Peroxide Crosslinking of Ethylene–Vinyl Acetate Copolymer

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Synopsis

The work reported here concerns the peroxide crosslinking of ethylene–vinyl acetate rubber. Calculated values for scission-to-crosslinking ratios are higher for EVA than for low-density polyethylene. In the temperature range from 150 to 200°C at a constant peroxide content, a rise in temperature results in a decrease in the obtained gel content. Some tensile and modulus–temperature results on crosslinked EVA samples are also reported on.

INTRODUCTION

Ethylene–vinyl acetate (EVA) copolymers are used as modifiers for wax and other systems and in hot melt adhesives.[1] EVA copolymers have a lower softening point than polyethylene, a phenomenon which has been attributed by Nielsen[2] to the formation of shorter sequences of polyethylene, thus lowering the melting point of the crystalline zones. EVA copolymers with low VA content (below 20% by weight) can be used directly, while the high VA-content copolymers are often used as modifiers for other systems. Contrary to the melting or softening point decrease, the glass transition temperature increases as the VA content in the copolymer is increased.[3] For the homopolymers, the T_g of poly-(vinyl acetate) is about 30°C, as compared to about −85°C for polyethylene. EVA copolymers containing about 45% weight vinyl acetate are completely amorphous rubbers.

Technical information on EVA is available mainly from the manufacturers who also claim that it can be readily crosslinked.[4-7] EVA rubbers are cured with either dicumyl peroxide or Varox peroxide (2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane). The Mooney rheometer[8] and Monsanto capillary extrusion rheometer[9] have been used to study the peroxide crosslinking of EVA rubbers. EVA rubber vulcanizates can be obtained by compression and injection molding. EVA rubbers are also curable in open steam. Oven curing, however, at atmospheric pressure is inappropriate. Loan[10] explains that the crosslinking mechanism of EVA is somewhat more complicated as compared to polyethylene due to the presence of two active sites in addition to the methylene groups in the polymer chain (tertiary and methyl hydrogens). Kuckro et al.[11] were mainly interested in the insulating properties of the copolymer and studied the effects

of parameters like VA content and carbon black loading on the physical properties of the crosslinked copolymer.

Pollac et al.[12] have studied the thermoelastic properties of crosslinked EVA. Mittelhauser and Graessley[13] were able to crosslink branched poly(vinyl acetate) by gamma irradiation with a cobalt-60 source. The work reported herein describes the chemical crosslinking of EVA copolymer characterized by a high content of VA.

EXPERIMENTAL

Levapren 452, EVA copolymer (45% VA content, Bayer, Germany) was crosslinked with different concentrations of dicumyl peroxide 40C (Dicup, 40% active). The copolymer was thoroughly mixed with the peroxide at 110°C in the mixing head of a Brabender Plastograph. Crosslinking was initiated by raising the temperature of the mixing head while recording torque–time and temperature–curves. The point at which the torque started to rise was chosen as representing the onset of crosslinking. Crosslinked sheets (6 in. × 6 in. × ⅛ in.) were prepared by mixing EVA/Dicup mixtures on a two-roll mill at 50–70°C and subsequently compression molding at 150°C for 1 hr in a Carver press.

Gel per cent was determined in boiling xylene according to ASTM D2765. Tensile properties were studied at 50 cm/min with an Instron tester, and the 10-sec shear modulus, $G(10)$, was measured from −70° to 40°C with a Gehman instrument.

RESULTS AND DISCUSSION

Results of experiments carried out in the Brabender Plastograph are summarized in Table I. It will be seen that, at a constant circulating bath temperature, higher peroxide levels cause onset of crosslinking at lower stock temperature and generate higher gel contents. The torque difference ΔM (the difference between the torque applied by the crosslinked mass in the Brabender and that applied by the melt prior the crosslinking) is also shown in Table I.

As expected, ΔM increases with an increase in the peroxide content while its temperature dependence is not clear. Based on the present results for EVA and past results on crosslinking of polyethylene,[14] one can conclude that ΔM can be used as a rough criterion only for the degree of crosslinking.

