

Effect of EPDM on LDPE/LLDPE Blends: Mechanical Properties

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ABSTRACT: Blends of two polyethylenes and an elastomer were prepared to investigate the effect of the latter polymer. The blends contain equal parts of low density (LDPE) and linear low density polyethylene (LLDPE), and ethylene-propylene-diene rubber (EPDM) with variable content ranging from 0 to 17.5%. Melt-mixed blends were prepared using a single-screw extruder. The influence on the mechanical properties of the following factors were analyzed: EPDM content, stretching rate in the range from 10 to 750 mm/min, and two cooling conditions. From the equilibrium torque the miscibility was analyzed. The structure exhibited by the stress-strain ($\sigma-\epsilon$) curve of the polyethylenes blend is reduced with the addition of the elastomeric phase, and the ultimate properties increase because the amorphous phase becomes softer and reduces its capability to transmit the applied stress to the crystalline particles. The slope of the $\sigma-\epsilon$ curve in the strain hardening region shows a maximum value at the stretching rate $\sim 50-80$ mm/min, which is explained partially in terms of the strain-induced crystallization of the polyethylene components. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 677-683, 1997

Key words: ternary blends; stretching rate; ultimate properties

INTRODUCTION

In recent years there has been much commercial interest in the development of polymer blends from large volume commodity plastics. Polyolefin blends have been studied to improve the properties and processability of the homopolymers involved.¹⁻³ In addition to the improvements of the mechanical and overall physical behavior, study of such blends is important because mixtures of such polymers often occur in plastic scrap and waste and affect their possible reuse. Blends of low density polyethylene (LDPE) and linear LDPE (LLDPE) are regarded as excellent materi-

als for film manufacture because they combine the good processability of LDPE and the good mechanical properties of LLDPE.⁴ This blend system has been studied by several authors; crystallization,⁵ thermal,^{6,7} mechanical,⁷ and rheological⁴ properties have been reported. The blends were found mechanically compatible in all the compositions.⁸ On the other hand, it has been suggested that the presence of a rubbery interphase between the heterophases in binary mixtures of incompatible polymers may be an important factor necessary to achieve good impact resistance and elongation at break, and that satisfactory tensile strength depends more on the dispersant properties of the rubbery component.⁹

In this paper we present the effect of the ethylene-propylene-diene rubber (EPDM) on the mechanical properties of a melt-mixed blend of LDPE and LLDPE containing equal proportions of both

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polyethylenes. In the analysis are included the effects of elastomer content, stretching rate, and cooling conditions.

EXPERIMENTAL

Materials

The characteristic parameters of the commercial polymers used to prepare the blends are as follows. The LDPE sample was obtained from Pemex, México, the LLDPE from Chem Int., and the elastomer EPDM from Montedison. The LDPE is marked under the name PX 17070, has an MFI value of $7.0 \text{ g (10 min)}^{-1}$ and a density of 0.917 g cm^{-3} . The LLDPE sample has the product name GB 5010, a melt index of $1.0 \text{ g (10 min)}^{-1}$, and a density of 0.919 g cm^{-3} . The EPDM has the name Dutral CO 038, a Mooney viscosity ML (1 + 4) 121°C of 65, and a specific gravity of 0.865, as reported by the producer. These polymers were used without any modification.

Preparation of the Blends and Test Samples

The materials were pulverized in a Brabender-type mill and the powders were physically mixed in the desired weight ratios. Sheets with a uniform thickness ranging from 0.5 to 0.7 mm were prepared using a single-screw Brabender extruder operated at 180°C and 40 rpm. The hot sheets obtained directly from the extruder were cooled down to room temperature in air. Sheets obtained in this way will be referred to as rapidly cooled sheets. To study samples with a distinct thermal history, some of these sheets were placed in a vacuum oven and slowly cooled sheets were obtained by holding the vacuum oven at 120°C for 20 min and then allowing it to cool down freely. From the rapidly and slowly cooled sheets, samples with the standard dumbbell shape with dimensions $22 \times 7 \text{ mm}^2$ were punched out for tensile tests. All blends contain equal relative amounts of each polyethylene (i.e., their weight ratio is kept fixed in the relation 1 : 1). The compositions labeled in the order LDPE/LLDPE/EPDM have elastomer content ranging from 0 to 17.5%. The rapidly cooled blend without elastomer will be referred to as the "reference blend."

