

Chemically Crosslinked High-Density Polyethylene

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Synopsis

Chemical crosslinking of high-density polyethylene was studied. The amount of gel produced by a given peroxide concentration depends on the molecular weight of the polymer. More scission reactions, during the crosslinking process, occur in low-density than in high-density polyethylene crosslinked with Varox and Luperox 130 peroxides. The rheological behavior of partially crosslinked polyethylene is useful and convenient for quality control, for characterization, and for studies on the various mechanisms associated with the crosslinking process.

Introduction

Low-shear rheometry proved a useful tool for rapid characterization of chemically crosslinked low-density polyethylene.^{1,2} At a constant shear rate, the melt viscosity of partially crosslinked low-density polyethylene increased with gel content, and its value was shown to depend on the original polymer viscosity, sol viscosity, and gel content.³

During the crosslinking process, molecular details of the flowing phase, or sol fraction, vary due to degradation, branching, and preferential removal of larger molecules into the gel fraction.^{4,5} Sol viscosity was shown to decrease with crosslinking propagation; this decrease was more pronounced for lower melt-flow indices.³ Crosslinking propagation and variation of sol viscosity depend on the initial molecular weight of the polymer, on molecular weight distribution and on the degree of branching. In these circumstances, viscosity-gel curves at a common shear rate should be determined for each polymer.

Comparison of the viscosities of artificial sol-gel mixtures with partially crosslinked polyethylene at the same gel content showed high interaction which could not be achieved in the artificial mixtures, even under prolonged mixing at high temperatures. In addition, study of the shear dependence of the viscosity showed that higher pseudoplasticity is associated with higher gel contents.

A parallel study was carried out on crosslinking of high-density polyethylene, whose crosslinking behavior was expected to differ from that of low-density polyethylene; the latter is characterized by higher molecular weight distribution and larger amounts of both short- and long-chain branching. (Branching is the origin of tertiary carbon atoms, believed to be potential sites for degradation.)

Experimental

High-density polyethylenes were crosslinked in the roller measuring head of a Brabender Plasticorder (model PL 3S) at 200°C (bath temperature). A liquid peroxide, 2,5-dimethyl-2,5-di(*tert*-butylperoxy)-hexyne-3, was used for crosslinking (Luperox 130, Wallace and Tiernan, Germany). Experimental procedures for crosslinking, gel determination and melt viscosity measurements were given previously.^{1,3,6}

Three high-density polyethylenes HD6, HD1.5, and HD0.5, with melt flow indices of 6, 1.5 and 0.5 g/10 min, respectively, were studied.

Results and Discussion

It has been shown¹ that in order to obtain well-cured low-density polyethylene (60–70% gel content), different peroxide concentrations are required; the higher the molecular weight of the polymer, the lower the concentration. Figure 1 shows that up to about 60% gel, a higher peroxide concentration is required at lower molecular weight in order to produce a certain gel content. The curves for HD0.5 and HD1.5 intersect at about 60% gel; this circumstance is unaccounted for at present, in the absence of molecular details of these polymers, but it should be borne in

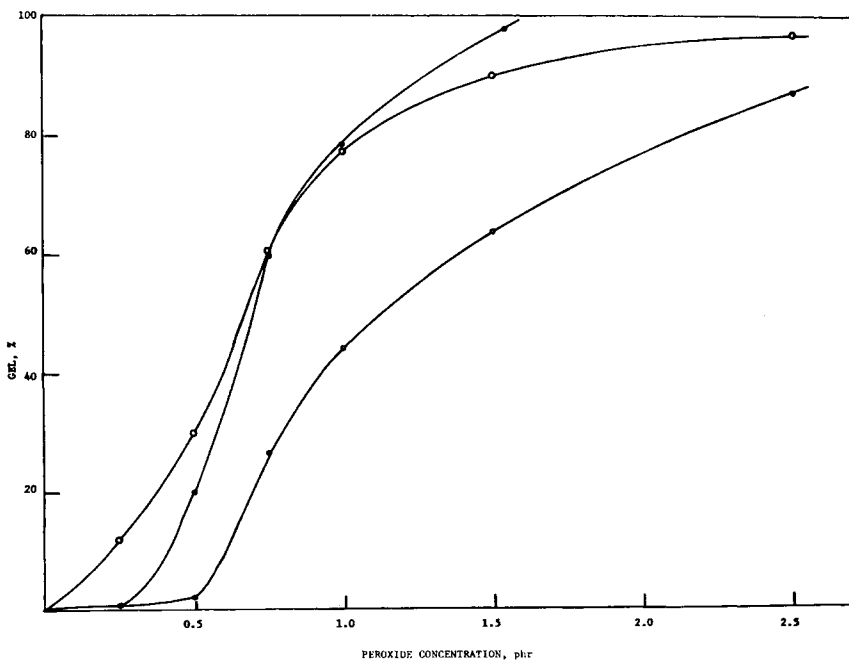


Fig. 1. Dependence of gel content on Luperox 130 concentration for different high-density polyethylenes. $T = 180^{\circ}\text{C}$, $\gamma_w = 7.3 \text{ sec}^{-1}$. ○) HD 0.5; ●) HD 1.5; ○) HD 6.

