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Double yield points in triblends of LDPE, LLDPE and EPDM

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Factors that affect to the proposed mechanisms that produce the double yield phenomenon in semicrystalline polymeric materials were studied. The systems under study were ternary blends of low-density polyethylene (LDPE), linear LDPE (LLDPE) and ethylene propylene diene (EPDM). The influence on the yield mechanisms of the following different factors were analysed: processing conditions, composition, stretching rate, cooling conditions and different types of elastomers. The behaviour of these blends in the region where the double-yield points occur was found to be different for those LDPE-rich blends from those LLDPE-rich ones. These differences are explained in terms of the two mechanisms in the double yield phenomenon; that is, the slip of the crystalline blocks and the shear on the crystalline blocks. The stretching-rate effect is explained in terms of the stress relaxation time. The effects of EPDM content, cooling conditions and type of EPDM are found to be equivalent to a smaller stretching rate.

1. Introduction

A yield point in polymers is conventionally accepted as being the point where the stress–strain curve shows a local maximum. For samples which initially deform homogeneously, this maximum occurs as a result of the internal plastic strain rate of the material increasing to a point where it becomes equal to the applied strain rate. In some instances a maximum in the force also relates to the onset of necking, where strain hardening of the necked materials is not sufficient to counteract the reduction of the cross-sectional area, leading to a reduction in load [1]. This maximum may become less defined as the testing temperature is increased or the strain rate is decreased, until it disappears. The temperature at which the local maximum disappears is lowest for the most branched material and highest for the unbranched, high-density material.

The yielding phenomenon of semicrystalline polymers has been associated with a change in the morphology of the material where a spherulitic structure transforms into a fibrillar one [1, 2]. During the stretching, this change occurs through shearing and fragmentation of the crystalline lamellae into blocks which rearrange into the form of parallel microfibrils. Investigations of the yield process in polyethylene have also been performed from a phenomenological point of view to establish the constitutive equations of the plastic flow [3, 4], and from the viewpoint of mechanics [5].

Works published recently [5–8] for polyethylenes and their blends under tensile loading, demonstrated clearly the existence of double yield points. Because there is a strong correlation between the character of the yield region and permanent deformation, understanding the yield process is very important to understand the complete deformation process. Popli and Mandelkern [6] reported double yield points for branched and linear low-density polyethylenes (LDPE), and suggested that the double yielding phenomenon arose from the very broad distribution of the crystalline lamella thicknesses. Seguela and Rietsch [7] studied the double yield behaviour of a medium-density polyethylene with a narrow crystal thickness distribution. Their explanation is in perfect agreement with the proposal by Yamada and Takayanagi [9] that the onset of plastic deformation in semicrystalline polymers is governed by two structurally well-defined processes: a slip of the crystal blocks past each other in the mosaic crystalline structure, and a homogeneous shear of the crystal blocks. Seguela and Rietsch [7] proposed that both processes could explain the two yield maxima observed, and the changes that these maxima experienced with changing deformation temperature or strain rate.

The effects of branching on the yield behaviour have been investigated by Brooks *et al.* [5] in polyethylene samples with different degrees of branching. The experimental results showed the existence of double yield points for all samples over a range of temperatures. The first yield point marked the onset of plastic strains which are slowly recoverable at least in part. Deformation beyond the second yield point is

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effectively irrecoverable and was associated with a sharp necking of the samples. The yield points were interpreted mechanically as the yield of two dashpots and the model used to describe the yield is of two non-linear Maxwell elements in parallel.

More recently, Balsamo and Müller [8] studied the cooling conditions and strain-rate dependence of double yielding in LDPE, linear LDPE (LLDPE) and their blends. The experimental results were interpreted in terms of the model proposed by Seguela and Rietsch [7]. The activation volume evaluated from Eyring's theory for the second yield process is greater than that for the first, which is consistent with the proposed model of a different deformation mechanism for each yield process.