Curves of gel content versus peroxide concentrations at different crosslinking temperatures are shown in Figure 1. The upper curve in this figure represents the results of compression molded samples at 150°C, while the other curves represent data on samples crosslinked in the Brabender mixing head. All the curves level off at about 3 phr Dicup, and the 180° and 200°C experimental data points practically coincide. In the temperature range studied, one may conclude that at a lower crosslinking temperature more gel is formed for the same Dicup concentration. In addition, conditions of compression molding (practically no shear and no oxygen) are favored over Brabender crosslinking conditions as far as higher gel contents are concerned.

It is known that in chemical crosslinking as well as in irradiation crosslinking experiments, two competing processes are involved; namely, crosslinking and degradation.[10] Whether the polymer will finally be classified as crosslinked or

TABLE I
Summary of Results from Brabender Plastograph Experiments

Bath temp., °C	Dicup 40C, phr	T_c,[a] σ_C	Gel content, %	ΔM, m-g
160	0.2	145	1.5	80
160	0.5	143	16.0	200
160	1.0	137	38.0	300
160	2.0	137	66.0	630
160	3.0	135	74.2	1290
180	0.5	139	3.2	300
180	1.0	137	21.8	530
180	2.0	134	50.6	1100
180	3.0	133	55.6	1265
200	1.0	—	21.4	495
200	2.0	—	51.0	1090
200	3.0	—	57.4	1315

[a] Beginning of crosslinking.

degraded depends on which one of the two competing reactions predominates. The behavior shown in Figure 1 can be explained in terms of the two competing chemical reactions where a higher temperature results in more degradation and consequently less gel. In the laboratory, the characteristic odor of acetic acid, which undoubtedly reflects the scission process, was clearly noted at the higher temperatures. Polypropylene is a typical polymer which shows more degradation than crosslinking using peroxides.[10] Polypropylene cannot, therefore, be crosslinked successfully only with peroxides.
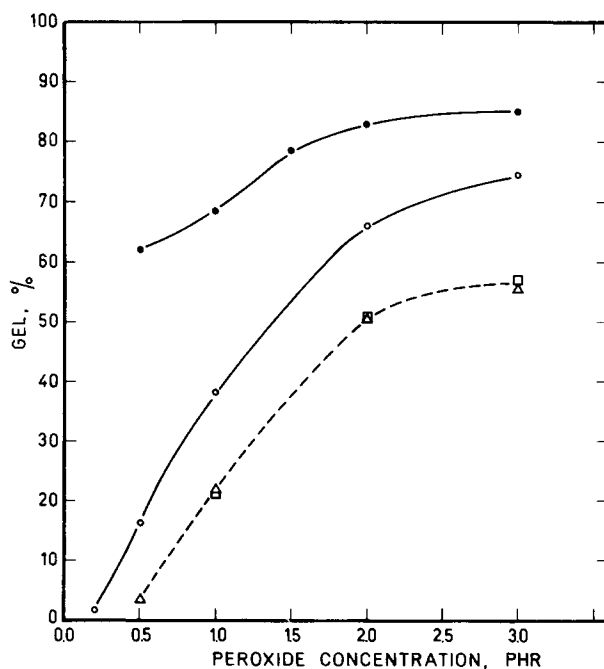

