

Tensile Mechanical Behavior of Linear High-Density Polyethylenes Modified With Organic Peroxide

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The molecular structure of several high-density polyethylenes of different molecular weights and vinyl contents was modified without altering their thermoplastic character using an organic peroxide. Chain linking was the main chemical event that occurred during the modification process. Samples of these polymers were crystallized from the melt, generating materials with different morphologies. Two crystallization procedures were followed: slow cooling and quenching. The density and crystallinity of the polymers were found to be slightly dependent on the molecular structures generated by the modification process. Tensile tests were performed at room temperature to evaluate the mechanical behavior of the polymers. The mechanical response of some of the slowly cooled samples changed from brittle to ductile when increasing concentrations of peroxide were added to the formulation. All the quenched samples displayed ductile behavior. The elastic modulus and yield stress were found to increase linearly with the crystallinity of the polymers independently of the molecular structure generated by the modification process. The molecular weight of the modified polymers appears to be the main structural property that influences the draw ratio after break and the ultimate tensile stress of the samples. The draw ratio diminishes, while the ultimate tensile stress increases with the molecular weight of the polymers, irrespective of the evolution of other molecular parameters.

INTRODUCTION

The treatment of polyethylene (PE) with organic peroxides at temperatures above its melting point is a well-known process used to change the thermo-mechanical properties of these polymers (1, 2). Many authors have analyzed the effect of adding a relatively large amount of peroxide to form a thermally stable macroscopic molecular network (1–8). Other studies have focused their attention on the modification of PE with peroxide concentrations below the critical one to obtain a molecular network (9–18). Under these conditions, the molecular structure of the original polymers is modified to generate new materials with different amounts of chain branching. The properties of the polymers are changed in this way without altering its thermoplastic character.

The treatment of PE with peroxide produces macro-radicals, which participate in combination reactions leading to crosslinking, long-chain branching and

chain extension reactions. Consequently, the polymers obtained using amounts of peroxide below the critical gel-concentration exhibit viscous and elastic properties in the molten state that grow significantly with the concentration of peroxide used in the reaction (9–18). The molecular structure of the original polymer significantly affects the degree of modification generated by the process. In that sense, the vinyl content and the molecular weight of the original PE are the most important parameters that should be taken into consideration. It has been observed that, for similar molecular weights and for a given peroxide content, the vinyl-containing polyethylenes display the largest molecular changes and, consequently, the largest changes in the rheological parameters (18). Furthermore, the amount of gel obtained from a given reaction increases with the initial vinyl content of the polymer when it is modified with peroxide concentrations beyond the critical concentration to induce gelation (8).

The different characteristics of the molecular structure, as well as the conditions of crystallization, determine the morphology and, consequently, the mechanical properties of the solid PE samples (19–29). For

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example, the level of crystallinity, which depends on the molecular weight, the degree of branching of the polymer, and the cooling rate from the melt, is one of the morphological variables that determines the value of properties such as the elastic modulus and yield stress. For molecular weights of linear PEs greater than about 1×10^4 g/mol, there is a continual decrease in the level of crystallinity until very high molecular weights are reached (30). In addition, in polyethylenes with short chain branches, i.e. ethylene copolymers, the level of crystallinity decreases monotonically with the branching level (26). The influence of crystallinity on the stress-strain properties is notorious. The yield stress increases almost proportionally and the modulus increases in a sigmoid-like form with the level of crystallinity (22–29). The ultimate mechanical properties, such as the stress and the draw ratio at break, depend on the molecular weight and branching level rather than on the degree of crystallinity. The stress at break displays a maximum, while the draw ratio at break decreases monotonically, when the molecular weight increases (22–28).

Since the treatment with peroxide produces significant changes in the molecular structure and the properties of molten PE, it is of interest to analyze the effect of such changes on the morphology and the mechanical behavior of the semicrystalline modified polyethylenes. To our knowledge, there is only one work that has studied the behavior of polyethylenes modified with low concentrations of peroxide (10). In this work, Kim and Kim found that the crystallinity level tends to decrease while the flexural modulus and the yield strength tend to increase with the concentration of peroxide.

In the present work, we have analyzed the changes produced in the morphology and the tensile mechanical behavior of high density polyethylenes as a consequence of the chemical attack with an organic peroxide. The peroxide concentrations considered are below the critical value needed to produce a gel. This work complements a previous one that was recently published on rheological behavior of molten modified polyethylenes (18).

EXPERIMENTAL

Materials and Sample Preparation

Four polyethylenes were used in this study. They are labeled PE1, PE2, PE4 and PE5. PE1 was supplied by DuPont de Nemours (USA) while the other three were provided by Petropol S.A. (Argentina). PE1 has a vinyl concentration of 0.033 mol/l, which was calculated from the absorbance of the 908 cm^{-1} band of the FT-IR spectra (18). The other polyethylenes have very low vinyl concentrations, under 0.005 mol/l.

The chromatograms of the polymers were obtained by gel permeation chromatography (GPC) using a Waters 150-C ALP/GPC system equipped with a set of 10 mm PLGel columns from Polymer Labs with nominal pore size of 10^6 , 10^3 and 500 \AA . The solvent was 1,2,4-trichlorobenzene at 140°C . More details about the procedure and the chromatograms can be found in a previous publication (18).

