performed at room temperature and at different cross-head speeds. The relative stress-strain curves for PE and PP are shown in Figs. 6 and 7, respectively. The calculated yield stress for both polymers, as a function of $\log v$, is plotted in Fig. 8 for both the polyolefins. As can be seen from Fig. 8, there is a maximum σ_y at a speed, v_B , of about 100 mm min^{-1} . Such a maximum represents the limit between the two

different drawing mechanisms described previously concerning the melting of other wise of the the polymer crystallites.

Summarizing, one can say that the drawing mechanisms acting in a semicrystalline polymer specimen under stretching depend both on the chamber temperature, T , and on the cross-head speed, v , values. Furthermore the homogeneity of the deformation depends on the chemical nature and/or the molecular characteristics of the examined polyolefin. This feature can explain why, generally speaking (as already known in the literature) to obtain high modulus fibres (corresponding to very high elongation ratios) it is sufficient to operate in one step for PE specimens [7-10] whereas at least two steps are necessary for PP specimens [11, 12].

3.1.2. PE/PP blends

Stress-strain curves of PE/PP mixtures, having 25/75, 50/50 and 75/25 weight ratios, are shown in Figs. 9, 10 and 11, respectively. In contrast to the PE and PP homopolymers, which exhibit

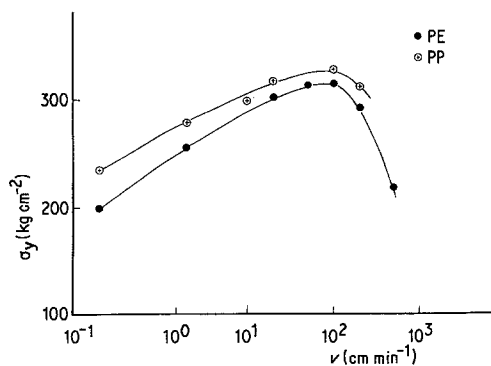


Figure 8 Yield stress σ_y for PE and PP homopolymers as a function of the cross-head speed v .

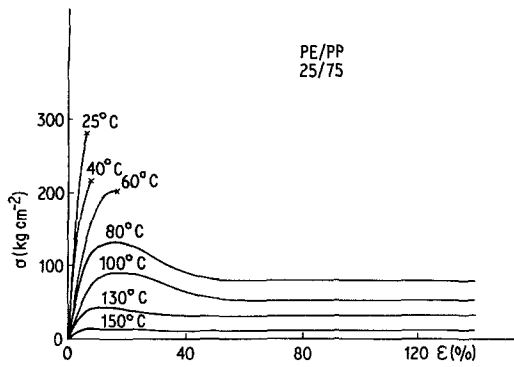


Figure 9 Stress-strain curves for PE/PP (25/75) blend obtained at a cross-head speed of 50 mm min^{-1} and at the temperatures shown.

a ductile behaviour at all the operating temperatures (Figs. 1 and 2), the blends show brittle failures at some temperatures. In fact for the 25/75 mixture these ruptures occur at 25, 40 and 60°C ; for the 50/50 mixture at 25 and 40°C , and finally the 75/25 blend shows a semiductile behaviour at 40°C and a brittle failure only at 25°C . At higher temperatures the blends exhibit a completely ductile behaviour. The moduli, E , calculated from these curves, are plotted as a function of the oven temperature, T , in Fig. 12 (no yield stress values are plotted because of the brittle failures at low temperatures for some blends). The trend is very similar to that of the homopolymers. Also in this case it is possible to obtain by extrapolation a break point, T_B . The occurrence of the brittle ruptures shown by the stress-strain curves seems to be clear evidence of some kind of interaction existing between PE and PP in all the blends during the

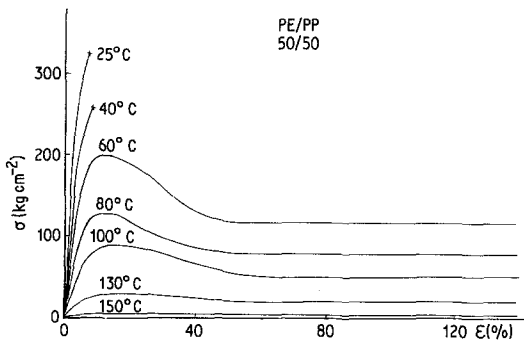


Figure 10 Stress-strain curves for PE/PP (50/50) blend obtained at a cross-head speed of 50 mm min^{-1} and at the temperatures shown.

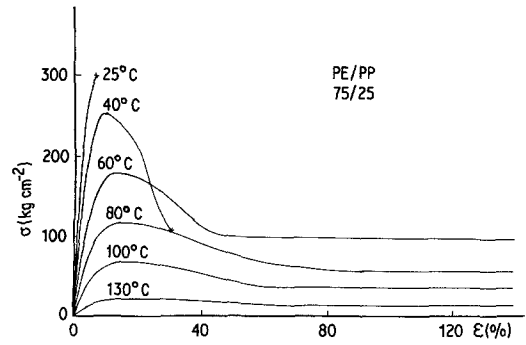


Figure 11 Stress-strain curves for PE/PP (75/25) blend obtained at a cross-head speed of 50 mm min^{-1} and at the temperatures shown.

drawing of the samples. The extent of such interactions depends strongly on the blend composition (the plasticity increased by increasing the PE content), which in turn seems to influence the break point, T_B , (Fig. 12), which may also represent in this case, the transition between two different drawing mechanisms. In particular, T_B decreases by increasing the PE content (this trend must be considered only in a very qualitative way).