In order to obtain a better understanding of the behaviour of the proposed two yield mechanisms of the double yielding in the case when an amorphous component is added to the semicrystalline material, we studied triblends of LDPE, LLDPE and ethylene propylene diene (EPDM). In this paper we analyse the yield behaviour by varying the processing conditions, composition, cooling conditions, and stretching rate, and using different types of elastomer, EPDM.

2. Experimental procedure

2.1. Materials

The commercial polymers used in this study were an LDPE manufactured in Mexico by Pemex (PX 17070), an LLDPE manufactured by Chem Int., USA (GB 5010), and three elastomers EPDM, one manufactured by Montedison (dutral 038) and two by DuPont (nordel 1040 and nordel 1070). The characteristics reported by the producers for these polymers are listed in Table I.

2.2. Preparation of the blends

The elastomeric materials were separately triturated to obtain particles with a size comparable to that of the pellets of the polyethylenes. The granulated materials were physically mixed in the desired weight ratios. Then the blends were powdered using a Brabender-type mill and the powder was collected after passing through a 0.1 mm hole mesh. Sheets with a uniform thickness ranging from 0.5–0.7 mm were prepared using a single-screw Brabender extruder, and the temperatures at the different zones (two in the barrel and one in the die) were set at the same value. In order to establish the effect of the processing conditions, two values for temperature and two for screw speed were used: 150 and 180 °C, and 40 and 70 r.p.m., respectively. The blends whose results are reported in all figures (except Fig. 1) were extruded at 180 °C and 40 r.p.m.. Samples with two different thermal histories were prepared. Rapidly cooled sheets from the melt were obtained directly from the extruder. Some sheets were placed in a vacuum oven and slowly cooled specimens were obtained by holding the vacuum oven at 120 °C for 5 min and allowing it to cool freely; it took about 3 h to reach near room temperature.

TABLE I Characteristics of the commercial polymers

Polymer	Name	MI (g (10 min)$^{-1}$)	Density (g cm^{-3})
LDPE	PX 17070	7.0	0.917
LLDPE	GB 5010	1.0	0.919
		ML (1 + 4)121 °C	Specific gravity
EPDM	dutral 038	65	0.865
EPDM	nordel 1040	40	0.86
EPDM	nordel 1070	70	0.86

2.3. Mechanical testing specimens

From the rapidly and slowly cooled sheets, specimens with the standard dumb-bell geometry with dimensions 22×7 mm^2 were cut for tensile tests. The uniaxial deformation of the samples was carried out at room temperature (25 °C) in an Instron tensile testing machine (model 4502). The influence of the stretching rates on the resulting stress–strain (σ–ε) curves was analysed over a wide interval ranging from 10–750 mm min^{-1}. In all the experiments, the deformation was carried out up to rupture. In general, seven specimens of each sample were obtained, whose average is reported.

2.4. WAXS measurements

Wide-angle X-ray scattering (WAXS) patterns of the samples were recorded with a Philips horizontal goniometer model PW 1380/60 fitted with a scintillation counter, pulse-height analyser, and a graphite crystal monochromator placed in the scattered beam. CuK_α radiation generated at 45 kV and 35 mA was used. The scattered radiation was registered in the angular interval (2θ) from 3°–45°. The degree of crystallinity in the blends and an estimation of the crystallite size were obtained in the standard way [10].

3. Results and discussion

All blends whose compositions are labelled in the order LDPE/LLDPE/EPDM, are grouped in two sets: in one set the polyethylene contents are different but the EPDM content is kept fixed at 0% or 5%, in the other set of blends the relative amounts of polyethylenes are kept fixed and equal to 1 (blends 1 : 1) but with different EPDM contents. To make the presentation of the results easier, results are divided according to the effect of the following variables: processing conditions (Fig. 1), composition (Figs 2–4), extension rate (Figs 5–6), cooling rate (Fig. 7), and type of EPDM (Figs 8 and 9). With the exception of the last two figures, the results presented correspond to blends prepared with EPDM dutral. The samples used to study the effect of the processing conditions and composition (Figs 1–4) were stretched at a rate of 80 mm min^{-1}. Finally, only the samples presented in Fig. 7 were rapidly or slowly cooled; in all other figures the samples were rapidly cooled.

