

## Mechanical Properties of Crosslinked Polyethylene and Crosslinked Ethylene-Ethyl Acrylate Copolymers\*

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### Synopsis

Stress-strain curves at various temperatures and secant modulus vs. temperature curves were used to investigate the differences that exist between peroxide crosslinked polyethylene, and vulcanized rubber. A series of hypotheses in terms of crosslinking density and crystallinity is advanced to help visualize the differences between crosslinked polyethylene and cured rubber. The same techniques were used to investigate the nature of crosslinked ethylene-ethyl acrylate copolymers. These copolymers, being more flexible than polyethylene, appear similar to "mechanical rubber," particularly after crosslinking. Recent experiments, however, indicate that profound differences exist. The performance of crosslinked polyethylene and of ethylene copolymers at elevated temperatures depends on crosslinking density, while at lower temperatures it is dominated by polyethylene crystalline morphology. This latter factor makes crosslinked polyethylene at ambient temperature a completely different product from vulcanized rubber. It also means that a crosslinked polyethylene will have lower crosslinking density than most rubber compositions of equivalent room temperature stiffness. A good indication of crosslinking density of crystalline polyolefins may be obtained by measuring mechanical properties such as modulus at elevated temperatures. Use of reactive co-agents is effective in raising crosslinking density to the point where fairly good elevated temperature properties are obtained without increasing the room temperature rigidity.

### INTRODUCTION

In recent years, the difference between certain plastic products and vulcanized rubber has become increasingly difficult to define. This has been particularly true with the advent of crosslinked low-density polyethylene and some rubberlike thermoplastic products such as the flexible ethylene copolymers.

It seemed advisable at this time to look more closely into some of the basic properties of crosslinked crystalline polyolefins and to see how they compare to a rubber product.

Since, for the purpose of this work, a profile of each material was sufficient, only one representative resin from each type was used. Carbon-reinforced vulcanized styrene-butadiene rubber controls were chosen because it would have been unrealistic to compare crosslinked rubbery poly-

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olefins to relatively weak, seldom used, nonreinforced rubber. On the other hand, the polyolefins could not be filled to the same degree as the rubber and retain any degree of rubberlike properties. As a result of these opposing factors, it seemed reasonable to work with crosslinked unfilled polyolefins and to compare these with carbon-reinforced rubber compositions. The data on the rubber controls can then be viewed as outside points of reference but are not comparable in every respect. For instance, the calculations of crosslinking density or the per cent gel make interesting reading, but the values do not mean the same thing as for the unfilled olefin systems.

## DISCUSSION

### Crosslinked Low-Density Polyethylene

Peroxide-crosslinked polyethylene has been known for many years;<sup>1</sup> it is an infusible product, somewhat more flexible than the regular polyethylene parent, but more rigid than most rubber formulations. At elevated temperatures it will not flow, but its mechanical properties are not outstanding. It has been used where the following properties are needed: excellent stress-crack and flex-crack resistance, very good elevated temperature performance from the point of view of no flow, little embrittlement, and good chemical resistance.

Peroxide-crosslinked polyethylene is qualitatively different from vulcanized rubber in a few other important aspects. Unlike rubber, it is not possible to increase the rigidity by increasing the amounts of vulcanizing agents; there is an optimum amount of peroxide that can be used. Crosslinked polyethylene is more flexible than the thermoplastic polymer, but the degree of flexibility cannot be varied at will.

A stress-strain curve of a low-density (0.919) product (DYNH) having a melt index of 2, uncrosslinked and crosslinked, shows that crosslinking decreases elongation, decreases modulus and increases ultimate tensile strength (Fig. 1, Table I).

Carbon black-reinforced styrene-butadiene type rubber compositions show a totally different stress-strain pattern. This means that crosslinking quantitatively alters a polyethylene. However, at room temperature it still is very different from a true rubber.

The effect of crosslinking at elevated temperatures was investigated by measuring the secant modulus at 1% extension at intervals of 5°C. from room temperature to 200°C. Figure 2 shows that the crosslinked polyethylene curve parallels that of the uncrosslinked parent up to about 100°C. and then levels out to a reasonably constant value until thermal degradation begins to affect the material. The vulcanized rubber, instead, shows virtually no change in modulus at 1% elongation over a very broad temperature range. There is, of course, a severe loss in per cent elongation and ultimate tensile strength at the higher temperatures (Fig. 3), but the stiffness at low extension is not affected.

