

# Effect of the Temperature on the Tensile Mechanical Behavior of Irradiated Linear Polyethylene

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**ABSTRACT:** The mechanical behavior of two  $\gamma$ -irradiated linear polyethylenes was determined at 75 and 105°C under tensile stress. Each polymer was crystallized from the melt after different thermal histories so that samples would be obtained with various degrees of crystallinity. Subsequently, they were irradiated *in vacuo* and at room temperature to total doses ranging from 20 to 200 kGy. The initial crystallinity, dose level, and test temperature determined whether the samples displayed ductile, brittle, or transitional behavior. The yield stress decreased as the temperature increased. The value of the yield stress at a given temperature showed a tendency to increase with dose; this became more evident as the initial crystallinity increased. The extensibility of duc-

tile samples, estimated from the draw ratio after break, decreased with the gel content. For ductile samples, the temperature affected the values of this property when the gel fraction that developed in the samples was relatively low. The effect of temperature became less noticeable when the gel reached values larger than 60%. The ultimate stress, normalized with the crosslinking density, correlated with the draw ratio after break in a way that resembled the type of relationship observed in other crosslinked systems. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1925–1935, 2003

**Key words:** polyethylene (PE); radiation; morphology; mechanical properties

## INTRODUCTION

The thermomechanical stability of linear high-density polyethylene is an important factor to be considered when the polymer is used at high temperatures. It is well known that at temperatures close to or above 70°C, its capacity to withstand deformation or stress is severely impaired.<sup>1–6</sup> Irradiation with high-energy ionizing radiation is a treatment widely used to expand the range of temperatures within which linear polyethylenes may be used and, therefore, to improve their thermomechanical performance. Different works dealing with the mechanical properties of  $\gamma$ -irradiated PE indicate that the tensile strength increases, the resistance to environmental stress cracking rises, and the creep properties are considerably improved.<sup>6–9</sup> The enhancement of these properties is directly related to the intermolecular crosslinks that are produced by irradiation. It has been established that various factors exist that control the amount of crosslinks generated by the radiation process.<sup>7,10–13</sup> When the irradiation is performed at temperatures close to room temperature, that is, 25–30°C, the crystallinity level is one of the factors that affects the efficiency of

crosslinking.<sup>10,13</sup> In a previous study, we presented results about the effect of the initial crystallinity on the efficiency of crosslinking, as measured from sol–gel relationships.<sup>13</sup> In the same study, we reported the consequences of irradiation on the tensile mechanical behavior and tensile mechanical properties at room temperature. This report is an extension of that work. Here, we pay special attention to the effect of the deformation temperature on the mechanical behavior and mechanical properties of irradiated linear polyethylene.

The mechanical behavior of irradiated polyethylene has most extensively been studied either at room temperature or at temperatures above the melting point of the polymer.<sup>6,8,13–19</sup> The information available on the combined effect of the morphology and dose on the tensile mechanical response of irradiated polyethylene for the range of temperatures between room temperature and the melting temperature, at which the polymer still remains in the semicrystalline state, is very limited.<sup>6,8,9</sup> One of these studies reports the effect of the morphology and irradiation dose on the drawing behavior of a linear polyethylene at 75°C.<sup>9</sup> No information about the molecular structure of the irradiated polymers is given in the article. Consequently, the aim of this article is to provide additional information about the tensile mechanical response of irradiated linear polyethylene in a range of temperatures of practical significance; this may also be of value for understanding some aspects of the mechanical behavior of this polymer. To accomplish this goal, we prepared a

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TABLE I  
Gel Content of the Irradiated Samples with Different Levels of Crystallinity as a Function of Dose

Dose (kGy)	PE1			PE2			
	Sample code (crystallinity, %)			Sample code (crystallinity, %)			
	IWQ (61.4)	SCA (73.0)	I110 (80.0)	IWQ (57.5)	SCA (68.0)	SCP (78.0)	I127 (82.0)
	Gel (%)			Gel (%)			
0	n/d	n/d	n/d	n/d	n/d	n/d	n/d
20	n/d	n/d	n/d	n/d	n/d	n/d	n/d
50	9.0	5.3	n/d	38.5	32.0	20.0	13.5
100	40.0	34.0	19.0	66.0	62.5	37.0	21.5
200	70.5	62.5	35.0	80.0	73.5	62.5	42.0

n/d = not detectable.

set of samples of two high-density polyethylenes with crystallinity levels varying over a broad range. The samples were  $\gamma$ -irradiated with doses between 20 and 200 kGy. They were subsequently characterized in terms of the changes in the molecular structure and gel content. The mechanical behavior of the original and irradiated samples was determined at 75 and 105°C under tensile force at a constant draw rate. The yield stress and ultimate tensile stress (UTS) were estimated from the stress–elongation curves. The draw ratio after break ( $\lambda_b$ ) was also measured. All the mechanical parameters were analyzed as a function of the initial crystallinity, dose level, and gel content.

## EXPERIMENTAL

### Materials

Two high-density linear polyethylenes supplied by Du Pont de Nemours and Oxy Petrochemical were used in this study. The polyethylenes termed PE1 and PE2 had weight-average molecular weights ( $M_w$ ) of 55,000 and 81,000, respectively. They were estimated from size exclusion chromatography (SEC) according to standard procedures. The polydispersity [weight-average molecular weight/number-average molecular weight ( $M_w/M_n$ )] was about 2.6 for both polymers.

### Sample preparation

Films of the initial material were prepared by compression molding at 150°C with a hydraulic press with thermostatically controlled platens. The samples were molded between 5-mm-thick aluminum plates lined with aluminum film and held apart by 0.5-mm-thick aluminum spacers. After molding, the samples were allowed to reach the semicrystalline solid state according to different procedures:

1. The first set of samples, denoted IWQ, was obtained by the quenching of samples of both polyethylenes to the temperature of ice water.

2. The second set was prepared by the slow cooling of samples to ambient temperature, with the samples kept between the press platens; these samples were named SCP.
3. For PE2, a third set was obtained by samples of PE2 being allowed to cool down to room temperature out of the press; these samples were labeled SCA.
4. The next group of samples was prepared by the quenching of PE1 at 110°C; this set was denoted I110.
5. The last group was obtained by isothermal crystallization at 127°C of PE2; these samples were named I127.