3.1. Effect of processing conditions

Samples with a composition of 47.5/47.5/5 were processed by operating the extruder at four different

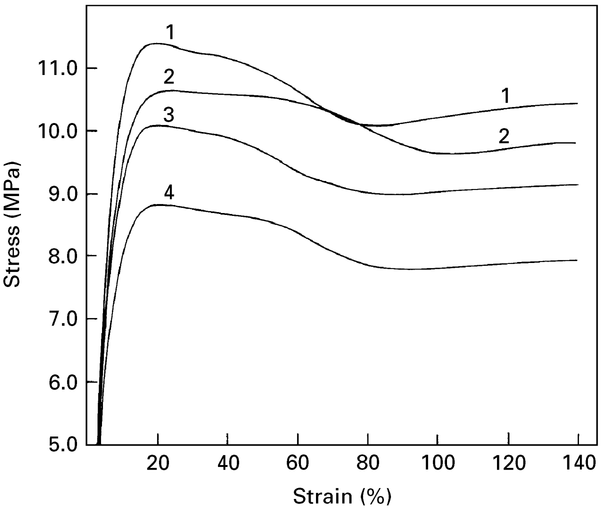

Figure 1 Stress–strain curves showing the effect of four processing conditions of screw speed V (r.p.m.), and temperature, T (°C). V/T: (1) 40/150; (2) 40/180; (3) 70/150; (4) 70/180.

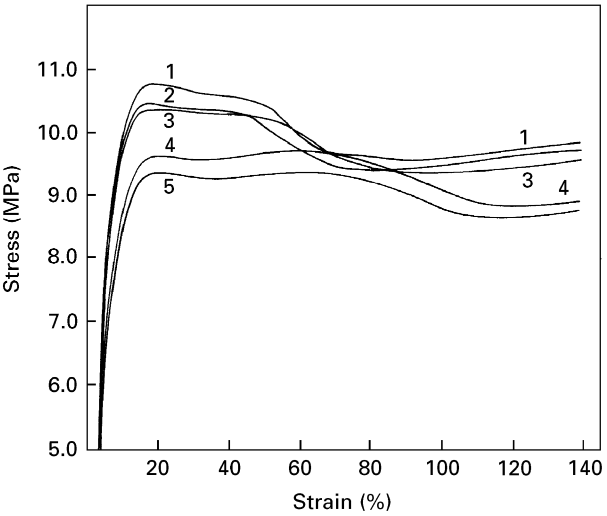

Figure 2 Stress–strain curves for polyethylene blends without elastomer obtained at a stretching rate of 80 mm min^{-1}. Blends were processed at 40 r.p.m. and 180 °C, and rapidly cooled. (1) 50/50/0; (2) 5/95/0; (3) 25/75/0; (4) 75/25/0; (5) 95/5/0.