Measurements of Mechanical Properties

The uniaxial deformation of the samples was carried out at room temperature (25°C) in an Instron

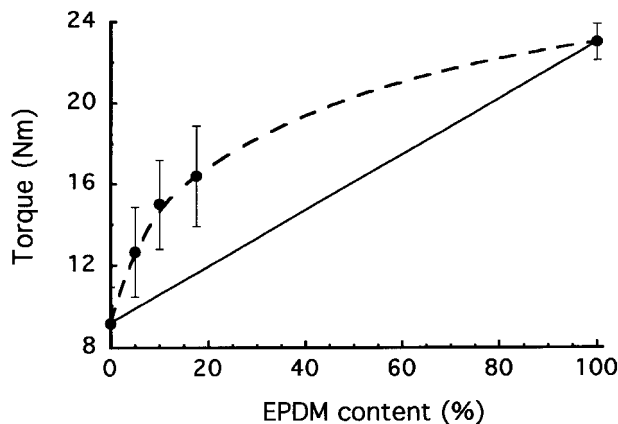


Figure 1 Mixing torque during extrusion process as a function of the elastomer content. The curve through the experimental points is drawn as a visual help.

tensile testing machine (4502). The influence of the stretching rate on the resulting stress–strain (σ – ϵ) curves was analyzed over a wide interval ranging from 10 to 750 mm/min. In all the experiments, the deformation of the specimens was carried out up to rupture. A considerable amount of scatter in the data is inherent in these types of measurements, particularly in the final properties. Therefore, at least seven specimens of each sample were tested in each case.

WAXS Measurements

The crystallinity and an estimation of the crystallite size were determined in the standard way¹⁰ by using the wide angle X-ray scattering technique (WAXS). The patterns were recorded with a Philips horizontal goniometer (PW 1380/60) fitted with a scintillation counter, pulse-height analyzer, and a graphite crystal monochromator placed in the scattered beam. $\text{CuK}\alpha$ radiation generated at 45 kV and 35 mA was used. The scattered beam was registered in the angular interval (2θ) from 3 to 45° .

RESULTS AND DISCUSSION

Extrusion Torque

The steady-state value for the mixing torque was measured during the extrusion process. This value depends on the blend composition, as shown in Figure 1. The torque increases with the EPDM content. The EPDM strongly affects the mixing

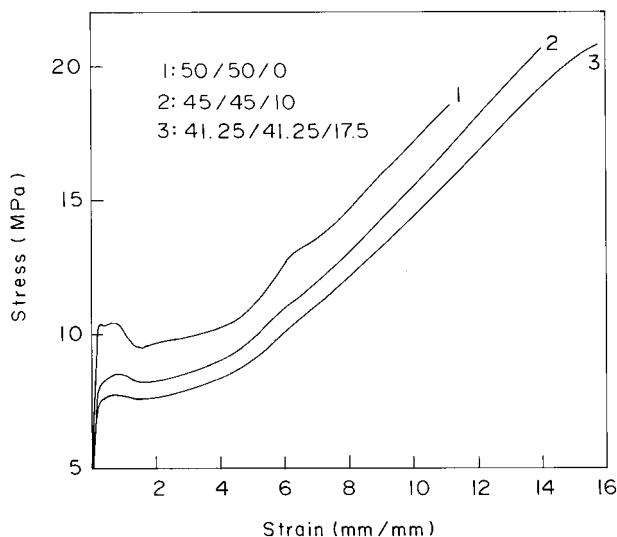


Figure 2 Stress-strain curves for blends LDPE/LLDPE/EPDM with different EPDM content, stretched at 100 mm/min.

torque, increasing it by $>75\%$ in going from the reference blend to that containing 17.5%. The error bars are included in the figure to emphasize the fact that the increment is nonlinear and that the measured torque, for these compositions, is higher than that predicted by the linear additive rule of ideal blends, which is represented by the straight line.

The equilibrium torque value may be taken as proportional to the viscosity of the system at the temperature and shear rate involved. The viscosity of the binary blend LDPE/LLDPE is reported to obey the logarithmic additivity rule.⁴ However, this rule is not obeyed by the extrusion torque when the EPDM is added to the reference blend. This seems to indicate that the binary blend LDPE/LLDPE and the EPDM at least partially are not miscible in the melt.