Table 1 includes the number- and weight-average molecular weights of the four polymers. The GPC chromatogram of PE5 shows a bimodal shape with a long molecular weight tail with a maximum at approximately 500,000 g/mol. Although less noticeable, PE4

Table 1. Average Molecular Weights Estimated from GPC and Mechanical Behavior and Crystallinity of the Original and Modified Polymers.

| | Peroxide concentration [ppm] | Molecular weight | | Mechanical behavior ¹ | |
|-----|------------------------------|-----------------------------|-----------------------------|----------------------------------|--------------------------|
| | | Mn $\times 10^{-3}$ [g/mol] | Mw $\times 10^{-3}$ [g/mol] | Quenched (Q) samples | Slow-cooled (SC) samples |
| PE1 | 0 | 22 | 53 | D (65) | B (83) |
| | 250 | 24.5 | 71 | D (66) | B (84) |
| | 500 | 29 | 78 | D (63) | T (77) |
| | 750 | 26 | 98.5 | D (61) | D (76.5) |
| | 1000 | 31.5 | 130 | D (58) | D (72) |
| | 2000 | 30.6 | 159 | D (55) | — |
| PE2 | 0 | 12 | 55 | D (68) | B (81) |
| | 250 | 16.5 | 70 | D (63) | B (80) |
| | 500 | 15.5 | 72 | D (66) | B (78) |
| | 750 | 13.5 | 76 | D (64.5) | B (77) |
| PE4 | 0 | 20 | 79 | D (62) | B (76) |
| | 250 | 18 | 85 | D (66.6) | T (71) |
| | 500 | 19 | 94 | D (62) | D (75) |
| | 750 | 20 | 95 | D (69) | D (77) |
| PE5 | 0 | 17 | 135 | D (56) | D (65) |
| | 250 | — | — | D (57) | D (69) |
| | 500 | — | — | D (62) | D (67) |
| | 750 | — | — | D (56) | D (67) |

¹These columns list the type of mechanical behavior of the studied polymers (D: ductile, T: transitional, B: brittle) and their crystallinity level measured by DSC (shown in parentheses) expressed as percentage.

also presents a long molecular weight tail. The rheological behavior of molten samples of PE4 and PE5 reveals that these polymers contain some degree of long-chain branching.

The 2,5-dimethyl-2,5-di(tert-butylperoxy)-hexane (Trigonox 101), kindly supplied by Akzo Nobel Química S.A. (Argentina), was the organic peroxide used for the modification of the polyethylenes. Samples of the polymers were dissolved in boiling xylene, then precipitated in cool methanol and afterwards dried to obtain fine powders free of additives. Fractions of these polyethylenes were then impregnated with different weights of a peroxide-hexane solution. After stirring the slurries to homogenize the mixtures, the hexane was allowed to evaporate under hood at room temperature leaving the PE powders impregnated with the desired amounts of peroxide. Three peroxide concentrations (250, 500 and 750 ppm) were used in the present study to modify the polyethylenes. In addition, PE1 was also modified with 1000 and 2000 ppm of peroxide concentration (see *Table 1*). The dried mixtures were compression molded at 170°C and 1 MPa in a thermostatically controlled hydraulic press using 3-mm-thick steel plates held apart by 0.5-mm-thick brass spacers. The molding pressure was kept for 5 min and then released. The modification reaction was allowed to proceed at 170°C for additional 15 min. This reaction time was chosen from rheological experiments, as the time needed to obtain constant values of the dynamic moduli (18). This time is used as indication of the complete reaction of the organic peroxide. Afterwards, the specimens were crystallized following two different procedures: 1) quenching from the melt to ice water temperature, and 2) slow cooling from the melt to ambient temperature keeping the samples between the plates of the press after the heaters were shut off. These procedures are identified as Q and SC respectively.

Morphological Characterization

The degree of crystallinity of the polymers was determined from the enthalpies of fusion measured in a Perkin-Elmer (DSC) Pyris 1 system. The calorimeter was calibrated using Indium as a standard. Specimens of about 7 mg of each polymer were sealed in aluminum pans and heated from 30°C to 150°C at a rate of 10°C/min. The enthalpy of fusion of each material was calculated from the area of the endothermic peak, defined by drawing a straight line from the onset to the end of the melting range. The degree of crystallinity was estimated considering a value of 69 kcal/kg for the fusion enthalpy of pure crystalline polyethylene (30). The reported results for the crystallinity of the different polyethylenes correspond to an average of the values determined for at least three samples of each polymer.

The density of the samples was determined at 24°C in a density gradient column filled with a mixture of isopropanol and triethylene glycol. The column was

calibrated with standard glass floats that allow density measurements with an accuracy of ± 0.2 kg/m³. The density values reported are the average of the measurements of at least four samples of each material. The degree of crystallinity on a density basis was calculated by the method of Chiang using values of 853 and 1000 kg/m³ for the densities of the non-crystalline and crystalline phases of the polyethylene samples respectively (31).

Tensile Mechanical Tests

Tensile measurements were carried out at room temperature (23–25°C) using an Instron 1122 tester at a crosshead speed of 2 cm/min. Dumbbell-shaped specimens of 12.0 mm gauge length and 4.0 mm width were stamped from 0.5-mm-thick plates obtained as previously described. The thickness of the testing specimens was measured to an accuracy of 0.01 mm. Equidistant ink marks were placed 2 mm apart on the deformation zone to facilitate the measurement of the draw ratio after break.