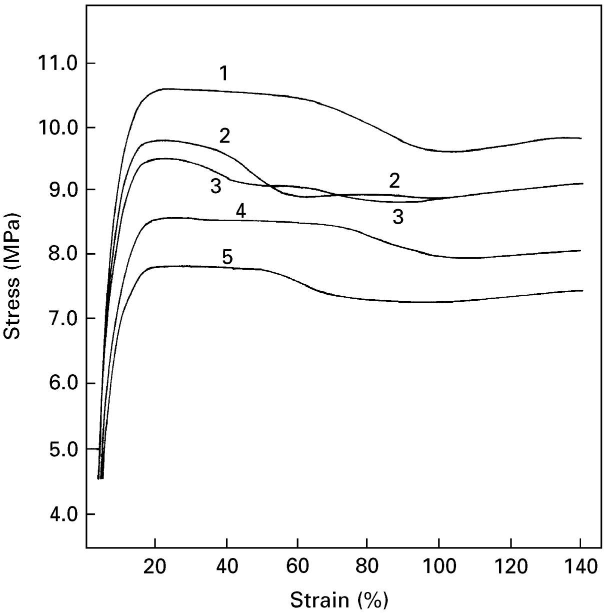

Figure 3 Curves for polyethylene blends with 5% EPDM dutral, with the same conditions as in Fig. 2. (1) 47.5/47.5/5; (2) 0/95/5; (3) 25/70/5; (4) 95/0/5; (5) 70/25/5.

conditions: screw speeds of 40 and 70 r.p.m., and temperatures of 150 and 180 °C. These samples were prepared with EPDM dutral and stretched at a rate of 80 mm min^{-1}. Their stress–strain curves in the yield region are shown in Fig. 1 (full curves and analysis of both initial and final properties will appear elsewhere [11]).

Those samples prepared at 40 r.p.m. have higher modulus than those prepared at 70 r.p.m. This is consistent with WAXS observations, because the measured crystallinity of the former is slightly higher (59%) than the latter (57%). These σ–ε curves could indicate that the mixing at 40 r.p.m. is better than at 70 r.p.m. because the material at 40 r.p.m. spent longer time in the extrusion machine. For a fixed screw speed, those samples prepared at 150 °C have higher modulus than those prepared at 180 °C. It can also be seen that the ratio between the stresses of the two yield points is not very different when we compare the two samples prepared with a screw speed of 70 r.p.m., meanwhile when we compare the ones at 40 r.p.m., the temperature difference makes the ratio change. One of the factors affecting the stress values of the first yield point may be the cooling rate, because the samples will cool faster when they are exposed to room temperature from a higher temperature, and when they move slowly they have more time to cool down so the slower they move the higher yield point they have. There may be other factors, such as the homogeneity of the blend, but this mainly affects the extreme mechanical properties [11].

3.2. Effect of composition

Blends of both polyethylenes containing 0 or 5 wt % EPDM prepared at 180 °C and 40 r.p.m., and stretched at a rate of 80 mm min^{-1}, have σ–ε curves as shown in Figs 2 and 3, respectively. The composition has a marked effect on the nature of the stress–strain curve in the double yield region. These curves exhibit well-defined double yield points. It is evident in both figures that those LLDPE-rich blends have higher stresses in the yield region and, also, that the elongation interval of this region is smaller than in those LDPE-rich blends. Indeed, the elongation range increases, although not regularly, with increasing LDPE content in the blend. These two effects can be explained in terms of the Seguela–Rietsch model. LLDPE-rich blends are more crystalline than these LDPE-rich blends; for instance, the measured crystallinity of 25/70/5 is 62% while that of 70/25/5 is 57%. Additionally, the differential scanning calorimetry (DSC) thermograms exhibit separate endotherms of each PE, which means the existence of separate crystalline particles of each material. On the other hand, because the LLDPE has a lower degree of branching than LDPE, it may have more perfect crystals and also the size of the block boundary regions are expected to be smaller than in LDPE. Consequently, the slip of the crystalline blocks of LLDPE (produced in the boundary regions) requires a higher stress, and at the same time the elongation interval is smaller than in LDPE because the attainable space where the blocks slip is smaller. Simultaneously to the slip in the LLDPE crystalline blocks, slip of the LDPE crystalline blocks is produced in their own boundary regions. Consequently, the slip of the crystalline blocks of both PEs is the cause of the increasing elongation interval of the yield region with the increment of LDPE content in the blend. This elongation interval is higher for LDPE-rich blends than for those with high LLDPE content. In between these extreme compositions the behaviour is irregular. These results are consistent with the elongation interval values that can be observed in the stress–strain curves corresponding to the pure polyethylenes reported elsewhere [8].

