

# Mechanical Properties of Crosslinked Polyethylene

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## Synopsis

The mechanical properties of crosslinked polyethylene were studied in an extended range of test conditions in order to determine the recommended service conditions for articles made of crosslinked polyethylene. On the other hand, this study can clarify the advantages of crosslinked polyethylene against the unmodified polymer. In fact, the results referred in the literature concerning the changes of mechanical properties of polyethylene introduced by crosslinking are contradictory and cannot clearly distinguish the two types of polymer. The above study concluded that tensile tests at elevated temperatures (above 70°C) with low stresses (about 0.5 MPa) can clearly describe the effect of crosslinking on the mechanical properties of LDPE, i.e. an improvement at least for deformation and service life.

## INTRODUCTION

The effect of the crosslinking on the properties of various types of polyethylene (PE) has been extensively studied.<sup>1-9</sup> In the related literature, there is an agreement concerning some of the basic properties changes of crosslinked polyethylene (XPE). Thus, many authors refer to the elevation of melting point, the improvement of the stress cracking, and solvent resistance,<sup>3</sup> as well as the improvement of low temperature embrittlement and weatherability.<sup>6</sup>

On the other hand, the results published on the changes of mechanical properties are contradictory. As a matter of fact, for tensile strength an increase<sup>2,8,10</sup> or a decrease<sup>3,7,9</sup> is referred to and for elongation the same disagreement exists.<sup>3,7,10-12</sup>

The reasons for such deviations are owned to the variety of PE types used and to the diversification of crosslinking processes (i.e., radiation or chemical technique). In fact, the molecular weight and crystallinity of PE are critical for the subsequent mechanical behavior of the product. From this point of view, the crosslinking process followed is of great importance. It is generally accepted that radiation does not affect crystalline regions<sup>13,14</sup> at least at the first stages of the process, while chemical processes conducted by melt techniques rearrange chains and affect crystallinity.

It also must be noted that XPE is a material consisted of thermoplastic and crosslinked fractions, both containing amorphous and crystalline phases. As a consequence, in the above structure some weak points appear to have a predominant role on the mechanical behavior of the material. The effect of such weak points on the behavior of a specimen is influenced by

the mechanical testing conditions, i.e., rate of strain, stress level, temperature, etc.

In the present work, an attempt was made to determine the effect of crosslinking on the mechanical properties of PE, selecting the testing conditions in order to minimize the role of weak points. In addition, the mechanical testing under different conditions evaluates the suitability of a test to predict the behavior of the material under normal service conditions.

## EXPERIMENTAL

### Materials

A low density polyethylene (LDPE) in powder form was used, having density  $0.925 \text{ g/cm}^3$  and MFI 70 dg/min. Dicumyl peroxide (DCP) [MERK-Schuchardt, bis( $\alpha, \alpha$ -dimethyl benzyl)peroxide for synthesis] was used as crosslinking agent in concentrations varying from 0.25 to 3 phr.

### Methods

For the preparation of crosslinked PE (XPE), a two-step (mixing and curing) process was followed. The mixing step leads to crosslinkable PE and provides dry blending of powdered PE with DCP, followed by melt mixing in a Brabender plasticorder (mixing head  $50 \text{ cm}^3$ ). The working conditions ( $120^\circ\text{C}$ , 5 min) were selected to exclude the beginning of the crosslinking reaction.<sup>9</sup>

The curing step was carried out during molding, in a heated plates hydraulic press (Dake Co, Michigan). The molding conditions were the following: temperature  $160^\circ\text{C}$ ; pressure 1000–1200 psi; curing time 7 min; cooling time 30 min (to  $25^\circ\text{C}$ ). The molded XPE were obtained in the form of sheets of 0.1–0.3 cm thickness.

The characterization of the molded samples was based on the determination of the gel content, defined by extraction in boiling toluene for 8 h.<sup>9</sup> The mechanical properties were examined according to ASTM D 638<sup>15</sup> using an Instron tensile machine, working at room temperatures or at elevated temperatures in combination with an oven.