Fig. 1. Dependence of gel content on Dicup 40C concentration for different temperatures: (●) 150°C (press); (○) 160°C; (△) 180°C; (□) 200°C (Brabender).
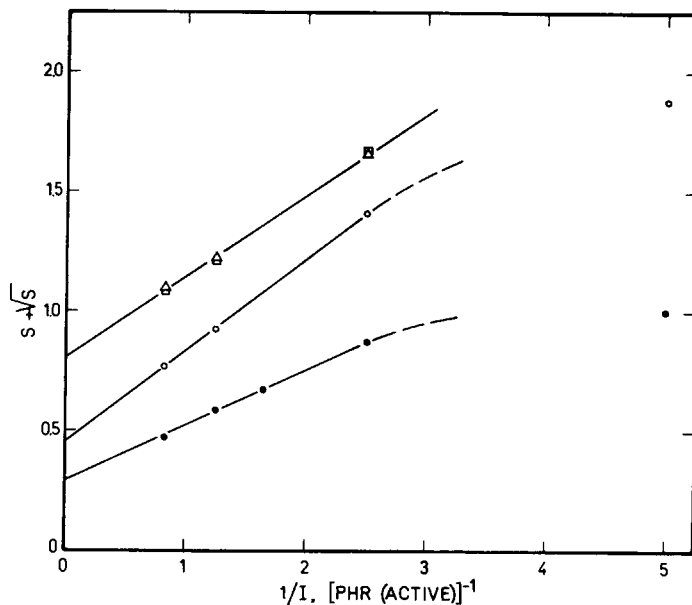
Fig. 2. Dependence of $S + S^{0.5}$ on reciprocal value of decomposed Dicup for different temperatures: (●) 150°C (press); (○) 160°C; (△) 180°C; (□) 200°C·(Brabender).

Charlesby and Pinner[15] have shown that, for a polymer of initially random distribution,

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

where S is the sol fraction at an irradiation 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. Barton[16] has modified eq. (1) for chemical crosslinking as follows:

$$S + S^{0.5} = \frac{p}{q} + \frac{1}{2mE\bar{y}_n(I)} \tag{2}$$

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

<div align="center">TABLE II
Summary of Results on Compression-Molded Sheets</div>

Dicup 40C, phr	Gel content, %	Tensile strength at 25°C, kg/cm²	Relative elongation at 25°C[a]	Tensile strength at 80°C, kg/cm²	Relative elongation at 80°C[b]
0.5	62.2	70.4	1.00	—	—
1.0	68.6	68.2	0.84	6.1	1.00
1.5	78.4	58.8	0.72	—	—
2.0	82.9	59.2	0.62	3.9	0.65
3.0	87.6	59.7	0.58	4.9	0.47

[a] Elongation related to the sample containing 0.5 phr Dicup 40C.
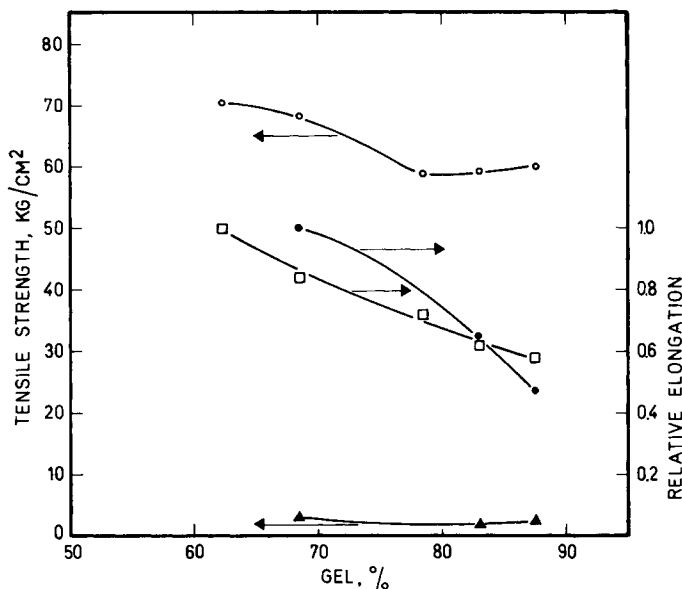[b] Elongation related to the sample containing 1 phr Dicup 40C.

Fig. 3. Tensile strength vs. gel content: (O) 23°C; (▲) 80°C; and elongation vs. gel content: (□) 23°C; (●) 80°C.