One important feature in Figs 2 and 3 is the higher modules and yield stress observed for the 50/50/0 and the 47.5/47.5/5 samples. These blends with equal parts of both polyethylenes exhibit higher initial properties than at other compositions. In particular, the Young's modulus as a function of the LDPE content shows a maximum value for the 50/50/0 sample and a similar behaviour for the 47.5/47.5/5 sample. This effect is ascribed to the different morphologies in the blends containing equal or different contents of both polyethylenes. A full discussion of the effect of the morphology of the phases is given elsewhere [11].

The effect of the elastomer content on the blend behaviour is illustrated by the stress–strain curves shown in Fig. 4. The double yield phenomenon decreases until it disappears with increasing elastomeric component in the blend. In the absence of the elastomer component, the region surrounding the crystalline block mosaics is formed by the amorphous phases of both polyethylenes. Because of the mixing method used here, it is more reasonable to expect the incorporation of the elastomeric component predominantly in the amorphous phase of the polyolefines, thus increasing the amorphous phase surrounding the crystalline regions rather than in the defective region between the crystalline blocks. Thus, the amorphous region is increased with the addition of the elastomer and, at the same time, becomes softer, reducing its capability to transmit the applied stress to the crystalline regions. Therefore, the double yield phenomenon is reduced until it disappears with increasing EPDM content.

3.3. Effect of stretching rate

The stress–strain curves for the 1:1 rapidly cooled blend without elastomer, stretched at different rates are shown in Fig. 5. A yield maximum takes place at the highest stretching rate. On the right-hand side of the yield maximum, a hump appears and develops with decreasing stretching rate. This hump turns into a second yield maximum and at a stretching rate of 100 mm min^{-1} its stress is comparable to that of the first yield maximum, then this second maximum becomes predominant at smaller stretching rates. This clearly indicates that in the yield process there are two mechanisms which are strongly affected by the stretching rate. However the stress–strain curves for a blend with 10% EPDM dutral have some differences (Fig. 6): all the curves represent smaller values for the stress, the yield maxima are still present although relatively less pronounced, and the two maxima have comparable stress values at the higher stretching rate of 300 mm min^{-1}. In these figures the effect of the elastomer content is again evident, as discussed before in relation to Fig. 4.

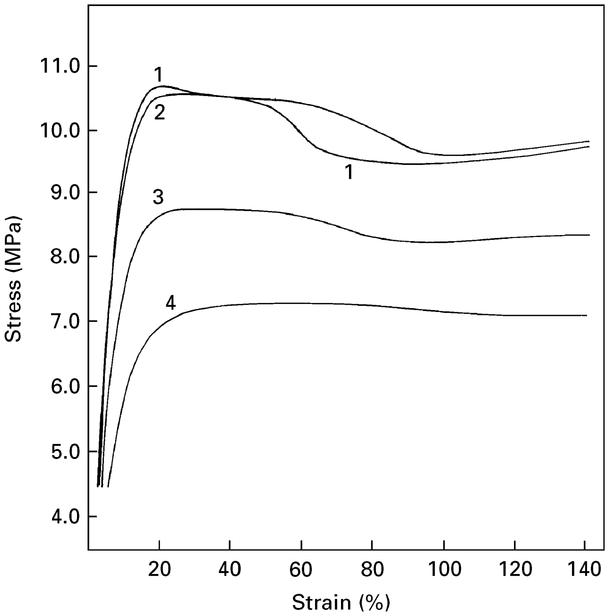

Figure 4 Effect of EPDM dutral content in blends containing fixed relative amounts of both polyethylenes; see Fig. 2. (1) 50/50/0; (2) 47.5/47.5/5; (3) 41.25/41.25/17.5; (4) 35/35/30.