mind that HD0.5 and HD6 on the one hand, and HD1.5 on the other, are from different sources.

Charlesby and Pinner⁷ have shown that for a polymer of initially random distribution

$$S + S^{0.5} = (p_0/q_0) + (1/q_0\bar{y}_n D) \quad (1)$$

where S is the sol fraction at dose D , p_0 and q_0 are the probabilities of degradation and crosslinking per monomer unit per unit dose, respectively, and \bar{y}_n is the number-average degree of polymerization. Several authors have used eq. (1) for determining the ratio of degradation to crosslinking (p_0/q_0) in irradiation-crosslinking experiments. Charlesby and Pinner have found an intercept of about $p_0/q_0 = 0.3$ for high- and low-density polyethylenes irradiated under vacuum. Lyons⁸ has shown that extrapolation of eq. (1) at high doses yields, for polyethylene, an intercept of $p_0/q_0 \cong 0$. In a recent publication⁵ on sol fractions of irradiated polyethylene, studied by gel-permeation chromatography, Lyons and Fox report that the crosslinking process described by Charlesby is followed closely by low-density polyethylenes, while high-density polyethylenes show deviations attributed to endlinking through vinyl decay or other factors. Chain degradation to crosslinking ratio is less than 0.03 in a low-density polyethylene.

Equation (1) has also been used for chemical crosslinking. In that case, the rate of radical production decreases with time, while in irradiation experiments the dose rate is generally constant. On the other hand, crosslinking studies at a wide range of dose rates have shown that the dose rate does not appreciably affect the crosslinking yield.⁴

Bristow⁹ has studied chemical crosslinking of natural rubber and synthetic polyisoprene and found very low values for the ratio of degradation to crosslinking; in his paper, $S + S^{0.5}$ is plotted against the reciprocal of the crosslinking density, calculated from swelling data. Barton¹⁰ has studied chemical crosslinking of poly-*n*-alkyl methacrylates, plotting $S + S^{0.5}$ against $[i]^{-1}$ (where $[i]$ is the peroxide concentration in moles per gram polymer) and modifying equation (1) as follows:

$$S + S^{0.5} = \frac{p}{q} + \frac{1}{2mE\bar{y}_n[i]} \quad (2)$$

where p and q are the scission and crosslink densities respectively, m is the molecular weight of the monomer, and E is the crosslinking efficiency or the number of crosslinks per decomposed peroxide molecule. Several other authors^{11,12} have shown that the crosslinking efficiency of dicumyl peroxide in polyethylene is close to unity and E is independent of the peroxide concentration. Crosslinking efficiencies of 2,5-dimethyl-2,5-di(*tert*-butylperoxy)-hexyne-3 and 2,5-dimethyl-2,5-di(*tert*-butylperoxy) hexane, for high- and low-density polyethylenes, respectively, were not found in the literature. Figure 2, plotted from the data in Figure 1 for high-density