The elastic modulus of each specimen was determined from the slope of the stress-elongation curve at 1% of calculated strain. The yield stress was obtained from the maximum force observed at low deformation levels divided by the initial cross-area of the specimen. The draw ratio after break was calculated dividing the spacing of the ink marks measured immediately after break by the initial spacing. Finally, the ultimate tensile stress was estimated from the force at the breaking point divided by the initial cross-area. The values of the reported properties correspond to the average of 10 to 15 measurements obtained from different specimens. The standard deviation of the elastic modulus, yield stress, draw ratio after break and ultimate tensile stress is of approximately 10%, 4%, 2%–9% and 10%–20%, respectively.

RESULTS AND DISCUSSION

Molecular Characterization

Table 1 displays the weight- and number-average molecular weights of the four original polyethylenes and the new materials obtained after modifying the polymers with different amounts of peroxide. No results are available for the modified PE5 materials due to experimental difficulties to measure the large molecular weight tail with sufficient accuracy. However, these materials remain soluble, and their rheological characterizations correspond to thermoplastic polymers. All the values of the molecular weights listed in *Table 1* were estimated from GPC chromatograms under the assumption that the polymers have a linear molecular structure. Consequently, for all the modified polymers, the reported molecular weights should be lower than the true ones since the peroxide treatment introduces long chain branches into the otherwise linear polyethylene molecules (18). GPC-light-scattering (GPC-MALLS) measurements performed in

modified PEs obtained from polymers not included in the present work show that the difference between the values of M_w obtained by GPC-MALLS and GPC alone increases as the concentration of peroxide increases. A maximum difference of about 30% was observed for PEs modified with peroxide concentrations close to the gel point (see, for example, ref. 18). Nevertheless, the data listed in Table 1, although underestimated, indicate that the molecular weights of all polyethylenes increase with the concentration of peroxide. This increment is induced by the chain-linking reactions that occur between molecules as a consequence of the combination of macro-radicals (9, 32, 33). Comparing the results for the different polyethylene families, it may be observed that PE1 displays the largest increment in M_w relative to its initial value. This effect may be attributed to the vinyl groups initially present in the molecular structure of this polymer, which enhance the chain-linking processes, as was shown in a previous publication (18).

The morphology of PE in the solid state is determined by the structure of the polymer molecules and by the crystallization procedure used to go from the molten to the solid state (30). Figure 1 shows the density and crystallinity data as a function of the peroxide concentration used in the modification process. For the sake of clarity, when two data in Fig. 1 fell in the same place, one of them was shifted 20 ppm to the right. Several details may be observed: a) for a given crystallization mode, the higher the molecular weight of the original PE, the lower the crystallinity and density of the material; b) all the SC samples have higher crystallinity and density than the corresponding Q samples; c) both the crystallinity and the density of the Q and SC samples of the PE1 family of polymers decrease with the peroxide concentration; d) in the case of the other three polymers, the crystallinity and the density are practically unaltered by the modification of the polymers with peroxide except, perhaps, a small decrease that may be observed in