The sample code is summarized in Table I.

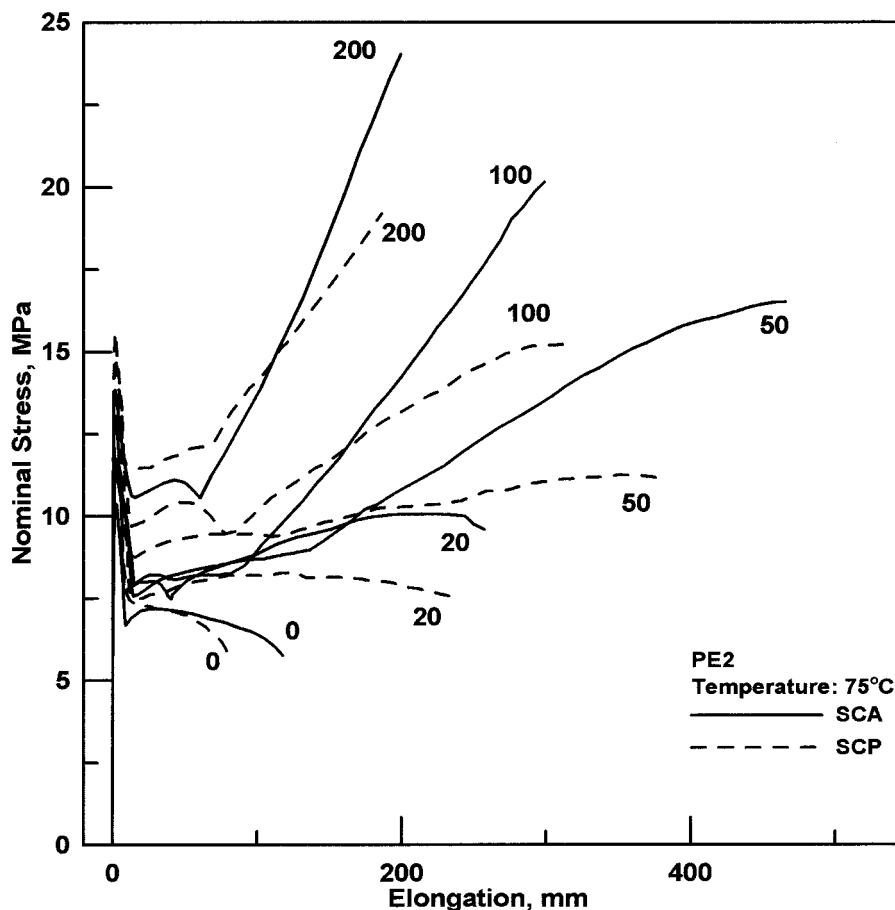
### Sample characterization

The degree of crystallinity of the samples was estimated from measurements of the enthalpy of fusion with a PerkinElmer DSC-2 calorimeter calibrated with an indium standard. The fusion endotherm was obtained at a heating rate of 10°C/min. The area of each endothermic peak was delimited by a straight line drawn from the onset to the end of melting and was measured with a planimeter. The degree of crystallinity was calculated with 69 cal/g for the enthalpy of fusion of completely crystalline polyethylene.<sup>20</sup> The average crystallinity measured for each set of samples is presented in Table I.

The heat of fusion of the irradiated samples was also determined. We observed no substantial differences in the heats of fusion between the irradiated sample and the corresponding parent sample beyond the experimental uncertainty.

### Irradiation procedure

Dumbbell-shaped samples with a gauge length of 12 mm, a thickness of about 0.5 mm, and a width of 4 mm



**Figure 1** Stress–elongation curves for SCA and SCP samples of PE2 at 75°C. The dose (kGy) is indicated beside each curve.

were cut from the films and inserted into glass tubes. The tubes were evacuated to  $10^{-4}$  Torr for 2 days and then sealed off. Subsequently, these samples were exposed to  $\gamma$ -rays generated by a  $^{60}\text{Co}$  source at room temperature. The dose rate was 3.3 kGy/h, which was determined by dosimetry with a radiochromic thin-film dosimeter.<sup>21</sup> Equal total doses of 20, 50, 100, and 200 kGy were applied to each set of samples. The dose error was estimated to be  $\pm 10\%$ . After irradiation, samples were stored *in vacuo* at room temperature for 1 week before the tubes were opened for sample characterization.

### Sample analysis

The gel fraction was determined by the extraction of the soluble portion of the different samples with xylene at 125°C. The extraction was performed by about 30 mg of each sample being placed into a basket made from a stainless steel mesh. Then, the baskets were immersed in hot xylene for periods of 6 h. After each of these periods, the samples were dried in a vacuum oven at 60°C to a constant weight. The extraction was considered complete when, after two consecutive periods of extraction, there was no detectable change in

the weight of the dried gel. The total time of extraction varied from 36 to 48 h, depending on the sample. The solvent was exchanged for fresh solvent between each consecutive extraction. The percentage of gel reported is from an average of three samples. The standard deviation was about 3%. The samples irradiated to a dose below the critical point were analyzed by SEC according to standard procedures.

### Mechanical behavior

The uniaxial tensile behavior of the dumbbell-shaped specimens was determined at 75 and 105°C with an Instron tester equipped with an environmental chamber. The draw rate was 20 mm/min. Specimens were equilibrated for 5 min at the appropriate temperature before testing. For the measurement of  $\lambda_b$ , ink marks placed 2 mm apart were drawn on the deformation zone of the sample. The reported stress was the engineering stress, which was conventionally defined as the force divided by the initial transversal area.