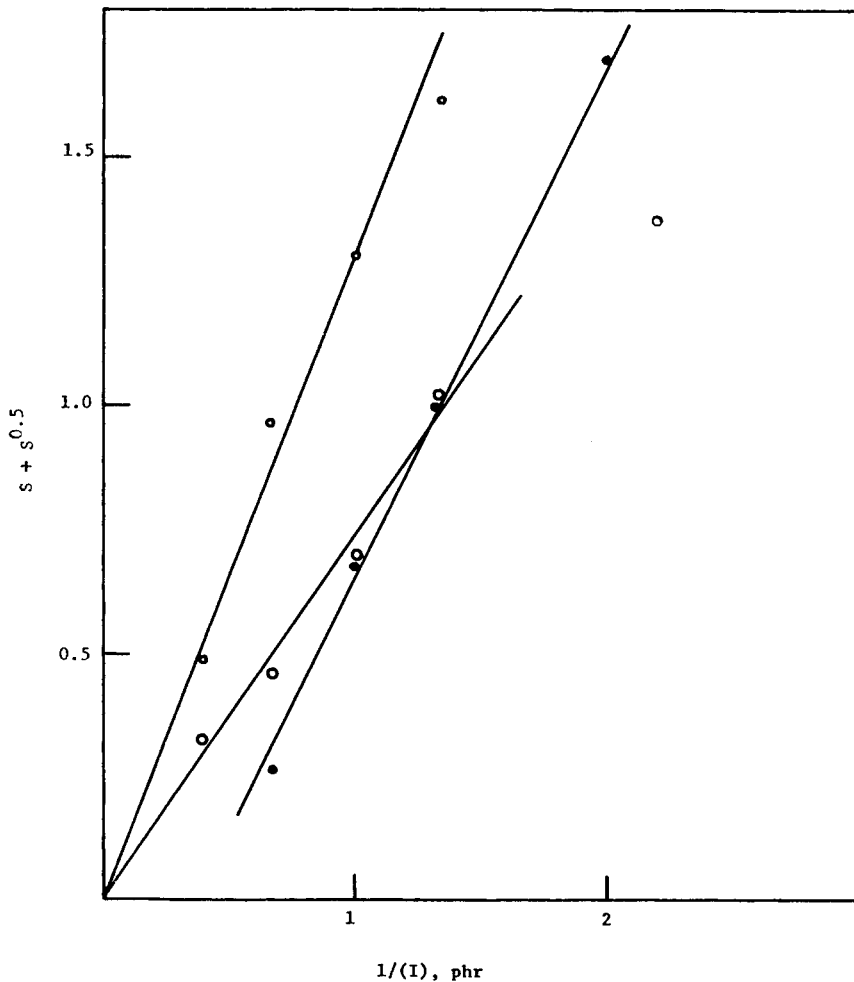


Fig. 2. Dependence of $S + S^{0.5}$ on reciprocal value of decomposed Luperox 130 (phr) for different high-density polyethylenes. $T = 180^\circ\text{C}$, $\gamma_w = 7.3 \text{ sec}^{-1}$. \circ) HD 0.5; \bullet) HD 1.5; \circ) HD 6.

polyethylenes, shows that polymers HD0.5 and HD6 suffer no practical degradation. HD1.5 shows a negative intercept, which is meaningless. The reason for the marked deviation of HD1.5 from Charlesby's theory is not clear.

Figure 3 is based on our previous data¹ for low-density (LD) polyethylenes crosslinked by Varox peroxide (Vanderbilt).

It shows that the ratio of degradation to crosslinking lies within the range of 0.16–0.36, in good agreement with the irradiation results reported by Charlesby and Pinner⁷ and Baskett and Miller.¹³ The p/q ratios for LD7 and LD2 are similar and smaller than for LD0.3, in good agreement with

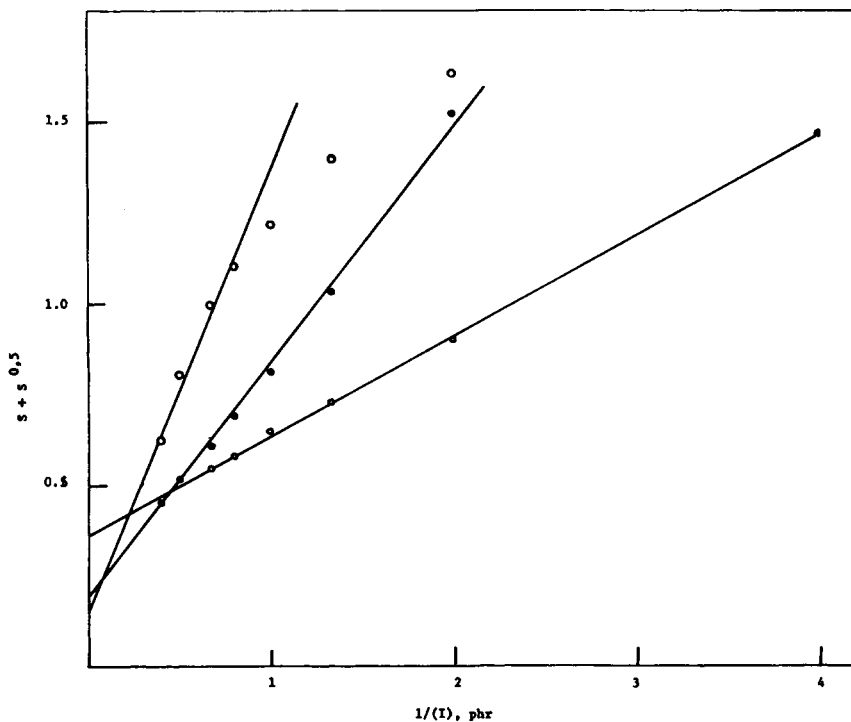


Fig. 3. Dependence of $S + S^{0.5}$ on reciprocal value of decomposed Varox (phr, 100% active) for different low-density polyethylenes. $T = 180^\circ\text{C}$, $\gamma_w = 7.3 \text{ sec}^{-1}$. \circ) HD 0.5; \bullet) HD 1.5; \circ) HD 6.