## RESULTS AND DISCUSSION

### Degree of Crosslinking

In order to correlate the mechanical properties with the degree of crosslinking, a number of samples was prepared containing different DCP concentration and cured under the same conditions. The results obtained, after the extraction process, are presented in Figure 1.

As the curve indicate, there is a continuous increase of the gel content with peroxide concentration up to about 2 phr. Then a limiting effect is evident.

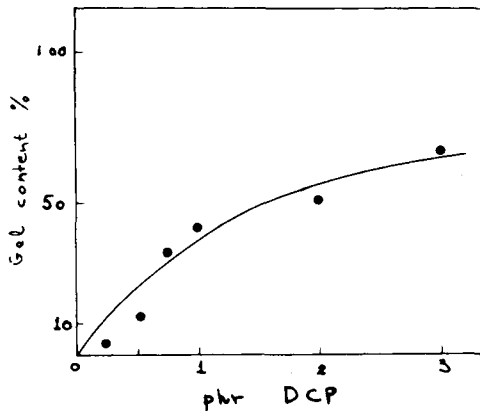


Fig. 1. Effect of DCP concentration on the gel content of cured samples.

### Tensile Strength at Room Temperature

The results obtained from tensile strength measurements at room temperature, correlated with gel content measurements, are shown in Table I and in Figures 2-4. As the curves of Figure 2 indicate, for low gel content, there is a little effect concerning the tensile strength. The effect is stronger for gel content values above 30% where the tensile strength is observed to increase continuously with gel content. The strain rate seems to have no influence on the curve form, but an increase in tensile strength values with strain rate is evident as normally expected.<sup>16</sup>

The results obtained from the measurements of the elongation at break, for samples of various gel content and for two different strain rates, are shown in Figure 3. As the curves of Figure 3 indicate, within the limits of the experimental conditions followed, there is an about linear increase of the elongation with gel content for both strain rates. It is also evident that the higher values correspond to the lower strain rate and the curves decline, leading to a greater percentage increase for the lower strain rates. Concerning the effect of the gel content on the elasticity moduli of XPE (Fig. 4), there is a decrease reaching a limiting value for gel content above 50%.

TABLE I  
Effect of Gel Content on Tensile Characteristics of LDPE<sup>a</sup>

Gel content (%)	Tensile strength		Elongation (%)		Young modulus
	A	B	A	B	
0	8.8	9.1	400	200	—
3	8.9	9.2	405	187	55.7
13	9.1	9.5	425	232	47
33	9.0	9.4	480	262	40
42	9.1	9.6	512	275	35
50	10.4	10.4	570	290	32
68	10.3	10.7	625	325	30

<sup>a</sup> A20 mm/min, B50 mm/min strain rate; tensile strength and Young modulus in MPa.

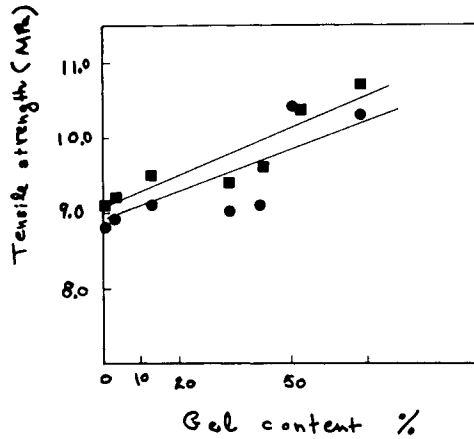


Fig. 2. Correlation of the tensile strength with gel content of cured samples. Strain rates (mm/min): (●) 20; (■) 50.

The above measurements indicate that for gel content lower than 50% the normal test conditions show no remarkable influence of the gel content on the mechanical properties.