Effect of Composition

The average σ - ϵ curve for the blend 50 : 50 : 0 stretched at an intermediate rate is shown in Figure 2. It closely resembles the curve that usually is presented as typical of a semicrystalline polymer^{11,12}; this curve has a yield region and is typical of a material which cold-draws with necking down of the cross section in a limited area of the specimen. The curve can be schematically subdivided into three parts. Part I: the Hookeian region, characteristic of very low strains. Part II:

the curve displays one (or two) sharp force maximum at low deformation corresponding to a single (or double) yield point; beyond this maximum there is a decrease in the force with a further increase in elongation; the force then can be either essentially constant or varying with a small slope. Part III: this part of the curve may be identified as the well-known strain-hardening region where stress increases with a slope higher than in part II.

The curve shape just described is considered typical only as a reference. Now it is known that there is not a typical stress-strain curve. There is a profound influence of molecular constitution (molecular weight and chain irregularity), as well as crystallization conditions, on the general deformation characteristics of semicrystalline polymers. Popli and Mandelkern¹³ have reported nominal force-elongation plots for a selected set of linear and branched polyethylene samples in which the curve exhibits a variety of shapes.

The curve for the blend without elastomer (50 : 50 : 0 in Fig. 2) shows the improvement of the mechanical properties from the combination of the individual mechanical properties of both polyethylenes. Particularly, the average value of the elongation at break for the blend is $\sim \epsilon_B = 11$, which contrasts with that for the pure LDPE, which is at about one-half, while the pure LLDPE does about the same value as the blend. The hump exhibited by the blend at $\epsilon \approx 6$ is a characteristic coming from the pure LLDPE, since it was observed in all the specimens of this homopolymer.

The shape of the σ - ϵ curve for the reference blend is modified with the addition of the elastomer. Figure 2 illustrates this effect in rapidly cooled blends. The high strain modulus (at any fixed strain) decreases with the increment in the elastomer content, in contrast to the elongation at break, which generally increases. Also, the double yield phenomenon and the hump present in the reference blend become less pronounced with increasing the EPDM content until they disappear.

The three different parts of the σ - ϵ curves, describing different molecular phenomena, can also be distinctly identified for blends with small EPDM content. These blends exhibit well-defined double yield points on the stress-strain curves, whereas those with higher EPDM content do not. A complete analysis of the double yield phenomenon observed in these ternary blends was reported recently.¹⁴ Moreover, the exact initiation and termination of the different parts on the σ - ϵ curves are difficult to mark with the increase in the

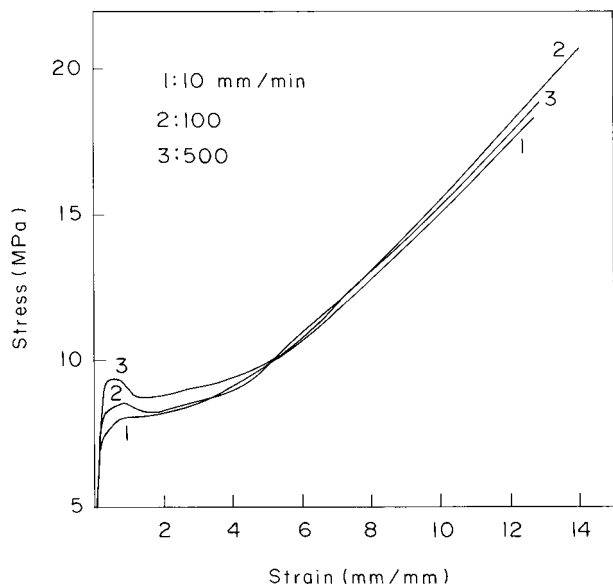


Figure 3 Stress-strain curves for the rapidly cooled blend 45 : 45 : 10 stretched at the different indicated rates in mm/min.

EPDM content. Parts II and III especially are overlapping in the blend containing 35% of EPDM (curve not shown). This means that the slippage and orientation of chains along the stretching direction take place simultaneously.