number of crosslinks per decomposed peroxide molecule. Using eq. (2), Barton plotted $S + S^{0.5}$ against $(I)^{-1}$, where (I) is the peroxide concentration in moles per gram of polymer, for poly(n-alkyl methacrylates), and Narkis and Miltz[17] used the same equation for high- and low-density polyethylenes. The data of Figure 1 are plotted in Figure 2 using eq. (2). The intercepts, or p/q values, representing ratios of degradation to crosslinking, are as follows: 0.3, 0.45, and 0.8 for 150°C (compression molded), 160°C (Brabender), and 180° or 200°C (Brabender), respectively. The p/q values for peroxide crosslinking of low-density polyethylenes (melt flow index 0.3 to 7 g/10 min) at 180°C were found to be in the range of 0.16–0.36, while practically zero intercepts (no scission) were found for high-density polyethylenes.[17] Contrary to the results for EVA, which show increasing p/q values with temperature, Bristow[18] reported that the p/q ratio for natural rubber does not vary with temperature. Charlesby and Pinner[15] found a value of $p/q = 0.1$ for poly(vinyl acetate) that was irradiated at room temperature with a 2-MeV electron source. This value is considerably lower than the p/q ratios for EVA reported in the present work. It should be mentioned, however, that the crosslinking and degradation reactions have a different temperature dependence, and therefore the end result of chemical crosslinking (carried out above the polymer softening point) is not necessarily similar to that of irradiation crosslinking (usually done at room temperature). It is therefore possible that the scission/crosslinking ratio of the EVA copolymer is controlled by the prevailing temperature.

Table II summarizes the results obtained with compression-molded sheets. The tensile strength and elongation at break at room temperature and 80°C are shown as function of the gel content in Figure 3. It can be seen from this figure that as the gel content is increased, there is a reduction of the relative elongation and tensile strength at room temperature. The tensile strengths at 80°C are
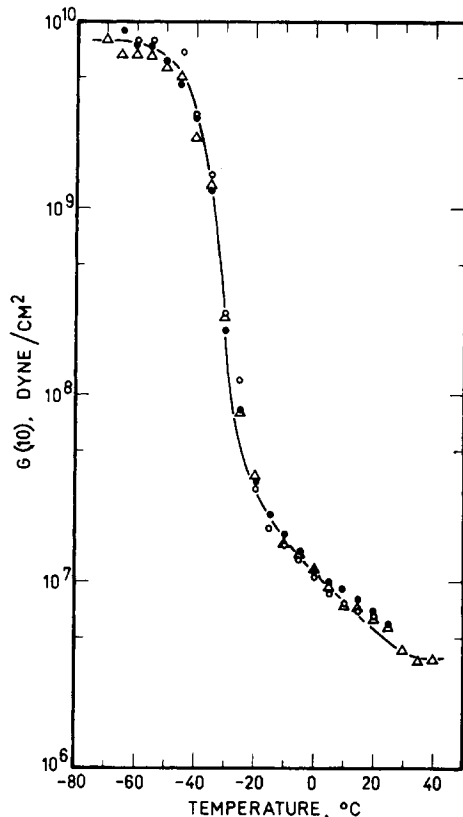
Fig. 4. Shear modulus vs. temperature for different gel contents: (●) 62.2%; (△) 78.4%; (○) 84.8% gel.

roughly independent of gel content and are about one order of magnitude lower than the values at room temperature. Crosslinked polyethylene was also shown to exhibit reduced elongations with increasing gel contents.[19] The tensile strength of the crosslinked polyethylene samples, however, increased with increasing gel content, in contradiction to the present results. It is important to note that crosslinked polyethylene is a semicrystalline polymer, while crosslinked Levapren EVA copolymer is amorphous due to the rather high VA content.

The shear modulus–temperature relationship, as shown in Figure 4, is practically independent of the gel content over the range studied, 62.2% to 84.4%. An estimate of the T_g for the EVA copolymer studied can be obtained using eq. (3) which relates the T_g of a copolymer to the T_g values of the component homopolymers:[20]

$$\frac{1}{T_g} = \frac{W_1}{T_{g,1}} + \frac{W_2}{T_{g,2}} \tag{3}$$

where W represents weight fractions, and the subscripts 1 and 2 represent the component homopolymers. Substitution of $W_1 = 0.45$, $W_2 = 0.55$, $T_{g,1} = 303°K$; $T_{g,2} = 188°K$[19] results in $T_g = 227°K = -46°C$ for the EVA copolymer. The actual T_g for the copolymer is expected to be in the range where the modulus begins to drop sharply as the temperature is increased. The calculated value falls within this range (see Fig. 4).

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