### Tensile Strength at 50°C

The mechanical response at elevated temperatures was examined by tensile strength measurements at the selected temperature of 50°C, where LDPE loses its 50% of tensile strength.<sup>9</sup> The results obtained are presented in Table II and Figures 5 and 6. The effect of the gel content on tensile strength is evident in Figure 5. As the curve indicates, the tensile strength increases with gel content up to 50% and then a slight decrease is shown. The elongation (Fig. 6) presents an increase with gel content.

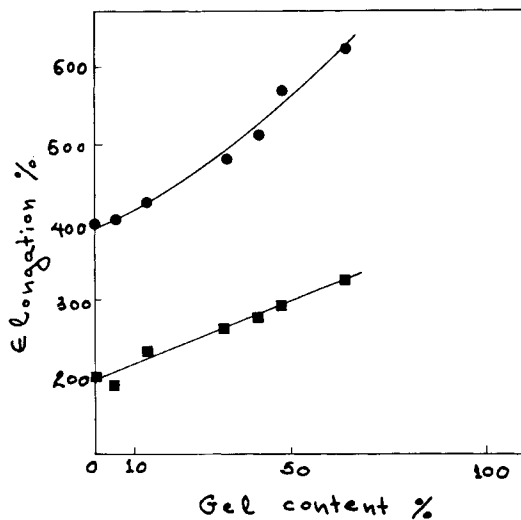


Fig. 3. The elongation at break vs. gel content. Strain rates (mm/min): (●) 20; (■) 50.

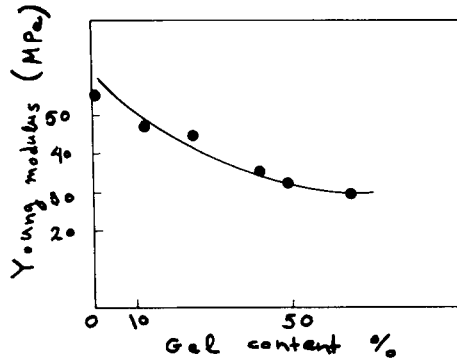


Fig. 4. Correlation of moduli of elasticity with the gel content.

TABLE II  
Effect of the Gel Content on the Tensile Characteristics of XPE at 50° C

Gel content (%)	Tensile strength (MPa)	Elongation (%)
0	4.4	100
42	6.0	250
50	6.7	210
68	5.8	200

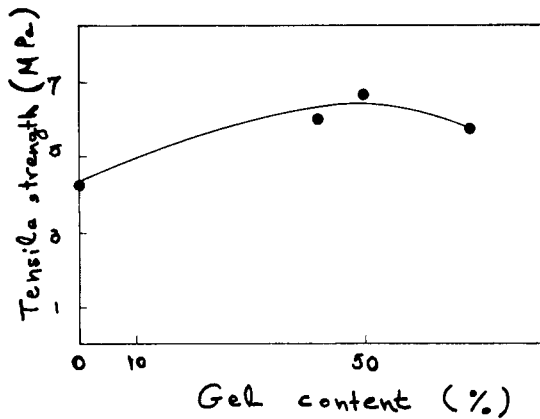


Fig. 5. Tensile strength vs. gel content at 50°C.

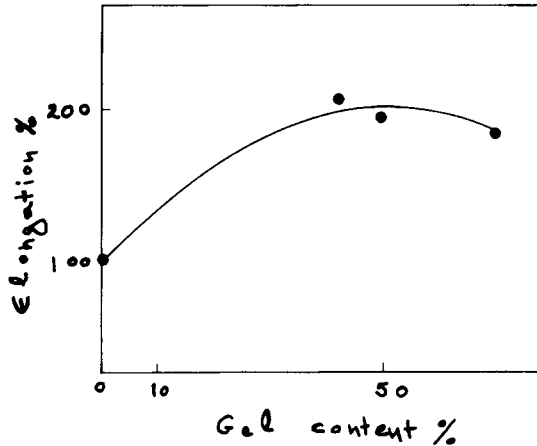


Fig. 6. Ultimate elongation vs. gel content at 50°C.