The yield stress was obtained from the maximum stress observed in the stress–elongation curves at low deformation levels, such as those shown in Figure 1.  $\lambda_b$  was obtained from the relationship between the final

**TABLE II**  
**Effect of the Dose on the Average Molecular Weights of Irradiated PE1 and PE2 Samples Below the Gel Point**

Sample	PE1				PE2	
	Dose (kGy)				Dose (kGy)	
	20		50		20	
	$M_w$	$M_n$	$M_w$	$M_n$	$M_w$	$M_n$
IWQ	92,000	19,500	—	—	161,000	34,000
SCA	n/a	n/a	125,000	23,000	143,500	25,500
I110	82,000	23,300	118,500	22,000		
SCP					129,000	30,000
I127					110,000	26,000

n/a = not available.

spacing of the ink marks measured after break and their initial spacing. The UTS was estimated from the ultimate force divided by the initial transversal area and multiplied by  $\lambda_b$ . The reported values of the different properties were obtained from an average of five to seven samples. The standard deviation of the data was about 2–7% for the yield stress, 2–5% for  $\lambda_b$ , and 10% for UTS.

## RESULTS AND DISCUSSION

### Sample characterization

The crystallinity levels of the samples that were studied in this work, together with the amount of gel developed upon irradiation, are given in Table I. The gel results were already reported in a previous publication.<sup>13</sup> We include them here for the purpose of facilitating the analysis of the mechanical results. These data indicate that the evolution of the gel content with the dose depended significantly on the initial crystallinity of the sample. At a given postgel dose, the gel content decreased as the crystallinity level of the sample increased. In addition, at doses below the gel point,  $M_w$  rose more rapidly for the samples with lower contents of crystallinity, as can be observed from the results presented in Table II. The values of  $M_w$  were estimated from an analysis of SEC chromatograms. It was assumed that the polymer had a linear molecular structure; that is, branching was not taken into account. For this reason, the reported molecular weights should be lower than the true ones, and these results are only valuable for the purpose of comparing the different samples. The gel and  $M_w$  data indicate that the gel point was located in the dose range of 30–50 kGy for PE1 and in the dose range of 20–40 kGy for PE2. The critical dose for gel formation increased with the crystallinity for each polymer.<sup>13</sup>

The reduction in the efficiency of crosslinking with crystallinity was attributed to the scavenging of immobilized free radicals by oxygen, which took place

when the samples were exposed to air during their manipulation for characterization.<sup>13</sup>

### Stress–elongation curves

Figures 1 and 2 present the nominal stress–elongation curves for some selected samples. They were chosen as examples to illustrate the effect of the crystallinity, dose, and temperature. In what follows, we use the classification given by Popli and Mandelkern<sup>22</sup> to identify the mechanical behavior of polyethylene. Therefore, we grouped the mechanical behaviors into three possible types: ductile, brittle, and transitional. The ductile behavior was characterized by a yield zone at low deformation followed by drawing with no significant changes in the nominal stress. Then, the samples either broke apart or showed strain hardening that was distinguished as an upturn in the stress before the breakage. The transitional samples showed a yielding zone in which a neck formed; after that, the samples broke apart because the deformed material was not able to sustain the drawing stress. The brittle samples broke at the yield point or immediately after yielding.

Figure 1 includes the stress–elongation curves obtained for the nonirradiated and irradiated SCP and SCA samples of PE2. They were chosen to illustrate the mechanical behavior exhibited at 75 and 105°C by all the samples of both polymers, except the I110 and I127 samples. In all the cases, the neck that was formed after yielding did not travel throughout the entire deformation. The samples break broke apart because the already deformed material was not able to sustain the drawing stress.

The mechanical behavior of the I127 and I110 samples, which had the highest crystallinity levels, was brittle at both testing temperatures. The samples broke at the yield point or immediately after passing this point (the stress–elongation curves are not shown).

The irradiation of the IWQ, SCP, and SCA samples induced ductility. As can be seen in Figure 1, the mechanical behavior changed from being transitional to ductile. All the irradiated samples displayed yielding followed by a strain-hardening process. A rather marked difference in the strain-hardening pattern among the irradiated samples was observed. The increasing slope of the last part of the stress–elongation curves with irradiation clearly showed that the strength of the samples grew with the applied dose. In addition, the upturn in the last part of the stress–elongation curves set in at a smaller elongation as the dose increased. These observations could be linked to the growth in the molecular weight with irradiation below the gel point and to the increase in the gel amount with the dose above that point. The shift toward lower elongation of the onset of the upturn in the stress and higher slopes in the terminal part of the