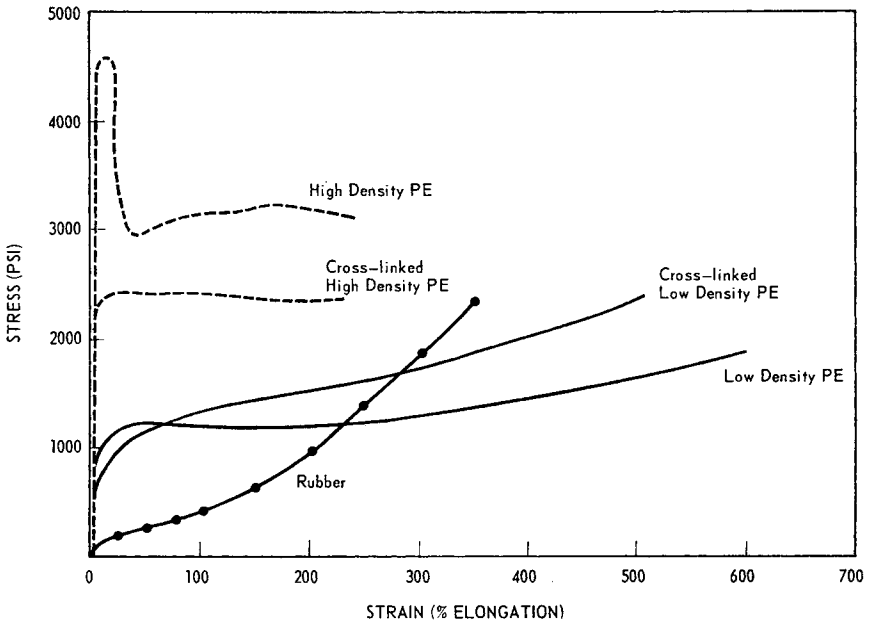


Fig. 1. Stress-strain curves at 23°C. for unfilled crosslinked polyethylene.

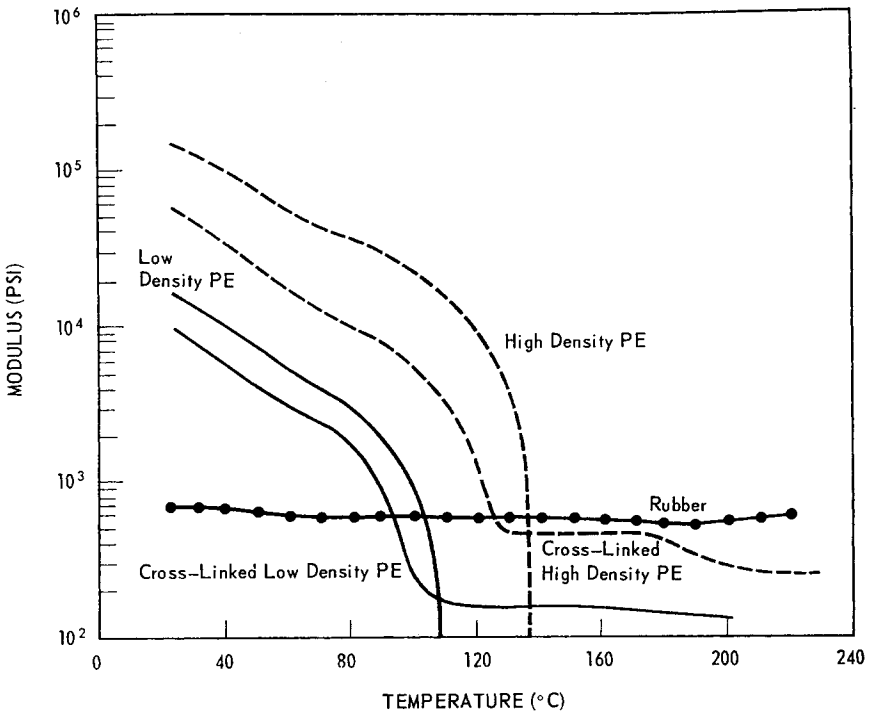


Fig. 2. Modulus vs. temperature curves for unfilled crosslinked polyethylene.

TABLE I  
Crosslinked, Unfilled Polyethylene

Polymer	Melt index	Ultimate tensile strength, psi		Elongation, %		Secant modulus, psi		Yield strength (23°C.), psi	Gel content, %	Cross-linking density factor, $\text{cm}^3/\text{mole} \times 10^{-3}$ <sup>a</sup>
		23°C.	160°C.	23°C.	160°C.	23°C.	160°C.			
		Flows	Flows	Flows	Flows	Flows	Flows			
Low-density PE <sup>b</sup>	2	1,800	Flows	600	Flows	20,000	Flows	1,200	—	—
Crosslinked low-density PE <sup>b</sup> (3% peroxide <sup>c</sup> )	0	2,280	66	500	100	11,000	166	d	88.3	0.16
Crosslinked low-density PE <sup>b</sup> (4.5% peroxide <sup>c</sup> )	0	2,360	118	490	100	10,400	237	d	88.3	0.23
Crosslinked low-density PE <sup>b</sup> (3% peroxide, <sup>e</sup> 10% triallyl cyanurate)	0	2,350	66	193	15	11,350	445	d	93.0	0.43
High-density PE <sup>c</sup>	5	3,000	Flows	270	Flows	150,000	Flows	4,600	—	—
Crosslinked high-density PE <sup>c</sup> (3% peroxide <sup>c</sup> )	0	2,300	245	265	80	55,000	474	2,400	98.0	0.45
Vulcanized rubber <sup>f</sup>	0	2,200	170	350	40	705	600	d	87.7	0.57

<sup>a</sup> See Experimental Section.

<sup>b</sup> DYNH, density 0.919.