### Tensile Creep at Elevated Temperatures

The above picture, concerning the tensile characteristics of XPE, is not convincing as an improvement of some critical properties of the polymer introduced by crosslinking. The elevated temperature seems to distinguish LDPE from XPE, but the effect of gel content on the tensile strength is not clear. It should be therefore useful to examine the mechanical properties of LDPE and XPE at elevated temperatures and low stress level, i.e., to examine the creep behavior at elevated temperatures.

The measurements are conducted at 70 and 90°C with 28 and 70 psi stress imposed. The results are shown in Figures 7–10. As the curves of Figure 7 indicate, there is no remarkable effect of the degree of crosslinking on the behavior of LDPE in the range of 0–80% gel content. For higher temperature (90°C) and the same stress (0.2 MPa) the curves of Figure 8 indicate that the effect of crosslinking becomes gradually more visible. The highest deformation rate corresponds to LDPE, while the samples with gel content 80% showed essentially lower deformation rate. Concerning the ultimate elongation, it is higher for LDPE and its drastic reduction is observed for gel content above 50%. Comparing the results of Figure 7 and 8, it is evident that, for the same stress, LDPE is more affected by temperature increase than XPE.

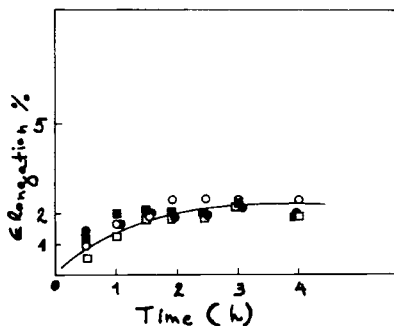


Fig. 7. Elongation vs. time for LDPE and XPE. Gel content (%): (■) 0; (○) 30; (●) 50; (□) 80. (70°C, 0.2 MPa.)

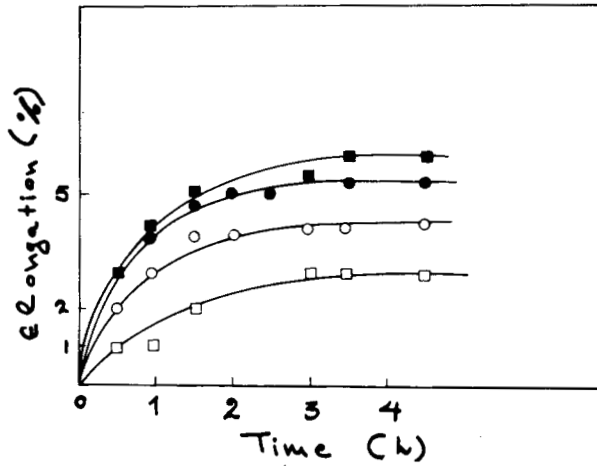


Fig. 8. Elongation vs. time at 90°C and 0.2 MPa. Gel content (%): (■) 0; (●) 30; (○) 50; (□) 80.

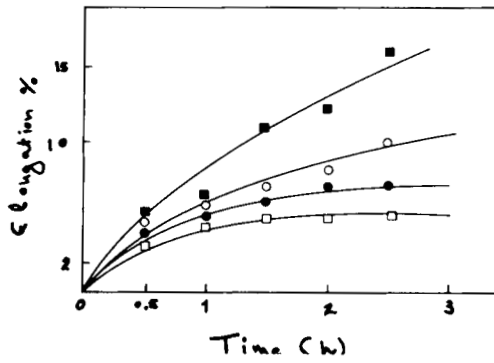


Fig. 9. Elongation vs. time at 90°C and 0.5 MPa. Gel content (%): (■) 0; (○) 30; (●) 50; (□) 80.