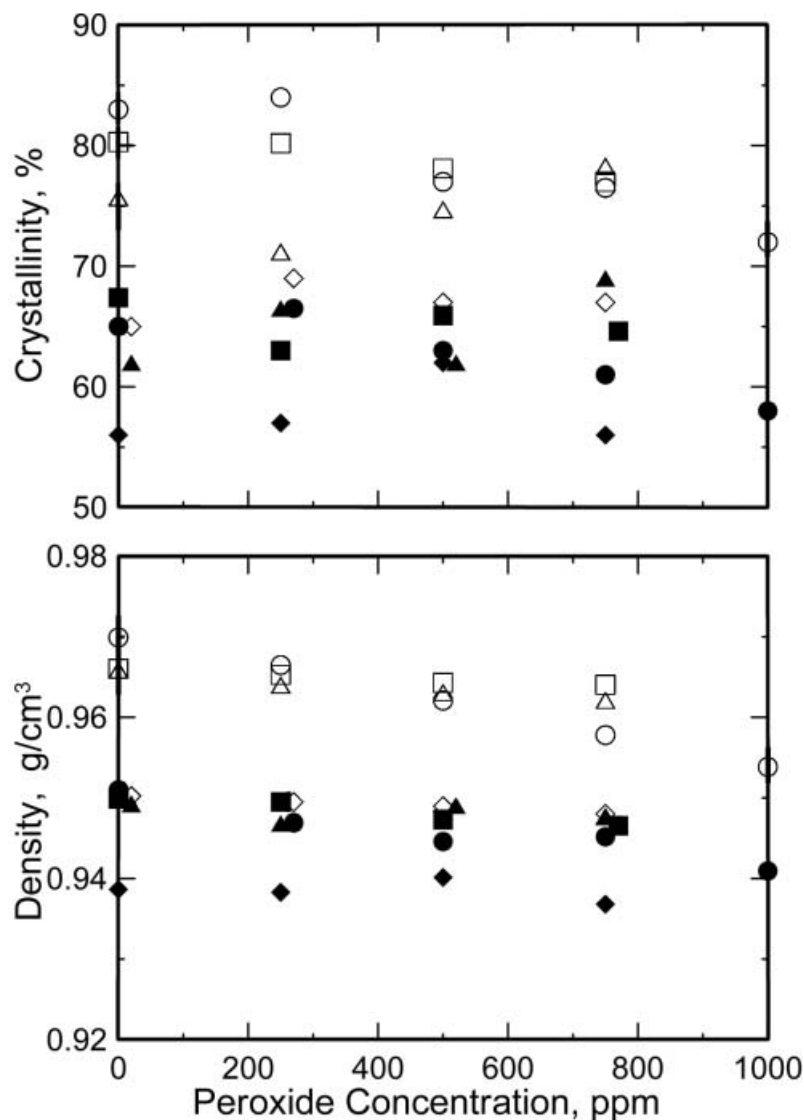


Fig. 1. Crystallinity calculated from enthalpy of fusion data and density of the polymers as a function of the peroxide concentration. Polymers: PE1 (○, ●); PE2 (□, ■); PE4 (△, ▲); PE5 (◇, ◆). Filled symbols: Q samples; open symbols: SC samples.

the case of the density of the SC samples. We attribute the larger change observed in the crystallinity and density of PE1 to the larger increase in the molecular weight experienced by this polymer with respect to the other three.

Mechanical Behavior

The modification of the molecular structure produced by the treatment with peroxide may induce important changes in the tensile response of a polymer. Figures 2 and 3 illustrate the changes observed in the PEs of the present study. These figures display the nominal stress-elongation curves corresponding to the Q and SC samples of the PE1 family of polymers. The quenched specimens of all the PEs (original and modified) display a ductile behavior, as illustrated in Fig. 2 for PE1. On the other hand, the SC samples of PE1 go from a brittle to a ductile behavior as the peroxide concentration increases (Fig. 3).

A yield region may be observed in Fig. 2 at low elongations. Although it is not clearly seen in this figure because of the scales used, the yield stress decreases slightly when the concentration of peroxide increases. Further analysis of this observation will be done later in the paper. Beyond the yield region, a stable drawing zone is observed until the "strain-hardening" process begins to occur. This process produces a continuous increase of the stress with elongation until the sample breaks. The drawing zone becomes shorter and the slope of the strain-hardening region increases with peroxide concentration. Furthermore, the elongation at break decreases and the stress at break seems to reach a maximum value as the concentration of

peroxide increases. The same qualitative behavior was observed in the Q samples of all the other PEs. This behavior can be associated with the progressive increase in molecular weight as the peroxide concentration employed in the modification process increases. The same trend in the evolution of the finale tensile properties with the molecular weight of the polymer has been observed for linear polyethylenes and ethylene copolymers (22–28).

Figure 3 includes a set of stress-elongation curves obtained from the SC samples of PE1 and the modified materials that were prepared from it. The original PE1 displays a brittle behavior, which is also observed in the SC samples of the original PE2 and PE4 materials. Specimens of these polymers either break at the yield point or immediately after yielding. However, the SC samples obtained from the original PE5 display a ductile behavior similar to the one described above for the Q samples. Above a given peroxide concentration, the modification of PE1 and PE4 produces a change from brittle to ductile behavior when they are allowed to crystallize slowly from the melt (see Fig. 3 and Table 1). The ductility of the materials increases with the peroxide concentration. All the SC modified materials obtained from PE2 display a brittle behavior.

It is known that the level of crystallinity plays an important role in the mechanical behavior of high-density polyethylene (HDPE) under tensile stress (23). The ductile-brittle transition in the behavior of HDPE takes place over a narrow range of crystallinity, which depends on the molecular weight. The results obtained in the present work agree with the expected behavior for polyethylenes with the corresponding crystallinity

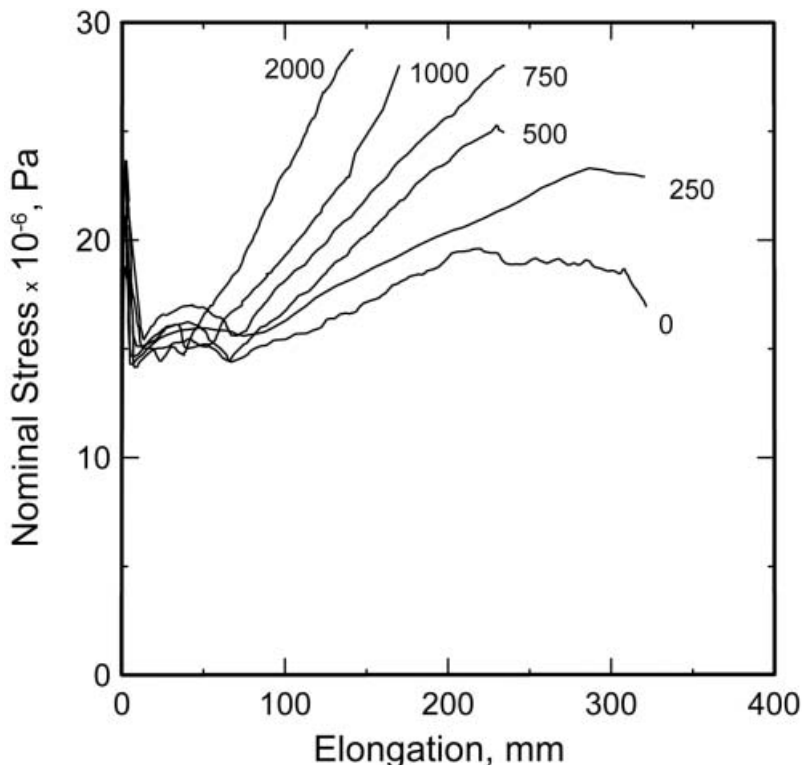


Fig. 2. Stress-elongation curves of the quenched PE1 family of polymers. The number beside each curve indicates the peroxide concentration used in the treatment of that sample.