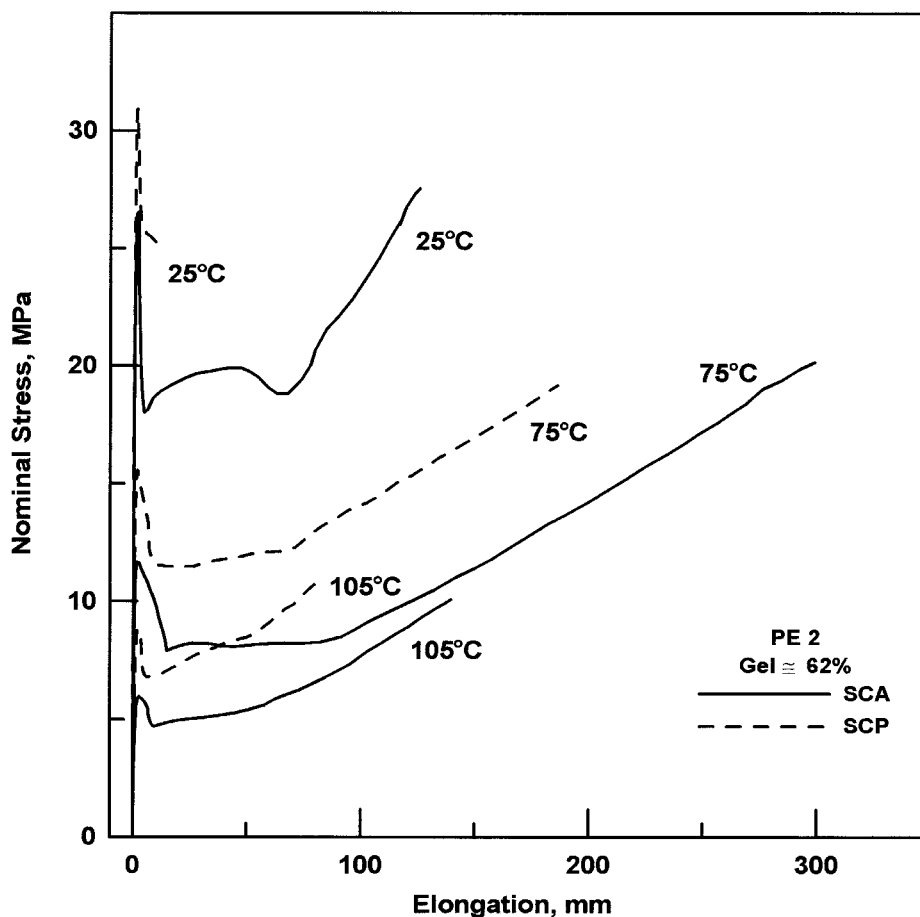


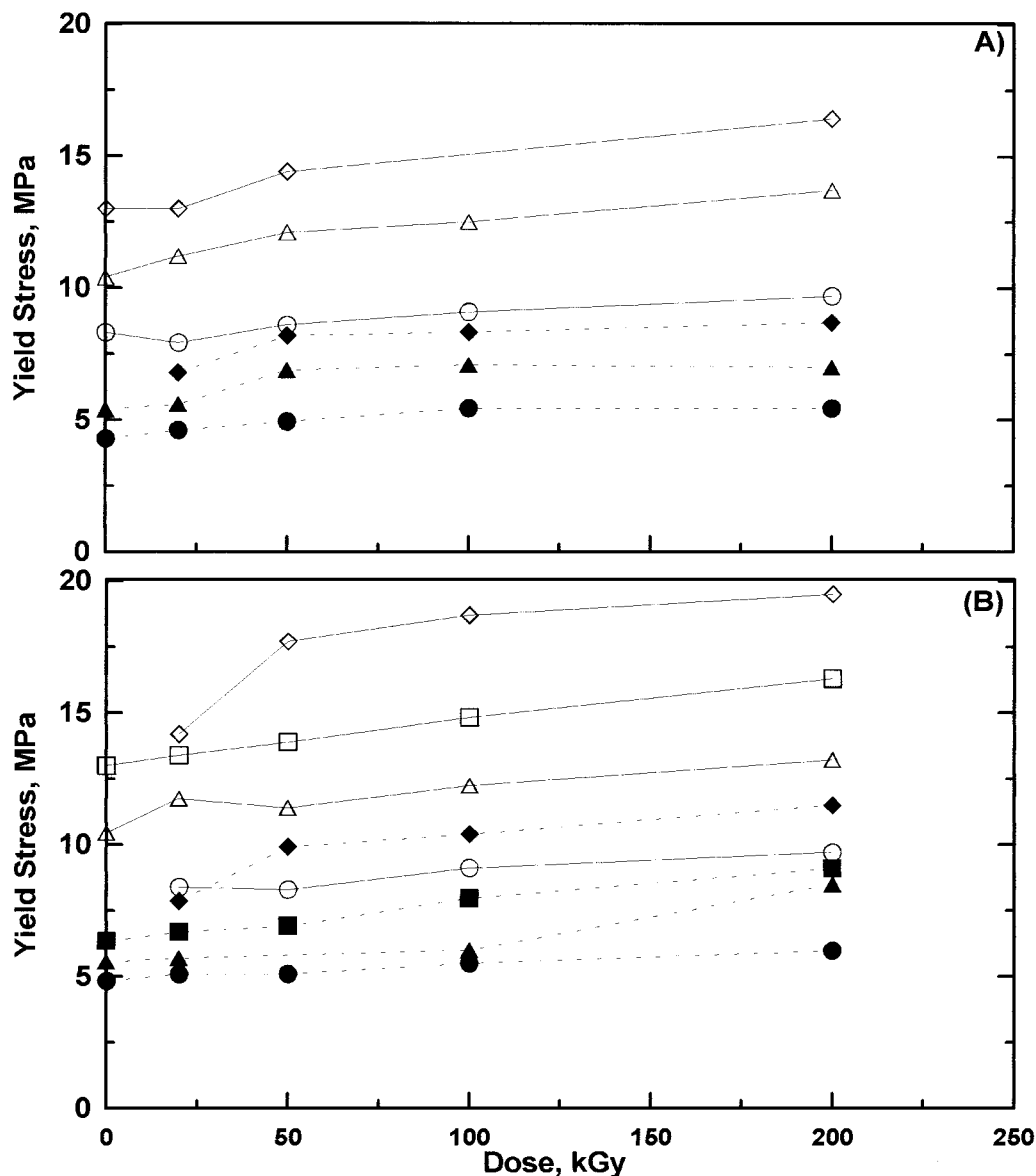
Figure 2 Stress-elongation curves for SCA and SCP samples of PE2 with a gel amount of about 62%. The test temperature is indicated beside each curve.

stress-elongation curves with the amount of gel has been observed experimentally in various crosslinked systems.<sup>1,9</sup> The molecular entanglement, which was enhanced by the growth in the molecular weight and branching that occurred during the initial part of the irradiation, helped to reach larger elongation levels, but soon after a molecular network formed and the crosslinking increased, the extensibility was severely limited.

The stress-elongation curves presented in Figure 1 allow a comparison of SCA and SCP samples of PE2, which had different degrees of crystallinity. Although the yield region is not clearly distinguished in the figure, the SCA yielded at a lower stress than the SCP at the same dose. The difference in the yield stress is discussed in the next section. The most significant difference between the curves is in the region beyond the yield. The irradiated SCA shows a larger stress slope and stress at break than the SCP sample at a given dose. This may be associated with the fact that the SCA sample developed a larger amount of gel [large crosslinking density ( $x_e$ )] than the SCP samples at a given dose level.