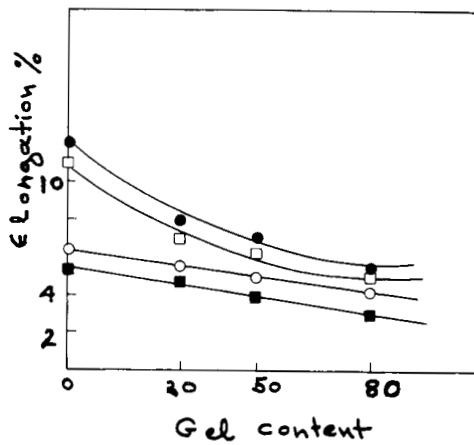


Fig. 10. Elongation vs. gel content at 90°C and 0.5 MPa: (■) 0.5 h; (○) 1 h; (□) 1.5 h; (●) 2 h.

A gradual increase of the stress from 0.2 to 0.5 MPa at 70°C gave results with no clear differences. At 90°C the same increase of stress gave results with differences which became clear enough at 0.5 MPa stress value.

As the curves of Figure 9 indicate, the effect of crosslinking is now clear and an increase in the gel content leads to a visible decrease of the elongation. Under the same conditions the specimens of LDPE break in 2.5 h, while these of XPE showed no failure after 10 h. Comparing the results of Figures 8 and 9, it is evident that at 90°C an increase of the stress is accompanied with greater elongation and elongation rate.

The curves of Figure 10 indicate that, under these conditions, the effect of crosslinking is clear and comparison with the results of Figure 2 certifies the suitability of such tests in order to examine the effect of the crosslinking process on the mechanical behavior of PE.

### CONCLUSIONS

The above discussion can lead to the following conclusions:

The effect of crosslinking on the mechanical behavior of LDPE can clearly be described by tests providing elevated temperatures and low stress level.

The results of these measurements can give information on the service life and the variation of dimensional stability of crosslinked PE. The above results are very useful for solving practical problems of constructions, e.g., pipes for hot water etc.

The increase in gel content of LDPE results in a decrease of the deformation rate and ultimate elongation, whereas, for the time to break (service life), an increase is observed.

The diversification of LDPE and XPE with various gel content is possible within a range of conditions including temperature, stress, and time.

### References

1. E. M. Dannenberg, M. E. Jordan, and H. M. Cole, *J. Polym. Sci.*, **31**, 127-153 (1958).
2. Ger. Pat. 1,169,126 (1964).
3. T. R. Manley and M. N. Qayyum, *Polymer*, **12**, 176 (1971).
4. T. R. Manley and M. N. Qayyum, *Polymer*, **13**, 578 (1972).
5. K. A. Kunert et al., *Polymer*, **22**, 1355 (1981).
6. M. Narkis, *M.P.I.*, Feb., 47 (1982).
7. J. de Boer and A. J. Pennings, *Polymer*, **23**, 1944 (1982).
8. S. K. Bhateja and E. H. Andrews, *Polymer*, **24**, 160 (1983).
9. A. Andreopoulos, doctoral thesis, NTUA, 1983.
10. J. Miltz and M. Narkis, *J. Appl. Polym. Sci.*, **20**, 1627-1633 (1976).
11. K. A. Kunert, *J. Polym. Sci.*, Pol. lett. Edn. 1981, 19, 479.
12. B. J. Lyons and C. R. Vaughn, *Irradiation of Polymers*, Adv. in Chem. Series, Vol. 66, R. F. Gould, Ed., Am. Chem. Soc., Washington, DC, 1967, p. 139.
13. A. G. Andreopoulos and D. C. Diakoulaki, *Interrelations between Processing Structure and Properties of Polymeric Materials*, Elsevier, Amsterdam, 1984, p. 569.
14. M. Kulkarni and R. Mashelkar, *Polymer*, **22**, 1665 (1981).
15. 1977 Annual book of ASTM, American Society for Testing and Materials, Easton, PA, 1977, pp. 215-228.
16. M. Silberberg and R. Supnik, in *Encyclopedia of Polymer Science and Technology*, Wiley-Interscience, New York, 1970, vol. 12, p. 602.

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