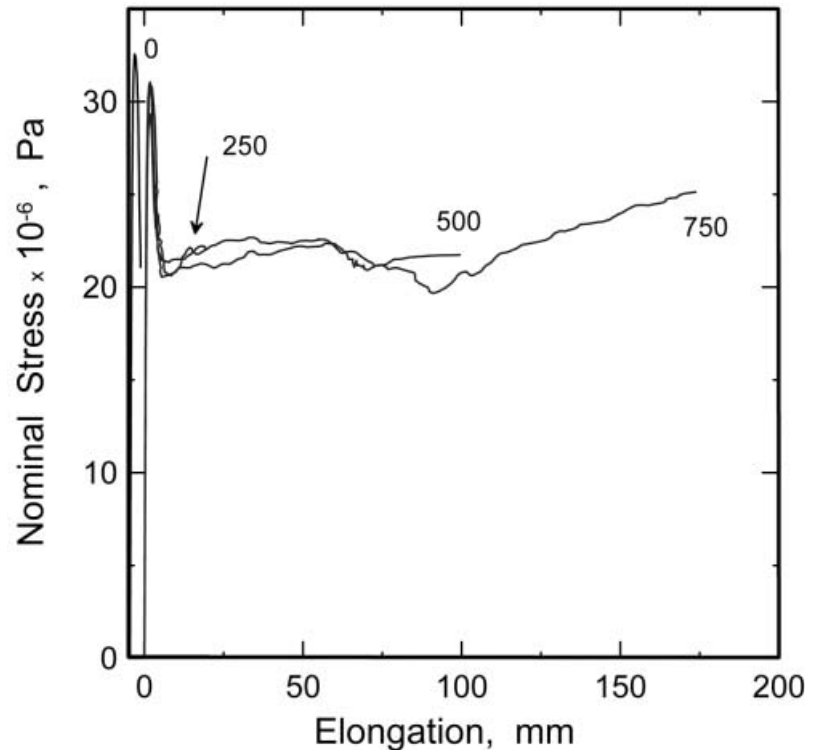


Fig. 3. Stress-elongation curves of the slow cooled PE1 family of polymers. The number beside each curve indicates the peroxide concentration used in the treatment of that sample.

level and molecular weight. For weight-average molecular weights of 54,000, 77,000 and 120,000 g/mol, the ductile-brittle transition is observed at crystallinities of about 65%, 72% and 76%, respectively (23). In the case of the originals PE1 and PE4, and the PE2 family of polymers, the combination of molecular weights between 55,000 and 79,000 g/mol and crystallinities from 76% to 83% justify the brittle behavior (see Table 1). In the case of PE2, the modification induced by the peroxide does not produce sufficient changes in the molecular structure of the polymer in order to reduce the crystallinity to a level where a ductile behavior may be observed. On the other hand, in the case of PE5 and the samples of PE1 and PE4 modified with the two larger peroxide concentrations, the combination of molecular weights larger than 80,000 g/mol and crystallinities lower than $\sim 77\%$ is the reason for their ductile behavior.

According to the stress-elongation results for both the Q and SC materials, the degree and length of the ramifications introduced by the treatment with peroxide seem not to have a noticeable effect. For example, Fig. 4 displays the stress-elongation curves of two Q materials with $M_w \sim 78,000$ g/mol (i.e., the original PE4 and the PE1 modified with 500 ppm) and two Q samples of $M_w \sim 130,000$ g/mol (i.e., the original PE5 and the PE1 modified with 1000 ppm). The two pairs of materials present very similar curves that break at comparable levels of stress and elongation, and have similar slopes in the stress-hardening region.

The mechanical properties at low elongation level of the polymers, i.e., the elastic modulus and the yield

stress, are plotted in Fig. 5 against the concentration of peroxide. When compared on this basis, both the moduli and the yield stresses for a given polyethylene family depend mainly on the crystallization procedure followed to prepare the sample. As expected, at a given peroxide concentration, the Q samples have lower values of both properties than the SC materials. Although the structural factors contributing to the elastic modulus and yield stress of polyethylene are not fully understood, it is known that the level of crystallinity is an important factor that affects the value of these parameters (19–26). The yield stress increases linearly with crystallinity while the modulus does not follow a simple relationship. The modulus and the yield stress of all the samples are plotted in Fig. 6 as a function of the crystallinity level determined from density data using the Chiang relationship (31). Both parameters increase monotonically with the crystallinity following roughly a linear relation. The data of both properties display a behavior that seems independent of the original polyethylene, the peroxide concentration used, and the crystallization procedure. These results reveal that the modification process, at the levels of peroxide used in this work, does not affect the relationship between the crystallinity level and the initial mechanical properties expected for ethylene homopolymers (19–26). Similar relations may be obtained if the crystallinity levels used are estimated from enthalpy of fusion instead of density.