our own earlier work,³ in which melt viscosities of separated sols were measured at a constant shear rate. The sol melt viscosity decreased with crosslinking propagation, and this decrease was much more pronounced for LD0.3 than for LD2 and LD7. On this basis of the agreement within the two aspects, it is believed that a scission mechanism does exist in chemical crosslinking of low-density polyethylene.

Comparison of Figures 2 and 3 shows that high- and low-density polyethylenes differ in their behavior with regard to chemical crosslinking, the latter being more susceptible to scission reactions. It should be noted here, however, that different peroxides were used for crosslinking the two types of polyethylene. The latter conclusion is in agreement with measurements on irradiated hydrocarbons, which have shown that branched hydrocarbons undergo more carbon-carbon bond scissions than normal alkanes.⁴

According to eq. (2), the slope of the curves should increase with decreasing initial number-average molecular weight. This is also confirmed in Figures 2 and 3.

In Figure 4, melt viscosity of partially crosslinked high-density polyethylenes is plotted against gel content. In view of the close dependence

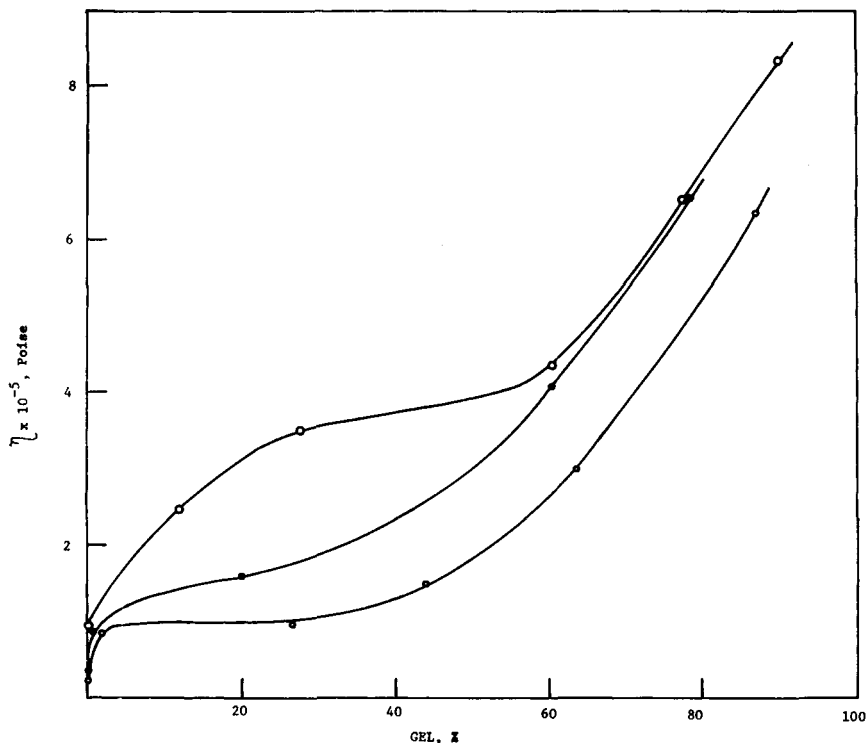


Fig. 4. Dependence of melt viscosity on gel content for different high-density polyethylenes. $T = 180^{\circ}\text{C}$, $\dot{\gamma}_w = 7.3 \text{ sec}^{-1}$. (○) HD 0.5; (●) HD 1.5; (○) HD 6.

in this case, the rapid and sensitive determination procedure for melt viscosity can serve as a useful quality-control test for both low- and high-density partially crosslinked polyethylenes. The initial increase in viscosity at low gel contents is due to the increase in molecular weight during the pregel stage. S-shaped curves of the same type were also found for low-density polyethylenes.³ It should also be noted that the curves for polymers HD0.5 and HD1.5 coincide at approximately the same gel content for which the gel-peroxide curves (Fig. 1) were found to intersect.