Ductile samples with about the same gel amount displayed a similar slope of the terminal zone of the stress-elongation curves. They showed a similar slope before breaking and broke at about the same stress level. An example is presented in Figure 2, which displays a set of nominal stress-elongation curves obtained at 75 and 105°C for the SCP and SCA samples of PE2 with a gel content of about 62%. The corresponding curve, obtained at 25°C, is also included in Figure 2 to better illustrate the effect of temperature on the stress-elongation pattern. It is clearly noticeable that the stress level at which the deformation proceeded decreased with the temperature. For the SCP sample, there was a change from brittle behavior to ductile behavior as the temperature increased. The SCA sample, which was ductile at all temperatures, displayed a decreasing stress at break, whereas the maximum elongation seemed to pass through a maximum. This type of evolution in the shape of the stress-elongation curve with the temperature is analogous to that observed in other crosslinked systems.<sup>1</sup>

The irradiation did not change the brittle character of the mechanical behavior of the I110 and I127 sam-



**Figure 3** Yield stress as a function of the dose for (A) PE1 samples and (B) PE2 samples: IWQ (circles), SCA (triangles), SCP (squares), and I127 (diamonds). Open symbols and solid lines indicate a temperature of 75°C; filled symbols and dashed lines indicate a temperature of 105°C

ples, which had the highest levels of crystallinity. Within the dose range studied, these samples displayed a brittle failure at all temperatures. These results clearly indicate that the initial crystalline structure plays an important role in the response of irradiated linear polyethylene to tensile deformation. In the following sections, we discuss some of the mechanical parameters measured at low and high deformation levels.

#### Yield stress

It is well documented that the yield stress of polyethylene is greatly affected by the crystallinity level and temperature, increasing with crystallinity and de-

creasing with temperature.<sup>1-6,22,23</sup> However, the effect of the crystallinity becomes less noticeable as the temperature increases. At a temperature very close to or above 100°C, it has been found that there are practically no differences in the yield stresses of samples of linear polyethylene with quite different levels of crystallinity.<sup>3</sup> The results for the yield stress presented in Figure 3 are in agreement with those observations. Figure 3 displays the nominal yield stress as a function of the dose level for all the samples measured at both temperatures that were tested. The yield stress values, measured at 75°C, are arranged according to the initial crystallinity level in the nonirradiated samples. The higher the crystallinity was, the greater the value was of the yield stress. At 105°C, the differences in the

values of the yield stress became less noticeable for the samples of both polyethylenes. However, the samples are still arranged according to their initial crystallinity.

In agreement with previous works, the irradiated samples displayed yield stresses slightly higher than those corresponding to the nonirradiated samples.<sup>9,13</sup> The value of this property increased with the dose at both temperatures. This effect seemed to be more significant as the initial crystallinity of the sample increased. For example, at 105°C, the yield stress values of the I127 and I110 samples irradiated to 200 kGy were roughly twice as large as the values corresponding to the nonirradiated samples. By contrast, the yield stresses for the IWQ samples irradiated to 200 kGy were only about 20% larger than the corresponding values of the nonirradiated samples. At this level of dosage, the major effect was the introduction of crosslinks and oxygenated species within the noncrystalline phase because it was expected that the irradiation process would not significantly affect the crystal core.<sup>10–12</sup> Therefore, the increase in the yield stress with dosage could be associated with the modification introduced into the noncrystalline phase. These modifications affected the mechanical response of that phase, mainly changing the stress level at which the yielding proceeded in the irradiated samples.

### $\lambda_b$

$\lambda_b$  is one of the mechanical parameters that is normally used to evaluate the magnitude of the changes produced by the irradiation process.<sup>1,6,14</sup> The data for  $\lambda_b$  are plotted against the dose level and gel amount in Figures 4 and 5, respectively. The lines in these figures were drawn with the purpose of indicating trends. Figure 4(a) represents the data for PE1 samples, whereas Figure 4(b) shows those for PE2 samples. In these plots, we have arbitrarily assigned a value of  $\lambda_b = 1$  to identify brittle samples. To illustrate better the effect of the temperature, we included  $\lambda_b$  for IWQ samples tested at 25°C that were reported previously.<sup>13</sup> As stated before, the initial samples displayed either brittle or transitional mechanical behavior at 75 and 105°C. Transitional samples, which are identified by the letter *T* in Figure 4, displayed  $\lambda_b$  values that had large errors because they represented the average of a broad distribution. The irradiation of the transitional samples produced ductile samples, and this was manifested as an increase in the value of  $\lambda_b$  at low dosages. Then,  $\lambda_b$  decreased gradually as the dose increased. This trend was observed for all the ductile samples and tested temperatures.

The effect of the temperature on the draw ratio at break was noticed for all dose levels, although it was less noticeable for the samples with the lowest crystallinity that were irradiated at the highest dose.  $\lambda_b$  for the sample drawn at 75°C was larger than that corre-