Figures 7 and 8 display the draw ratio after break and ultimate tensile stress of the ductile and transitional materials as a function of the weight average

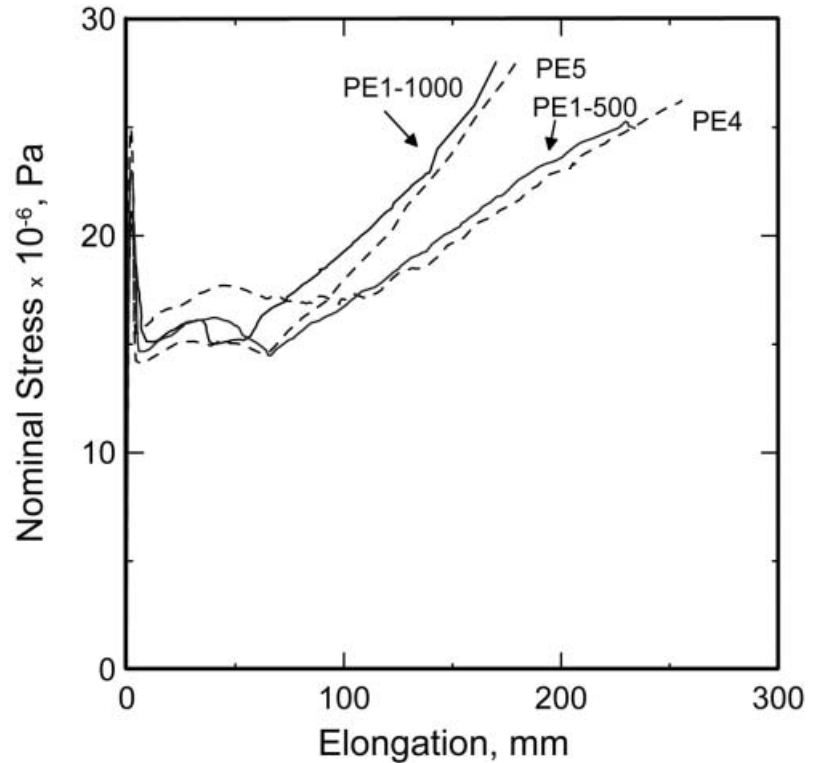


Fig. 4. Stress-elongation curves of selected ductile materials.

molecular weight measured by GPC. The solid line in Fig. 8 was drawn to indicate the trend of the measured ultimate tensile stress. The values of the draw ratio after break decrease, while the ultimate tensile stress increases with augmenting the molecular weight. The draw ratio after break data fall in the region of previously published data from HDPE obtained by Kennedy *et al.* under similar testing conditions (25, 26). The dashed lines in Fig. 7 limit the region of the data obtained by Kennedy and co-workers. The weight average molecular weight and the total degree of branching (short and long) have an important influence on the draw ratio after break of polyethylenes

(22, 25, 26). Results presented by Kennedy and co-workers for LLDPEs show that for a given molecular weight, the draw ratio after break strongly decreases as the concentration of short chain branches increases. For example, this property gradually decreases from 8 to 3 as the concentration of α -olefin increases from 1 to ~ 4 mol% for LLDPEs of 100,000 g/mol. Results from Mandelkern *et al.* show that for an equivalent molecular weight, low-density polyethylenes typically display a draw ratio after break between 5 and 7 (22).

It is interesting to notice that, although the treatment with peroxide produces some long chain branches in the polyethylene molecules, the draw ratios after

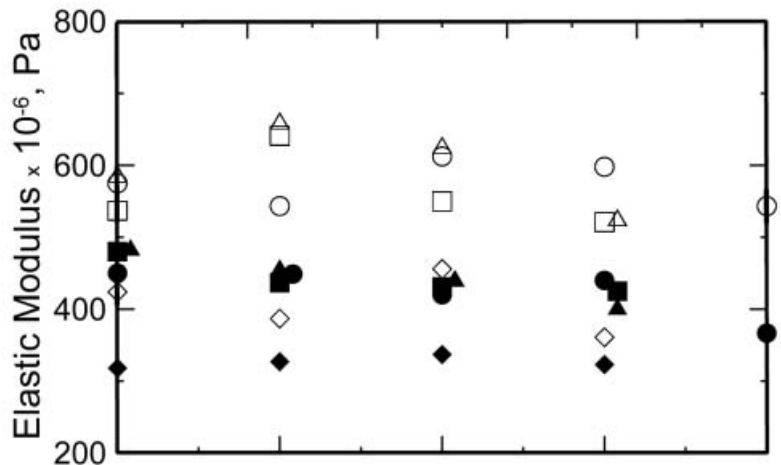


Fig. 5. Elastic modulus and yield stress of all the materials as a function of the peroxide concentration. Polymers: PE1 (\circ , \bullet); PE2 (\square , \blacksquare); PE4 (\triangle , \blacktriangle); PE5 (\diamond , \blacklozenge). Filled symbols: Q samples; open symbols: SC samples.

Fig. 5. Continued.