The shape of the viscosity-gel curves at a constant shear rate reflects changes in the sol fraction. This can be confirmed by hot extraction and filtration, followed by filtrate centrifugation, drying of the sol, and measuring its melt viscosity. This was done in our previous work on low-density polyethylene³ and for HD0.5 in the present work. In this case, a slow decrease in sol viscosity was observed up to about 40% gel content, followed by a steep decrease. This behavior is in agreement with the curve for HD0.5 in Figure 4, where the viscosity of the crosslinked polymer increases very slowly in the range of 30–60% gel; in other words, the viscosity increase due to higher gel content is offset by reduction of the sol viscosity.

It has been shown that viscosity-gel relations for low-density polyethylenes follow an empirical equation at limited gel contents:³

$$\frac{1-g}{\log(\eta_{cw}/\eta_{ow})} = a \log g + \log b \quad (3)$$

where η_{cw} is the viscosity of the partially crosslinked polymer with gel content g , and η_{ow} that of the corresponding noncrosslinked polymer, both at the wall shear rate; a and b are empirical parameters, the former shear-dependent and the latter nearly unity, i.e., $\log b$ is practically zero. The slope a at a constant shear rate depends on the rate of sol viscosity reduction, and the absolute value of a increases for higher rates of the latter. Viscosity-gel data for high-density polyethylenes according to eq. (3) are interpreted in Figure 5. Equation (3) is shown to be appropriate in this case as well, and as all curves being concurrent at $(1,0)$, we have $\log b = 0$. The absolute values of a are summarized in Table I, including those for low-density polyethylenes previously found³ at a shear rate of 33 sec^{-1} , and recalculated for 7.3 sec^{-1} .

Quantitative comparison for $|a|$ values for the two polyethylene types is difficult, since similar melt flow indices do not reflect similar molecular weights, or molecular weight distribution. In general, $|a|$ values for low-density polyethylenes are higher than their corresponding high-density counterparts, in agreement with the previous comparison between Figures 2 and 3.

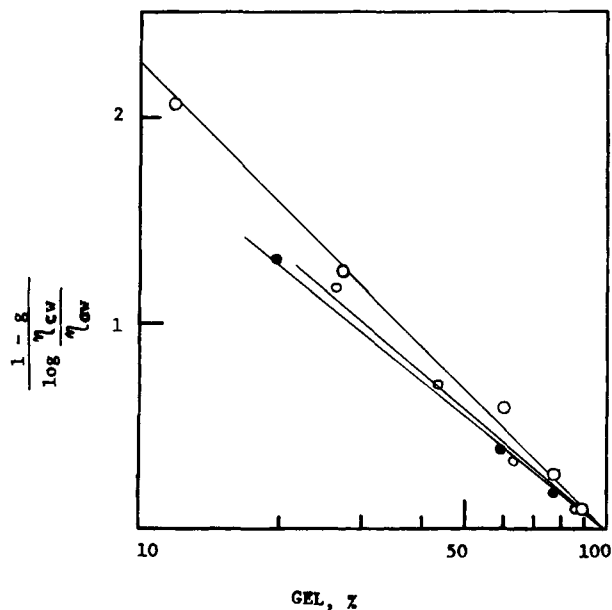


Fig. 5. Interpretation of viscosity-gel data for different high-density polyethylenes by eq. (3). $T = 180^\circ\text{C}$, $\dot{\gamma}_w = 7.3 \text{ sec}^{-1}$. \circ) HD 0.5; \bullet) HD 1.5; \circ) HD 6.

TABLE I
 $|a|$ Values for High- and Low-Density Polyethylenes
 at a Shear Rate of 7.3 sec^{-1}

Polyethylene	$ a $
HD0.5	2.25
HD1.5	1.85
HD6	1.92
LD0.3	4.0
LD2	1.82
LD7	2.2

A preliminary study on the shear dependence of melt viscosity of partially crosslinked high-density polyethylene was carried out. In the shear rate range of $3.75\text{--}33 \text{ sec}^{-1}$, the flow behavior of crosslinked and corresponding noncrosslinked polyethylenes followed the power-law equation:

$$\tau = K\dot{\gamma}^n \quad (4)$$

Higher K and lower n values are associated with increased gel content; thus the polymer becomes more pseudoplastic as crosslinking progresses. Values of n for the noncrosslinked HD0.5 and HD6 are 0.84 and 0.78, respectively, whereas after partial crosslinking $n = 0.37$ for the former and 0.27 for the latter polymer at gel contents of 48 and 52%, respectively. The steep increase in pseudoplasticity with crosslinking was also found for low-density polyethylene.³

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