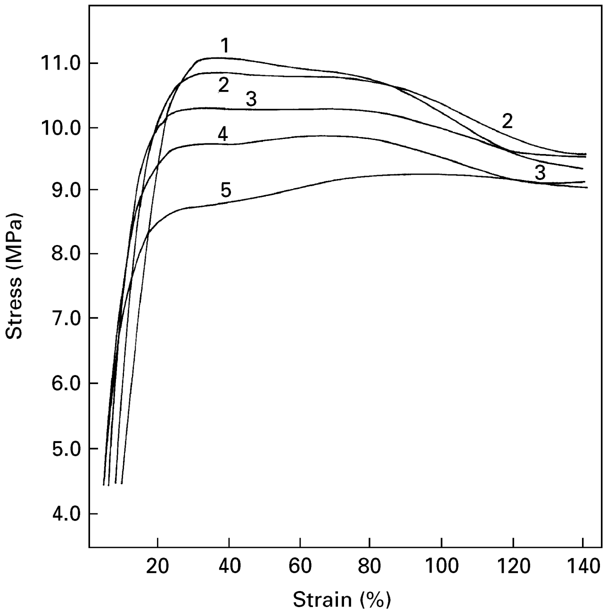

Figure 5 Effect of stretching rate on the stress–strain curve for the blend 50/50/0, rapidly cooled and prepared at 40 r.p.m. and 180 °C. Strain rates: (1) 500, (2) 300, (3) 100, (4) 50, (5) 10 mm min^{-1}.

The shape of the curves shown in Fig. 5 clearly indicates that at high stretching rate the mechanism involving the slip of the crystalline blocks predominates over the mechanism involving the deformation

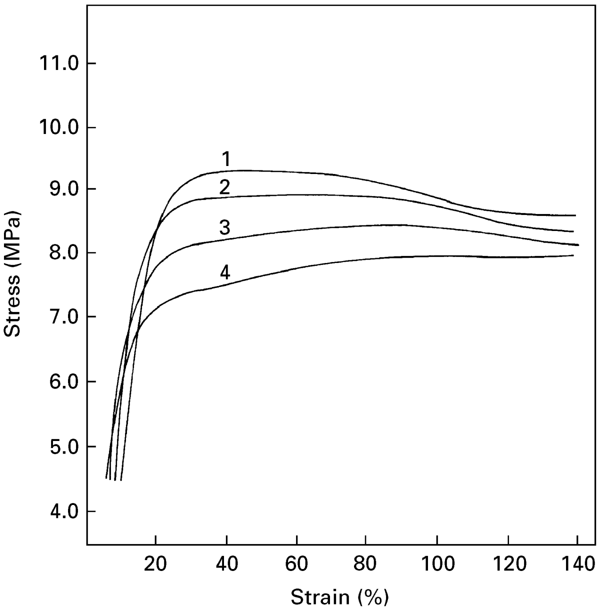

Figure 6 Effect of stretching rate for the blend 45/45/10, under the same conditions as in Fig. 5. Strain rates: (1) 500, (2) 300, (3) 100, (4) 10 mm min^{-1}.

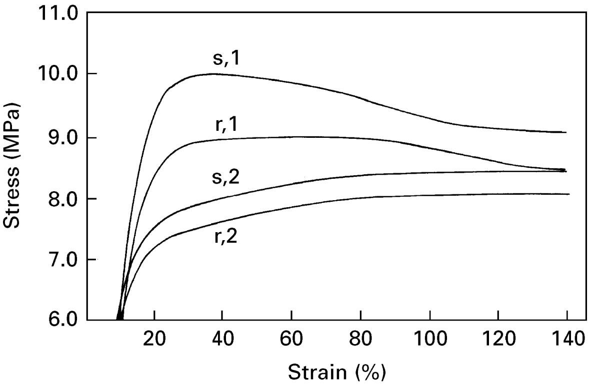

Figure 7 Effect of cooling rate on the σ–ε curve for the blend 45/45/10. (r) Rapidly cooled and (s) slowly cooled, (1) 300 mm min^{-1} and (2) 10 mm min^{-1}.