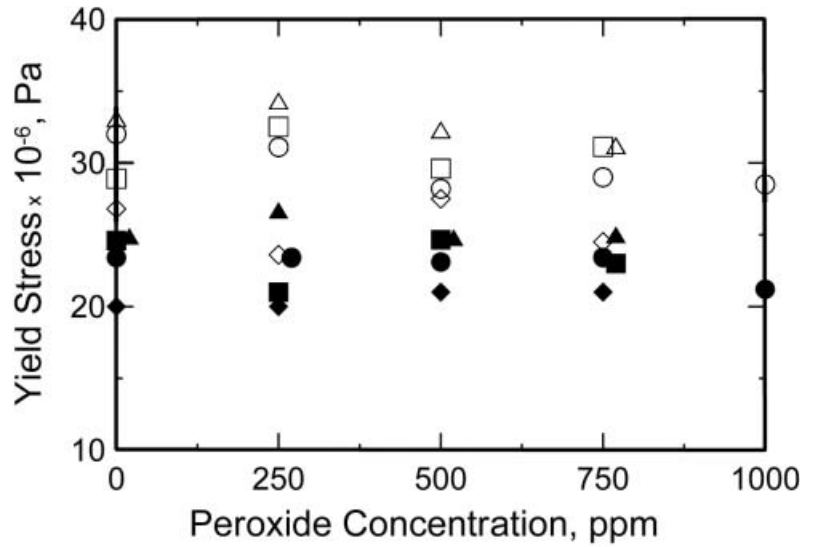


Fig. 6. Elastic modulus and yield stress of all the polymers as a function of the crystallinity level determined from density measurements. Polymers: PE1 (\circ , \bullet); PE2 (\square , \blacksquare); PE4 (\triangle , \blacktriangle); PE5 (\diamond , \blacklozenge). Filled symbols: Q samples; open symbols: SC samples.

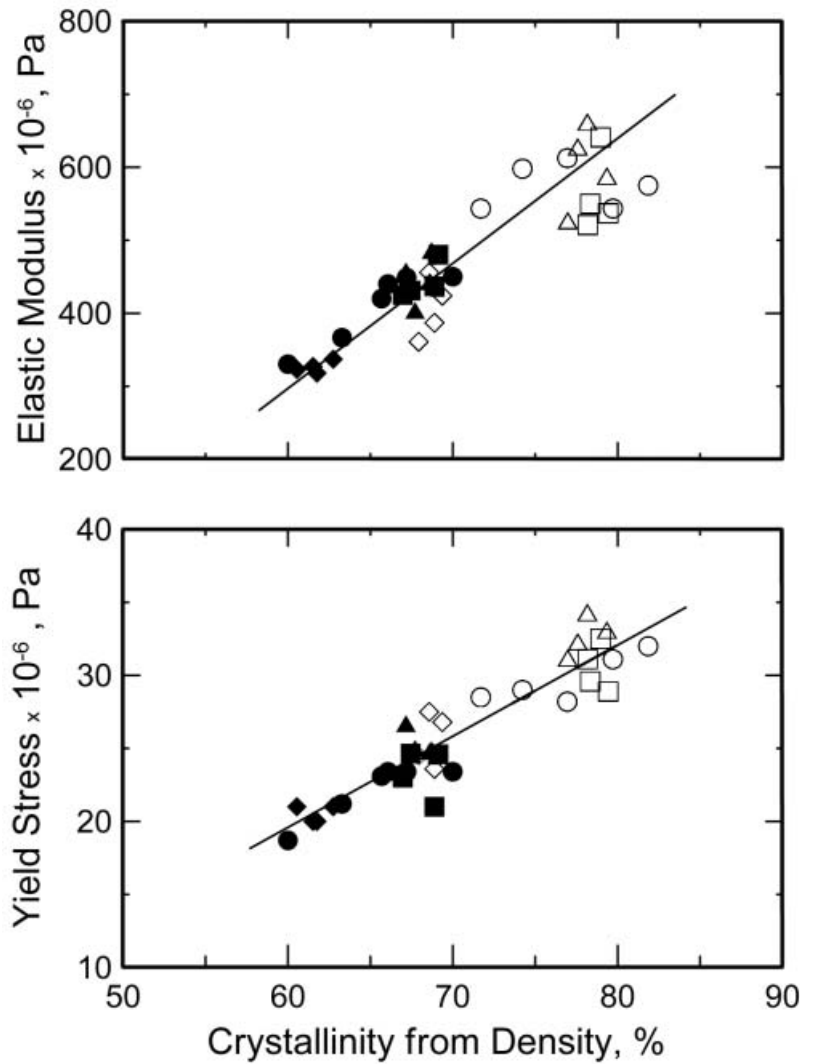


Fig. 7. Draw ratio after break of the ductile and transitional materials as a function of the weight-average molecular weight. Polymers: PE1 (○, ●); PE2 (□, ■); PE4 (△, ▲); PE5 (◇, ◆). Filled symbols: Q samples; open symbols: SC samples. The dashed lines limit the zone where the experimental data of Kennedy et al. (25, 26) are found.