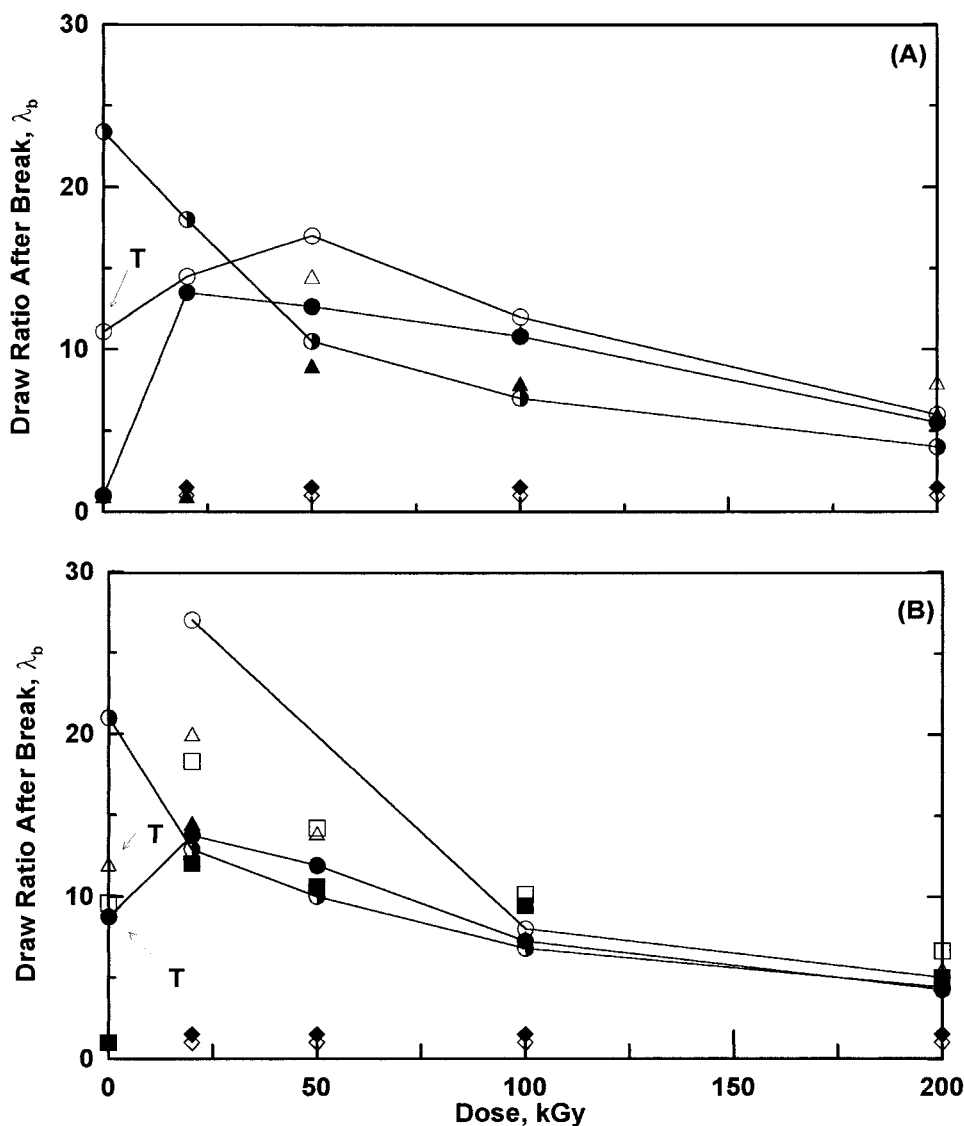
sponding to 25 and 105°C. The evolution of  $\lambda_b$  values through a maximum as the temperature increases has been observed for various crosslinked systems and also for nonirradiated linear polyethylenes.<sup>1,3,8</sup> The reduction in the extensibility indicated by the dependence of  $\lambda_b$  with the dose may be associated with the increases in  $x_c$ . At low doses, the increase in the molecular weight and branching produced a molecular structure capable of sustaining the drawing stress. Therefore, the transitional behavior became ductile. However, as pointed out previously, all the I127 and I110 samples that were brittle did not change with respect to this type of behavior after irradiation for the ranges of doses and temperatures covered by this work.

The effect of the crystallinity on the deformation was further analyzed by the plotting of the draw ratio at break against the gel amount, as presented in Figure 5. Here we have arbitrarily assigned a value of 2 for the percentage of gel of those samples irradiated at dose levels below the gel point to distinguish them from the original samples. The dependence of  $\lambda_b$  with the gel amount of all the ductile samples was similar for the samples of both polyethylenes, in that its value decreased continuously as the amount of gel increased. The dependence of  $\lambda_b$  at 75°C with the gel seemed to be roughly proportional to the gel content. This implies that for completely crosslinked materials, very low elongation levels could be expected.

When a comparison is made at a given gel amount, it can be seen that the higher the initial crystallinity was, the lower the draw ratio at break was. These differences seem to vanish for a gel amount greater than 50–60%. These results may be explained at least partially by the effect of the oxidation and the plausible heterogeneity of the network formed. For about the same amount of gel, the dose level had to be increased as the crystallinity increased (see Table I). Therefore, the oxidation level increased with the crystallinity of the samples for a given gel amount.<sup>13</sup> The phenomenon of embrittlement due to oxidation has been observed for various irradiated systems.<sup>16</sup> However, when the crystallinity increases, the concentration of chain links within the noncrystalline phase increases, and the spacing between links may change in such a way that the capacity for sustaining a large extension of this phase may be reduced.

### UTS

Another property that we have analyzed is UTS, estimated as mentioned in the Experimental section. For ductile polyethylene, this property describes a maximum, for fixed testing conditions, when it is related to  $M_w$  of the polymer.<sup>23</sup> For crosslinked systems, UTS also describes a maximum when plotted against  $x_c$ .<sup>1</sup> In addition, a correlation between the UTS and the max-



**Figure 4**  $\lambda_b$  versus the dose for (A) PE1 samples and (B) PE2 samples: IWQ (circles), SCA (triangles), SCP (squares), and I110 and I127 (diamonds). Half-filled symbols indicate a temperature of 25°C, open symbols indicate a temperature of 75°C, and filled symbols indicate a temperature of 105°C. For brittle samples,  $\lambda_b$  was 1. The lines connect the data for IWQ samples. T identifies transitional samples.

imum draw ratio has been found if the values of the former property are normalized by  $x_e$  and reduced to a common temperature.<sup>1</sup> Following that idea, we explored the possibility of relating UTS and  $\lambda_b$  in these irradiated samples.  $x_e$  for each sample irradiated above the critical dose was estimated theoretically according to the proposal of Saito<sup>24</sup> for an irradiated polymer with an initial Wesslau type of molecular distribution. This type of distribution well describes the molecular weight distribution of the polyethylenes used here. The gel amount developed for each sample was used for calculating  $x_e$ . We assumed that during the irradiation chain scission was minimal and that a gel fraction close to 1 could be reached if a sufficiently high dose was applied to each of the samples. We

considered that the crystallinity merely reduced the density of crosslinking that could be generated at a given dose.