of the crystalline blocks, while at slow stretching rate the second mechanism predominates. This effect may be explained in terms of the stress relaxation time, which is present at all rates. When the deformation takes place in a short time (i.e. high stretching rate) the effect of the stress relaxation is small. In the opposite extreme case, when the deformation is applied slowly (50 times smaller), the stress value is smaller because the relaxation has sufficient time to reduce the stress. On the other hand, the stress corresponding to the second mechanism (deformation of the crystalline blocks) is relatively rate independent as is evinced in the σ–ε curve.

The effect of the strain rate on the double yield phenomenon is opposite to the effect of the deformation temperature. Stress–strain curves obtained at different deformation temperatures have been reported [7], the shapes of which are similar to those shown in Fig. 5. Two extreme types of stress–strain curves can be identified [5]. One type of curve (similar to curve 1 of Fig. 5) is typically seen at low temperatures or high strain rates, where the shape of the stress–strain curve describing the first yield process is the major factor in determining the shape of the applied stress curve. The other type of curve (similar to curve 5 in Fig. 5) is typically seen at high temperatures or low strain rates where the shape of the second yield process becomes dominant. These two extreme types of curve can individually be interpreted mechanically in terms of two parallel processes, as reported by Brooks *et al.* [5].

3.4. Effect of cooling rate

The effect of two different cooling conditions on the yield behaviour are shown in Fig. 7, for samples stretched at two rates, where the stress–strain curves exhibit some differences. The slowly cooled samples (curves s, 1 and s, 2) exhibit higher stress than the rapidly cooled ones (curves r, 1 and r, 2); at small stretching rate the curves are parallel to each other, but at high stretching rate their shapes are different; at 300 mm min^{-1} the first yield maximum is higher than the second maximum in the slowly cooled sample (curve s, 1), while they have comparable values in the rapidly cooled one (curve r, 1). These results are expected because, as opposed to the rapid cooling, the slow cooling promotes the production of a higher proportion of thicker lamellar crystals and the formation of more perfect crystals. In fact, both the degree of crystallinity and the crystallite size in the slowly cooled sample are slightly higher than in the rapidly cooled one [11]. The different cooling conditions also may cause the size of the block boundaries (i.e. the phase between the crystal blocks) to be smaller in the slowly cooled samples. Consequently, it is more difficult to deform these regions in the slowly cooled samples as is evinced by the stronger stress needed to produce the slip of the crystal blocks. Similar observation has been reported for LDPE/LLDPE blends by Balsamo and Müller [8]. There are many ways to cause the first yield stress to become dominant over the second yield stress: increasing the degree of crystallinity, increasing the strain rate, decreasing the deformation temperature. These factors involve more perfect crystals or a reduction in the mobility of tie chains.

3.5. Effect of the type of EPDM

Blends with composition 45/45/10 using three different EPDMs, whose characteristics are listed in Table I, were stretched at the intermediate extension rate of 100 mm min^{-1}. In general, the mechanical properties of the blend prepared with the EPDM dutral have different values than those for the blends prepared with EPDM nordel, while the mechanical properties of those prepared with either EPDM nordel are similar to each other [11]. Fig. 8 shows the corresponding stress–strain curves in the region of elongation where the yield phenomenon occurs. The curves for blends containing nordel are almost parallel to each other but different in shape to that prepared

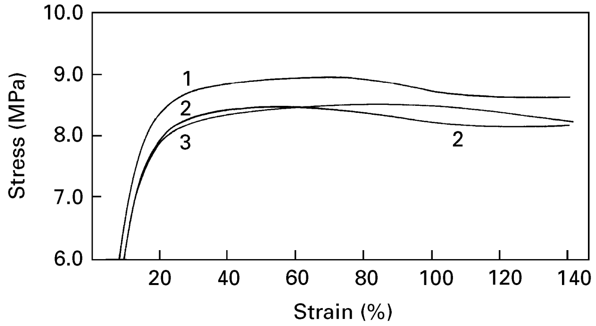

Figure 8 Stress–strain curves for blends 45/45/10, rapidly cooled, with different EPDM elastomers. (1) Nordel 1040, (2) nordel 1070, (3) dutral.