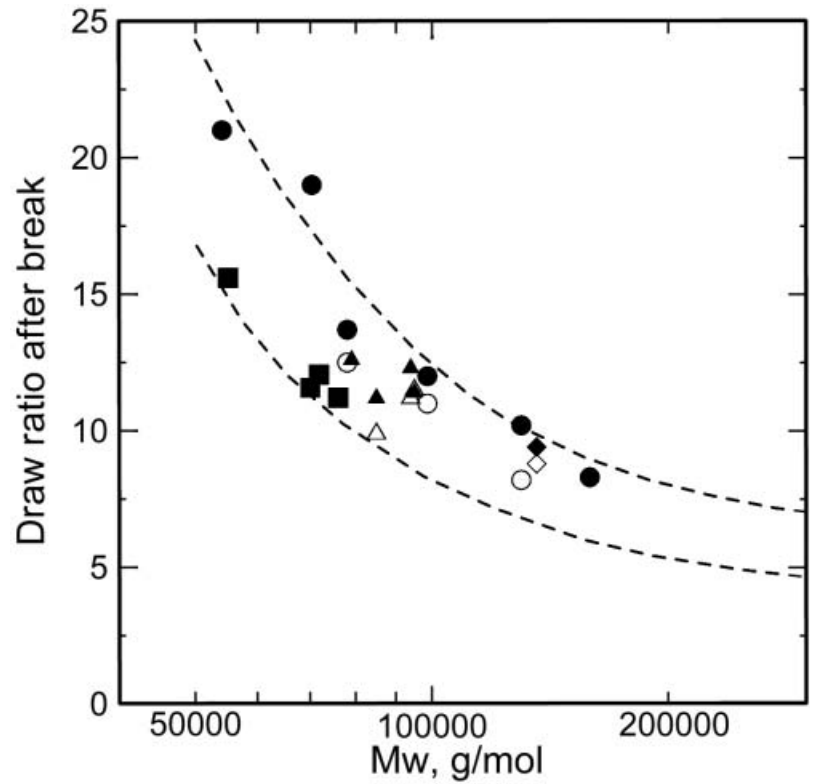
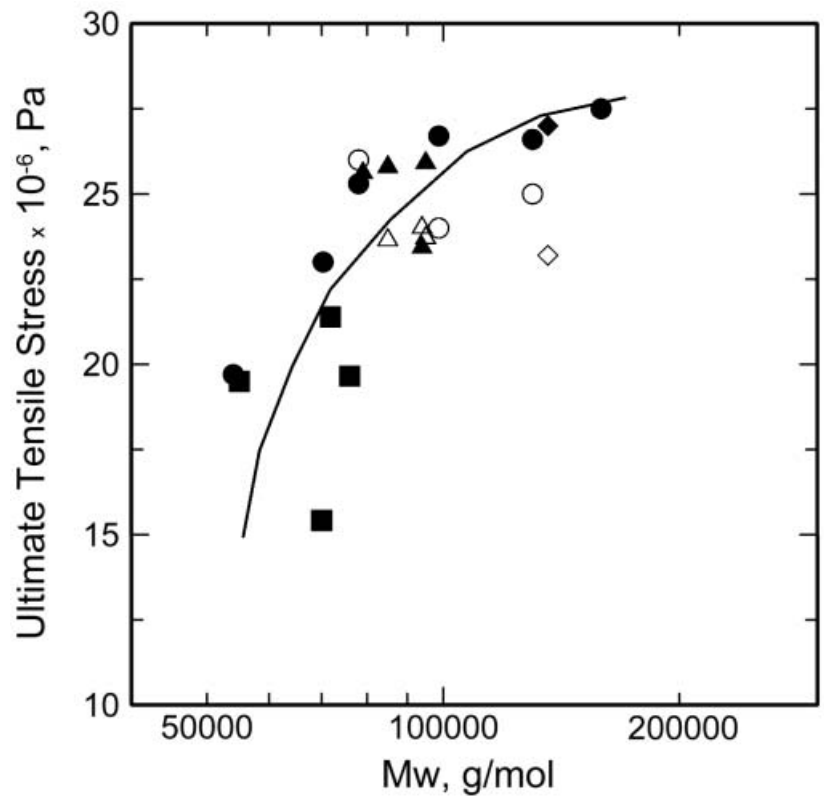


Fig. 8. Ultimate tensile stress of the ductile and transitional materials as a function of the weight-average molecular weight. Polymers: PE1 (○, ●); PE2 (□, ■); PE4 (△, ▲); PE5 (◇, ◆). Filled symbols: Q samples; open symbols: SC samples. The solid line indicates the trend of the results.



break of the materials reported in the present study are mainly affected by the size of the molecules and not by the degree of branching. A plausible explanation for this behavior is that the modified polymers have a low degree of branching. In the case of the ultimate tensile stress, the obtained results show the same qualitative behavior of previously published data (25). Although the values of the weight-average molecular weights may be somehow underestimated (see the **Molecular Characterization** section), the dispersion normally observed in the values of both ultimate properties does not justify a more precise determination of the molecular weight of the polymers.

CONCLUDING REMARKS

The experimental results presented have shown that it is possible to modify the molecular structure of linear polyethylene in order to obtain materials with different mechanical properties. Four high-density polyethylenes were successfully modified with different concentrations of an organic peroxide below the critical one to obtain a macroscopic molecular network. Samples of all the polymers were crystallized from the melt following two different procedures.

The density and the crystallinity of the obtained polymers were found to be slightly dependent on the molecular structure generated by the modification process. All the quenched samples display a ductile behavior. The slow-cooled samples show brittle or ductile mechanical response according to the crystallinity level and molecular weight of the material.

The elastic modulus and yield stress increase linearly with the crystallinity of the polymers. The relationship between these mechanical properties and the crystallinity seems to be independent of the molecular structure generated by the modification process. The draw ratio after break decreases and the ultimate tensile stress increases with the molecular weight of the polymers. These mechanical properties seem to depend solely on the molecular weight and not on the complexity of the molecular structure induced by the modification process.

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