Figure 6 shows the UTS normalized by  $x_e$  as a function of  $\lambda_b$  for the samples that displayed ductile behavior. It is rather surprising that the points corresponding to all of the irradiated polymers fall closely on a single curve for each tested temperature, within the rather large experimental error characteristic of tensile strength measurements. The lines in the figure were drawn just to indicate general trends. The normalized UTS grew as  $\lambda_b$  increased. It can also be observed that the normalized UTS values decreased with the temperature when compared at a given draw ratio. We reduced the normalized UTS values to a



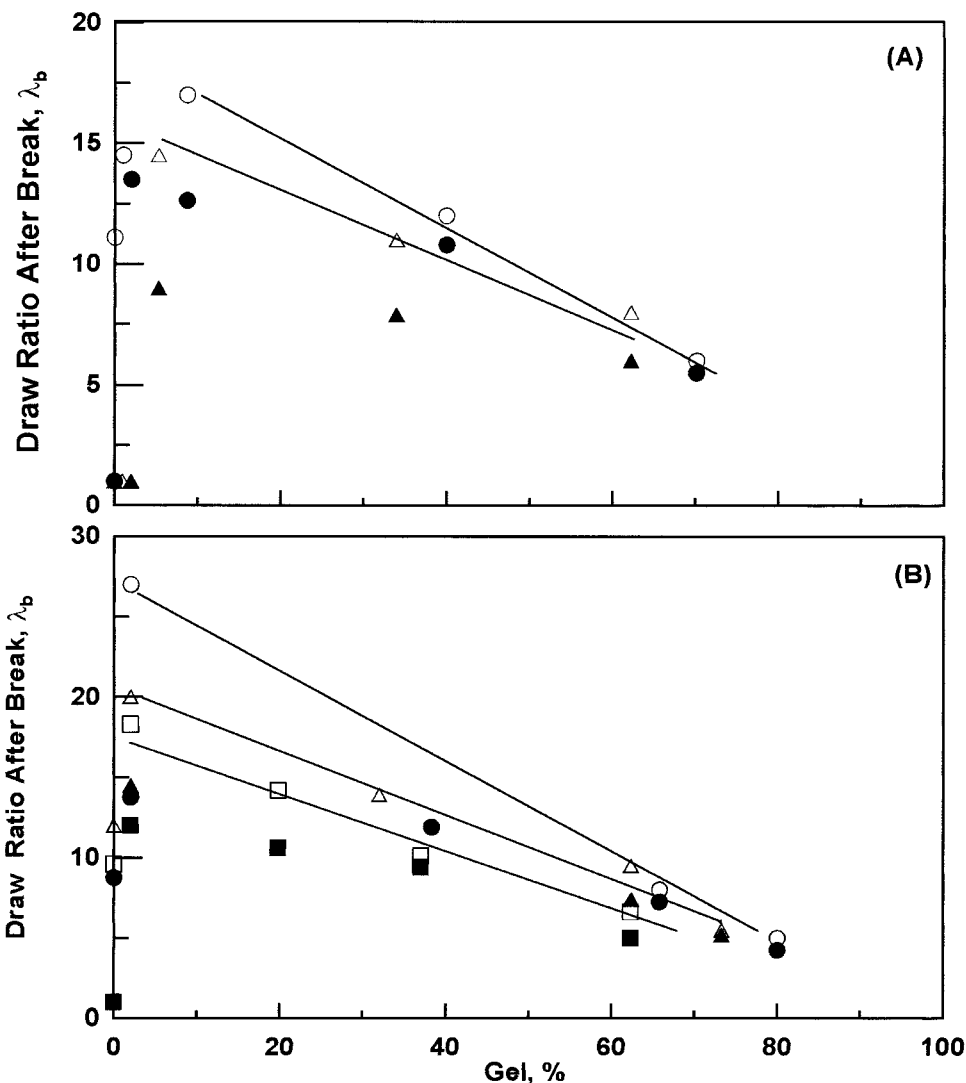


Figure 5  $\lambda_b$  against the gel for (A) PE1 samples and (B) PE2 samples. For brittle samples,  $\lambda_b$  was 1. For the definitions of the symbols, see Figure 4.

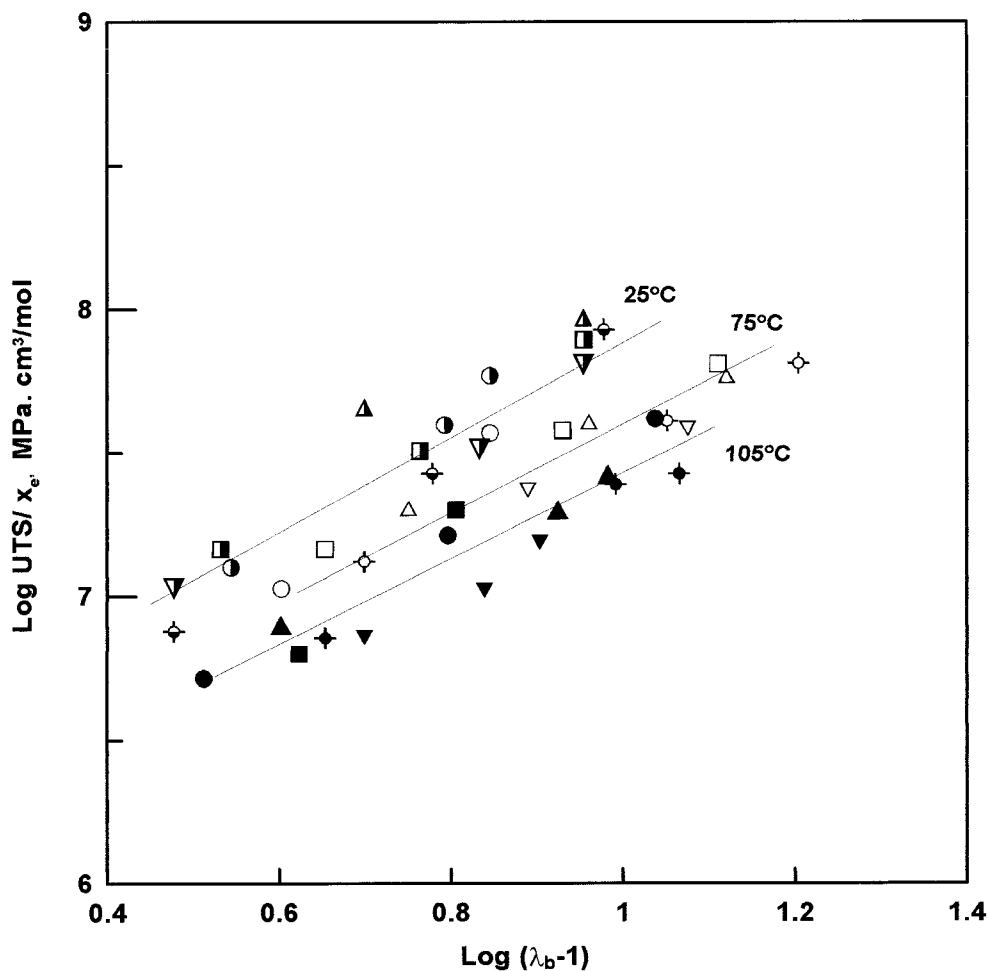
common temperature to build a failure envelope. However, they do not superpose on a single curve when plotted against  $\lambda_b$  in the same way as presented in Figure 6. This may be expected to happen in these irradiated polyethylenes.<sup>1,3</sup> On the one hand, a strain-induced crystallization mechanism has been considered to take place when polyethylene is stretched at large deformation.<sup>3</sup> On the other hand, separate failure curves are obtained in the temperature range in which crystallization of a strain-crystallizing rubber does occur during stretching.<sup>1</sup>