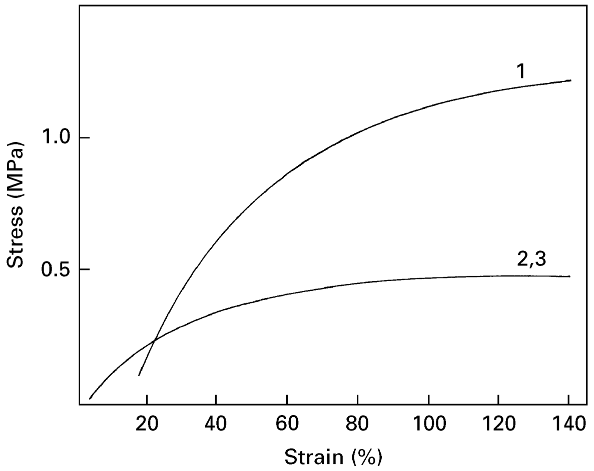

Figure 9 Stress–strain curves for the three pure elastomers stretched at 80 mm min^{-1}. (1) Dutral, (2) nordel 1040, (3) nordel 1070.

with dutral. The presence of the double yield phenomenon is still clear in the latter case, while it is disappearing in the former cases. As discussed before, because the main effect of the addition of EPDM to the blend is to increase the amorphous region surrounding the crystalline regions, the behaviour of nordel in the blend is as if the blend contained a greater amount of elastomer; this effect can be seen by comparing curves 1 and 2 of Fig. 8 with the evolution of the curves (Fig. 4) with increasing amount of EPDM. This difference is produced by the different behaviour of the elastomers; the σ–ε curves for the pure elastomers (Fig. 9) show that both EPDM nordel in the yield region are practically identical to each other and need a lower applied stress than dutral to reach the same elongation. This capacity of nordel to flow more easily than dutral is the reason why blends containing these elastomers behave in an equivalent way as if there were a greater amount of elastomer in the blend.

4. Conclusion

The composition of the triblends has three marked effects on the nature of the stress–strain curve in the double yield region: (1) the stress in those LLDPE-rich blends is higher than in LDPE-rich blends; (2) the elongation interval of the yield region is smaller in LLDPE-rich than in LDPE-rich blends; and (3) the double yield phenomenon in the polyethylenes decreases until it disappears with increasing elastomer component.

The first two effects can be explained in terms of the differences in the degrees of crystallinity and in the size of the defective regions surrounding the crystalline blocks of both PEs. The degree of crystallinity of LLDPE-rich blends is higher. Additionally, because the LLDPE has a smaller degree of branching than LDPE, the size of the defective regions surrounding the crystalline blocks is expected to be smaller. Therefore, the required stress to deform this defective region is higher and at the same time the elongation range is smaller. This conclusion is confirmed by the WAXS observation in slowly cooled samples.

The effect of the stretching rate on the predominance of either mechanism in the double yield phenomenon, i.e. the shape of the stress–strain curve, is explained in terms of the stress relaxation time. These conclusions reinforce the validity of the model proposed by Seguela and Rietsch.

The effect of increasing the elastomeric component (third effect) is to increase the amorphous phase that surrounds the crystalline regions and, additionally, the amorphous phase becomes softer. Therefore, the net effect of the elastomer component in the blend is equivalent to reducing the strain rate. This effect is also observed by changing the type of EPDM.

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