In the absence of the elastomeric component, the material surrounding the crystalline particles is composed of amorphous phases of both polyethylenes. Because of the mixing method used here, it is reasonable to expect the incorporation of the elastomeric component predominantly in the amorphous phase surrounding the crystalline particles, but not in their interior. Thus, the amorphous phase 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 particles. Therefore, the structure observed in the stress-strain curve of the reference blend is reduced until it disappears with increasing the elastomer content.

Effect of Stretching Rate

The stretching rate has two important effects on the general nature of the σ - ϵ curves: in the yield region and on the slope of the last part of the curve (Fig. 3). The stretching rate has maximum influence on the yield region where the stress is higher for higher rates. This effect may be ex-

plained in terms of the stress relaxation time. 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.

In the yield region the samples display neck formation. The deformation is confined to the region of neck formation, and the neck gradually propagates through the sample. After the neck has traversed the sample, the whole length of the sample deforms uniformly. The neck formation initiates about the elongation of the second yield point; these observations are in accordance with those reported earlier for pure polyethylenes.¹⁵ Upon formation of the neck, the deformed region whitens. This whitening may be due to void formation, as described elsewhere for polyethylenes.¹³

The last part of the curves resembles the characteristic shape found in the strain-induced crystallization (SIC) phenomenon.¹⁶ Figure 3 also shows that the curve representing the stretching rate of 100 mm/min has the highest value of the final slope. This would suggest that the strain-induced crystallization, if present, has the maximum value around this stretching rate. The possibility that the SIC phenomenon may be happening can be detected through the analysis of the final slope dependence on the stretching rate.

The final slope (f_s) as a function of the stretching rate (v) is shown in Figure 4 for blends containing different amounts of EPDM and the two thermal histories. The shape of the f_s versus v curves for all

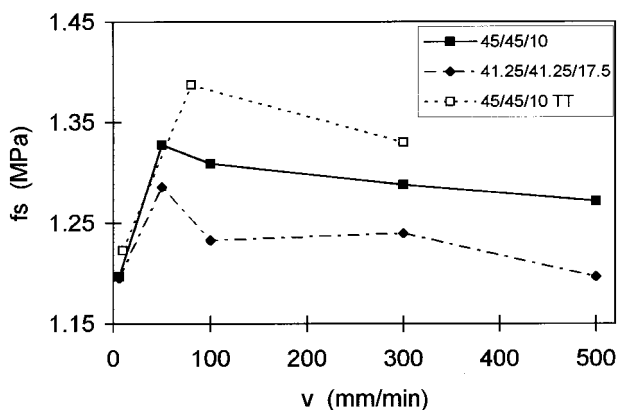


Figure 4 The effect of the stretching rate (v) on the final slope (f_s) of the stress-strain curves. The label TT refers to slowly cooled sample.

blends are similar to those exhibited by the examples of Figure 4. The final slope represents the conventional strain hardening $(\partial\sigma/\partial\varepsilon)_v$; the subscript v ($=d\varepsilon/dt$) means that the slope is taken at constant strain rate. For the purpose of this paper, we do not make an error if instead of the strain rate we use the stretching rate, since the initial length of the specimen had the same constant value in all the tests. The strain hardening has a maximum value for a stretching rate ~ 50 – 80 mm/min. The curves of the final slope values have in common an almost linear increasing behavior with decreasing the stretching rate up to 50 – 80 mm/min. However, for the rate of 10 mm/min the final slope value has a significant decrease. This may be an indication that at this stretching rate the SIC mechanism is reduced. These changes in the final slope are attributed exclusively to the polyethylenes components, since the stress–strain properties for the pure EPDM did not change in this range of stretching rates.

The strain hardening region characterized by a noticeable increase in the final slope value may be caused mainly by two mechanisms. Due to stretching, the polymers undergo plastic deformation leading to high orientation of chains in the amorphous regions as well as reorganization of crystallite structure in the stretching direction, since at this stage the originally present spherulitic order is already broken. Also, due to stretching, a part of the chains in the amorphous regions may be oriented in a perfectly crystalline fashion, which may increase the crystallinity content. One or both of these two main factors contribute to the strain hardening. Recently, Ray, Khastgir, and Mukunda¹⁷ studied stress–strain properties of LDPE as a function of the strain rate and found that the final slope increases with decreasing the strain rate in the range from 1000 mm/min to 100 mm/min. After failure, samples were studied by WAXS and DSC (differential scanning calorimetry) to estimate the change in the crystallinity. They reported that the strain hardening is mainly due to the change in internal order of crystallites with marginal increase in strain-induced crystallization. Investigations of the changes occurring in the crystalline morphology during the process of deformation are in progress in our laboratory, the detailed discussion will be communicated in future.