The data analyzed in the manner adopted here seem to indicate that the relationship between the ultimate properties and draw ratio is not related to the initial crystallinity and polyethylene type as long as ductile behavior is observed. They seem to be mainly dependent on the fact that they correspond to a crosslinked system. It is not the intention of this report to attempt either to explain this interrelationship or to suggest

that it can be applied in a universal way. However, it is worth mentioning that the breaking properties, as seen in the failure envelope, seem to be independent of the chemical nature of the crosslinked materials over quite wide ranges of temperatures and strain rates.<sup>1</sup>

## CONCLUSIONS

The results obtained from this study demonstrate that the tensile behavior of irradiated high-density polyethylene depends on the initial structure, dose, and temperature. The irradiation of ductile samples limits the extensibility of the material. The ductility is improved when transitional samples are irradiated at doses below or just above the gel point. The irradiation of brittle samples does not modify substantially the characteristics of the deformation pattern when the temperature is increased.



**Figure 6** Normalized UTS as a function of  $\lambda_b$  for PE1 samples [IWQ (crossed circles) and SCA (downward triangles)] and PE2 samples [IWQ (circles), SCA (upward triangles), and SCP (squares)]. Half-filled symbols indicate a temperature of 25°C, open symbols indicate a temperature of 75°C, and filled symbols indicate a temperature of 105°C.

The yield stress decreases as the temperature increases. The values of the yield, at a given temperature, show a tendency to increase with dose that becomes particularly more evident as the initial crystallinity increases.

$\lambda_b$  and UTS are substantially modified by irradiation. For ductile samples, the temperature affects the values of  $\lambda_b$  when the gel fraction developed in the samples is relatively low. The effect of temperature on this property becomes less noticeable when the gel reaches values larger than 60%.

The UTS normalized with  $x_e$  depends almost proportionally on the draw ratio at break for each temperature. Nevertheless, separate curves were obtained for each temperature. The initial structure and type of polyethylene do not seem to affect the relationship between the ultimate tensile properties. Additional experimental results are necessary to determine whether this relationship holds for other irradiated polyethylenes and test conditions.

## References

- Nielsen, L. E.; Landel, R. F. *Mechanical Properties of Polymers and Composites*, 2nd ed.; Marcel Dekker: New York, 1994.
- Ward, I. M.; Hardley, D. W. *An Introduction to the Mechanical Properties of Solid Polymers*; Wiley: New York, 1993.
- Peacock, A. J.; Mandelkern, L.; Alamo, R. G.; Fatou, J. G. *J Mater Sci* 1998, 33, 2255.
- Hillmansen, S.; Hobeika, S.; Haward, R. N.; Leever, P. S. *Polym Eng Sci* 2000, 40, 481.
- Brown, N. In *Failure of Plastics*; Brostow, W.; Corneliussen, R. D., Eds.; Hanser: New York, 1986; Chapter 6.
- Shultz, J. *Polymer Material Science*; Prentice Hall: Upper Saddle River, NJ, 1974; Chapter 11.
- Lyons, B. J. In *The Radiation Chemistry of Macromolecules*; Dole, M., Ed.; Academic: New York, 1973; Vol. 2, Chapter 14.
- Matusевич, Y. I.; Krul, L. P. *Khim Vys Énerg* 1992, 26, 124.
- Capaccio, G.; Ward, I. M.; Wilding, M. A. *J Polym Sci Polym Phys Ed* 1978, 16, 2083.
- Dole, M. *Polym Plast Technol Eng* 1979, 13, 41.
- Rijke, A. M.; Mandelkern, L. *Macromolecules* 1971, 4, 594.
- Turner, D. T. *J Polym Sci Part D: Macromol Rev* 1971, 5, 229.
- Failla, M. D.; Vallés, E. M.; Lyons, B. J. *J Appl Polym Sci* 1999, 71, 1375.

14. Lyons, B. J.; Vaughn, C. R. Irradiation of Polymer; Advances in Chemistry Series 66; American Chemical Society: Washington, DC, 1967; Chapter 10.
15. Spadaro, G.; Calderaro, E.; Rizzo, G. Eur Polym J 1992, 28, 257.
16. Audouin-Jirackova, L.; Papet, G.; Verdu, J. Eur Polym J 1989, 25, 181.
17. Kandeil, A. Y.; Kassem, M. Thermochim Acta 1991, 191, 333.
18. Seguchi, T.; Arakawa, K.; Hayakawa, N.; Machi, S. Radiat Phys Chem 1981, 18, 671.
19. Lyons, B. J. Radiat Phys Chem 1993, 42, 197.
20. Quinn, F. A., Jr.; Mandelkern, L. J Am Chem Soc 1958, 80, 3178.
21. Miller, A.; Batsberg, W.; Karman, W. Radiat Phys Chem 1988, 31, 491.
22. Popli, R.; Mandelkern, L. J Polym Sci Part B: Polym Phys 1987, 25, 441.
23. Kennedy, M. A.; Peacock, A. J.; Mandelkern, L. Macromolecules 1994, 27, 5297.
24. Saito, O. In The Radiation Chemistry of Macromolecules; Dole, M., Ed.; Academic: New York, 1973; Vol. 2, Chapter 11.