From the data presented above it seems possible to draw the following inferences about the PE-PP blends. The same two drawing mechanisms can be suggested for the blends as well as for the homo-

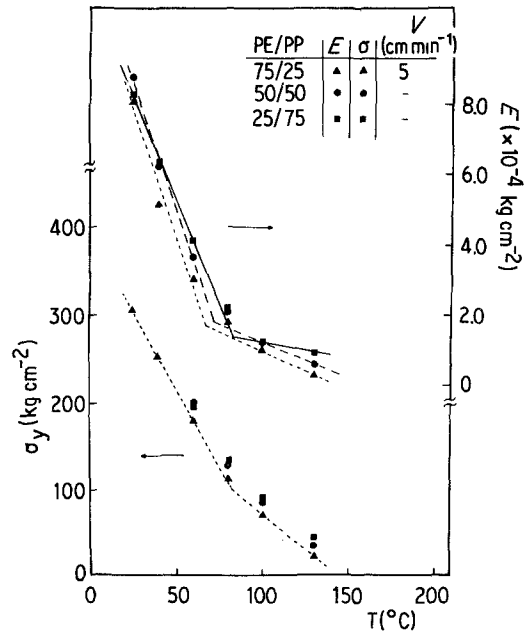


Figure 12 Yield stress and apparent modulus, E , for different PE/PP blends (weight ratios indicated) against temperature.

polymers: the cold drawing acting at $T < T_B$ and the hot drawing acting at $T > T_B$. In spite of this similarity (the existence of the break point, T_B , in both the cases), there is a substantial difference in behaviour between one-component and two-component systems. In fact, in the first case at $T < T_B$ (where no crystallite should melt) cold drawing is always possible even though very defective (crazed) fibres are produced. In the second instance no flow is possible at the same conditions and only brittle or semibrittle failures are obtainable for the blends. This is due to the interactions arising between the two components into the neck, where both undergo a strong morphological change (from a spherulitic to a fibrous structure). In this way the two interconnected species (PE and PP) can become entangled to some extent by the tie molecules anchored to the respective crystallites and the cold-flow is therefore highly hampered. The similarity of behaviour is restored at $T > T_B$, where in all cases good fibres can be formed by some partial melting of the crystallites and/or by easy chain unfolding of the macromolecules contained in the crystals. The dispersed phase, however, acts in some way as a disturbance during the flow of the matrix, yielding more defective fibres with respect to the homopolymer case.

3.1.3. Ultradrawn fibre formation

From the considerations reported in Sections 3.1.1 and 3.1.2 it seems that for all the materials examined, PE and PP homopolymers and their blends, the conditions for obtaining ultradrawn fibres (exhibiting high moduli and stresses) are those corresponding to the hot-drawing regime. Since the optimum temperatures and rates to be used during the hot drawing, depend on the chemical and molecular characteristics of the homopolymers, a trial and error procedure was used to establish them. So in this case a temperature of 80°C and a cross-head speed of 200 mm min^{-1} were used. As mentioned previously and also in the literature, only one step is needed for PE and for the 75/25 blend whose matrix is still PE.

For PP, 25/75 and 50/50 blends the T and v values used were 130°C and 200 mm min^{-1} , respectively. But even under these conditions only homogeneous deformations were obtained and hence low elongation ratios. Therefore a second step at $T = 130^\circ\text{C}$ and $v = 1\text{ mm min}^{-1}$

was performed to obtain high extension ratios for such material. Annealing at 130°C under tension was performed during which almost no relaxation could take place in the already crystallized samples, and the perfection of the PP crystals could be enhanced by chain unfolding and recrystallization under stretching (in this case one author [13] suggests the existence of a continuous crystal within the fibre) in order for them to yield better fibre properties.

3.1.4. Ultradrawn fibres properties: mechanical behaviour

The moduli of PE, PP and their blend fibres obtained at room temperature and at a cross-head speed of 10 mm min^{-1} are reported as a function of the elongation ratio λ in Fig. 13. The PE-rich blend PE/PP = (75/25) and the PP-rich blend (PE/PP = 25/75) show an increasing linear trend with increasing λ , qualitatively very similar to the PE and PP homopolymers. This result is to be expected since in these cases it is the matrix which plays the major role. The blend moduli are, of course, lower than those corresponding to the homopolymers because the dispersed phase acts as defects in the fibre structure. It is to be noted