The above discussion was made for rapidly cooled samples. The effect of the cooling conditions on the σ – ε curve is illustrated in Figure 5

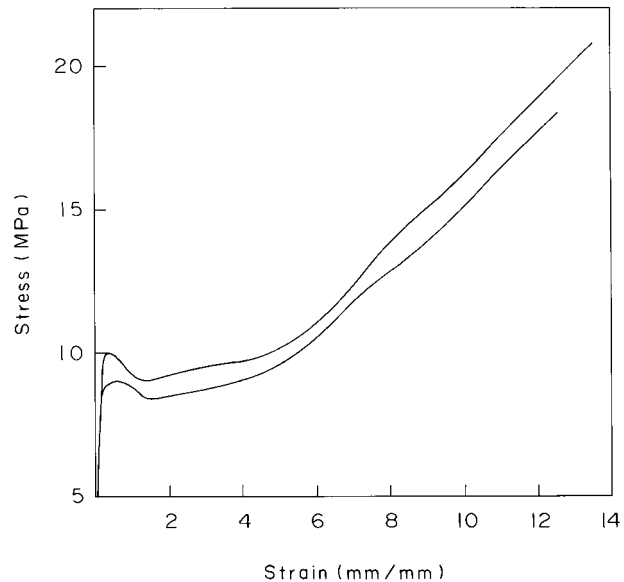


Figure 5 Cooling rate effect on stress–strain curves for blends 45 : 45 : 10 stretched at 300 mm/min. Lower curve: rapidly cooled sample; upper curve: slowly cooled sample.

for a fixed stretching rate. In general, the σ – ε curve for samples subjected to the slow-cooling treatment shows better mechanical properties. In particular, the stress at rupture as well as the stress at any fixed elongation have higher values in slowly cooled samples. However, the values of the strain at rupture are practically equal for both cooling conditions. The differences observed are due, as a consequence of the distinct thermal histories, to the slightly different crystallinity and crystal size in the unstretched state. For example, for the blend 45 : 45 : 10 the crystallinity and the estimated crystal size in the rapidly cooled sample are 42% and 14.1 nm, respectively; while for the slowly cooled sample these parameters are 44% and 15.1 nm. Also, the slow-cooling treatment causes that the strain hardening (measured by the final slope) be higher in these samples, as is represented in Figure 4. The final slope values for the slowly cooled samples could be anticipated to be higher than those for the rapidly cooled samples since, in addition to the possible present mechanisms during the strain hardening, the crystallinity in the unstretched state is higher, which in turn leads to a higher stress for the same degree of elongation.

Final Properties

The final polymeric properties investigated are the stress and the elongation at rupture. Typical

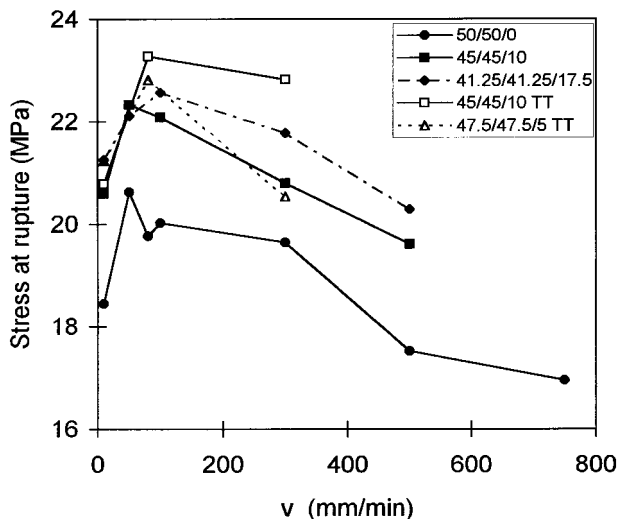


Figure 6 Stress at rupture as a function of the stretching rate. Effects of the elastomer content and the cooling rate. The label TT is used to identify the slowly cooled samples.

data of these properties for some blends are represented in Figures 6 and 7, respectively, as functions of the stretching rate, composition, and the two cooling rates. In general, both final properties increase with increasing the EPDM content; however, they show different dependence on the strain rate. The slow-cooling condition has a noticeable effect on the stress at rupture (σ_B), in contrast to the strain at rupture (ε_B), where the effect is practically null.