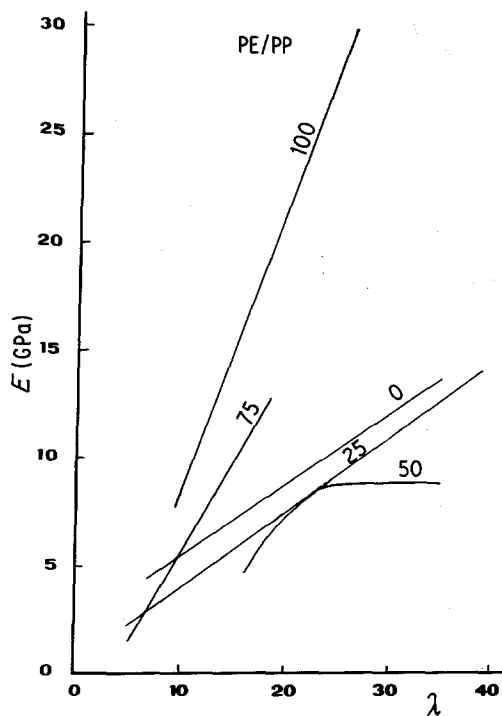


Figure 13 Moduli of ultradrawn homopolymer and blend fibres (PE weight percentages indicated) as a function of the elongation ratio, λ .

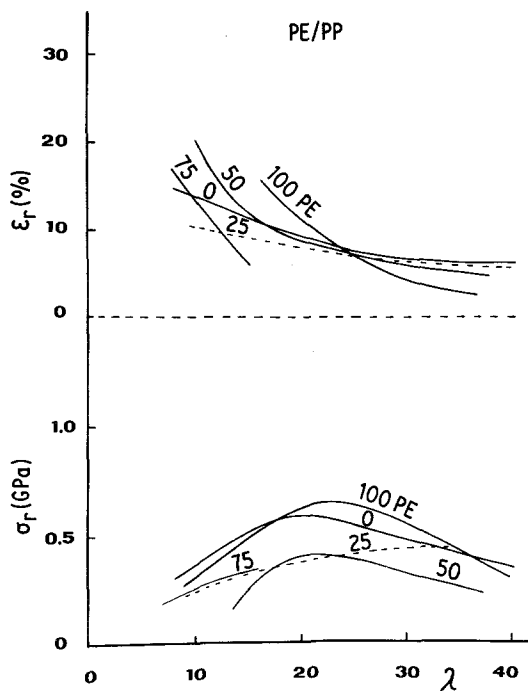


Figure 14 Ultimate strength, σ_T , and elongation-at-break, ϵ_T , for homopolymers and for different blends (PE weight percentage indicated) as a function of the elongation ratio, λ .

however, that the dispersed phase also becomes elongated to a great extent by the matrix, as qualitatively shown by WAXS tests [14].

The 50/50 blend modulus first increases with increasing λ and beyond $\lambda = 20$ it levels off at a value of about 9 GPa. Here it is difficult to assess which of the two components is the real matrix of the system.

However, since the same operating variables (T and v) and the two steps used for pure PP were necessary to obtain good ultradrawn fibres, it seems that it is the PP which plays the major role.

On possible explanation of the levelling off of the 50/50 blend is that, during the second step, equivalent to an annealing under slow stretching, the temperature (130°C) was sufficient to improve the PP crystalline structure but was too high for the PE phase. In fact very likely the PE domains were melted at that temperature, losing part of the orientation gained in the first step of drawing at the high elongation rate.

The strength and the elongation-at-break, as a function of λ , for the same materials are plotted in Fig. 14. The strengths of pure PE and PP as well as that of the 50/50 blend show a maximum

around $\lambda = 20$; those relative to the 25 wt% and 75 wt% PE blends seem to exhibit instead a monotonic increase. The elongation-at-break for all the systems decreases monotonically with increasing λ , reaching very low values ($< 5\%$). The slopes of the PE-rich blends are very steep whereas those of the PP-rich mixtures show a less drastic decrease. Such a behaviour is characteristic of very brittle materials. No simple explanation of the plots shown in Figs. 13 and 14 can be given at a molecular level without further investigation by other techniques such as differential scanning calorimetry (DSC), WAXS, small angle X-ray scattering (SAXS) and scanning electron microscopy (SEM).

In recent literature [15] ultradrawn blend fibres have been obtained by the "surface growth" procedure (from solutions in p-xylene PE, PP and a 50/50 blend have been drawn and heated at 120°C during the stretching) obtaining fibres whose moduli were about 20 GPa. These values are higher than those presented in this paper, and such a result is very reasonable because in our case the molecular weights ($\bar{M}_{wPE} = 9.2 \times 10^4$ and $\bar{M}_{wPP} = 3.1 \times 10^5$) are an order of magnitude lower than those used by Smith and Lemstra [16] ($\bar{M}_{wPE} = 1.5 \times 10^6$ and $\bar{M}_{wPP} = 3 \times 10^6$).

4. Concluding remarks

It has been shown in this paper that PE-PP blends can be very usefully analysed by stress-strain curves obtained with various operating variables. In this way a new definition of cold and hot drawing is proposed, different from that previously reported in the literature [16]. Furthermore by suitably choosing these parameters one can obtain ultradrawn blend fibres. Structural interpretation of the results presented in this paper would require the use of other characterization techniques such as WAXS and morphological observations by transmission and scanning optical and electronic microscopy. Such work is in progress at our institute.

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