The stress at rupture as a function of the stretching rate (Fig. 6) does not have linear behavior, it shows a maximum around the stretching rates of 50–100 mm/min. This behavior is consistent with that observed in the final slope. In both types of samples (rapidly and slowly cooled) the σ_B increases with the EPDM content. The effect of the slow cooling treatment is again evident. During strain hardening both the amorphous and crystalline components attempt to orient along the stretching direction. These orientations lead to close packing of the chains, causing appreciable increase in the intermolecular forces of attraction, which account for high stress at rupture.

The values of the strain at rupture for the reference blend are practically independent on the stretching rate, within experimental errors, since the slope in the linear fitting of the data is very small (Fig. 7). This result agrees with those reported for pure polyethylenes. Andrews and Ward¹⁸ found that there was no effect of strain

rate on ε_B up to a critical rate, after which a rapid increase in ε_B was observed; in high molecular weight linear as well as branched polyethylenes it was reported¹³ that there was no change in ε_B for strain rates in the range from 0.2 mm/min to 1000 mm/min. In our case, Figure 7 shows that the ε_B values for blends containing EPDM are also practically independent on the stretching rate, and that they increase with the elastomer content. Because the incorporation of the EPDM predominantly increases the amorphous regions, as discussed above, the deformations take place to longer elongations.

CONCLUSIONS

One effect of the elastomer EPDM (up to 17.5% content) on the binary blend LDPE/LLDPE, with equal proportions of both polyethylenes, is to increase significantly the steady-state value of the mixing torque. The equilibrium torque does not obey either the linear or the logarithmic additivity rules. This may mean that the EPDM at least partially is not miscible with the blend LDPE/LLDPE in the melt.

The addition of the elastomeric phase has marked effects on the nature of the stress–strain curve of the binary blend. The high strain modulus decreases, the yield phenomenon becomes less pronounced until it disappears, and the typical

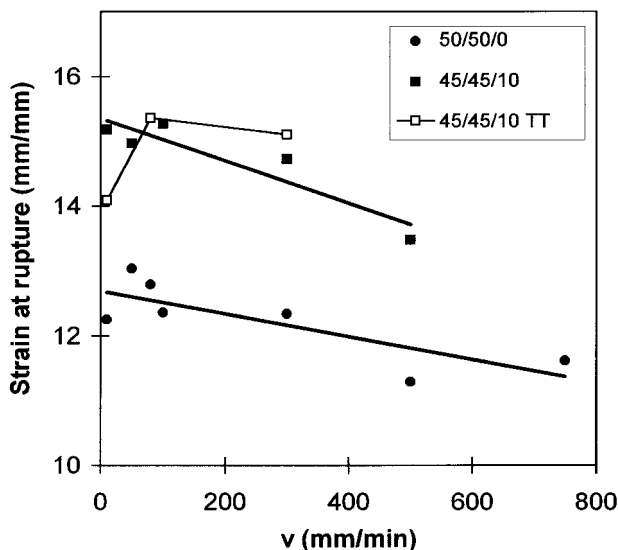


Figure 7 Stretching rate dependence of the strain at rupture. Same legend as in Figure 6.

shape of the stress–strain curve of semicrystalline polymers is modified. Because the amorphous phase, which surrounds the crystalline regions, increases with the incorporation of the EPDM, the whole amorphous phase of the system becomes softer and reduces its capability to transmit the applied stress to the crystalline regions.

The stretching rate has an important influence on the yield region where the stress is higher for higher rates, and on the strain hardening region where the final slope (of the σ – ε curve) has a maximum value at rates ~ 50 – 80 mm/min. The changes in the final slope are attributed in part to the strain-induced crystallization of the polyethylene components.

The slowly cooled samples have better mechanical properties than the rapidly cooled samples, since the former have slightly higher crystallinity and crystal size in the unstretched state. The EPDM has a positive effect on increasing the final mechanical properties of the polyethylenes blend.

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