<sup>c</sup> Dicumyl peroxide; cured at 160°C., 15 min.

<sup>d</sup> No true yield point.

<sup>e</sup> DMD-7000, density 0.96.

<sup>f</sup> SBR formulation: SBR rubber (100), HAF black (50), sulfur (1.33), Altax (1.0) cumate (0.16).

Although modulus-temperature curves give a good idea at what temperatures major changes occur, they do not indicate how useful the materials really are. For instance a brittle, low elongation product may have a respectable elevated temperature modulus. Since cure of molded items can conveniently be conducted at 150–160°C. it seemed pertinent to investigate the stress-strain behavior of these products at 160°C. This is an indication of the strength and over-all toughness of a part being removed from a hot mold. Figure 3 shows that crosslinked low-density polyethylene is much weaker than the rubber control. Also, the inflection or pseudo yield point has disappeared. This is reasonable if it is assumed that the inflection point is caused solely by crystallinity and that, as reported in the literature, there is no polyethylene crystallinity remaining above 138.7°C.<sup>2</sup>

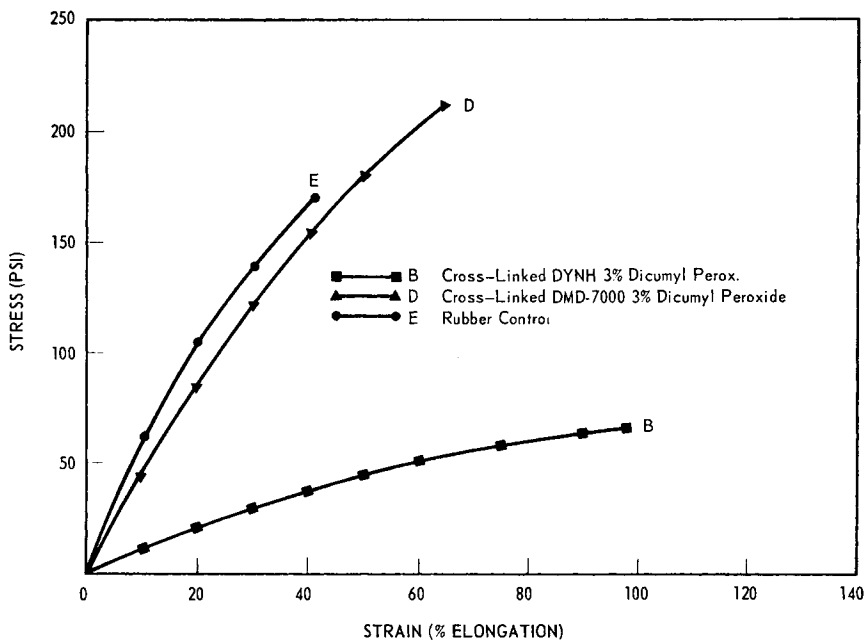


Fig. 3. Stress-strain curves at 160°C. for unfilled crosslinked polyethylene: (*B*) crosslinked DYNH, 3% dicumyl peroxide; (*D*) crosslinked DMD-700, 3% dicumyl peroxide; (*E*) rubber control.

In general, the data show that crosslinking lowers the degree of polyethylene crystallinity, but that this crystallinity is still a dominating feature up to the point where the crystals melt. Above this point, the material appears in every way similar to a weak rubber.

One may say that crosslinked polyethylene is a rubber that at room temperature is reinforced by polyethylene crystalline areas. It should be noted, however, that this reinforcement is of a completely different nature than that provided by carbon black and results in a pronounced yield point.

### Crosslinked High-Density Polyethylene

Properties of a high-density (0.960) polyethylene (DMD-7000) having a melt index of 5, both uncrosslinked and peroxide-crosslinked, were also investigated. In general the data show the same behavior as for the low-density product (Table I, Figs. 1-3), except that the data were much more erratic from experiment to experiment. Differences of 36,000-55,000 psi modulus were observed in the same system, depending on the conditions of mixing in the peroxide. The higher milling temperatures necessary to melt the high-density polyethylene probably tended prematurely to crosslink the material on the mill. It seemed that the higher the temperature, the lower the modulus and the higher the crosslinking densities of the finished compound. Despite these limitations that preclude rigorous comparisons, the behavior of the high-density polyethylene qualitatively parallels that of the low-density polyethylene.

It is interesting to note that these experiments indicate how the properties of the finished crosslinked product can, to a degree, depend on the crystalline state of the material at the moment of crosslinking. This is in agreement with Flory's theories.<sup>2</sup>

### Crosslinking Density

Many methods<sup>3</sup> have been used to obtain an indication of the degree of crosslinking. Some are based on mechanical properties such as compression set, some on solvent effects such as swelling, or extraction of low molecular weight fractions.

In this work, crosslinking density was followed by measuring the per cent gel, that is, the per cent polymer that cannot be dissolved in hot ethylbenzene. In addition to this rather empirical test, an attempt was made to measure the moles of crosslinks per unit volume by assuming that the rubbery plateau of a modulus temperature curve is a measure of crosslinking density.

This concept, besides being intuitively reasonable, also has theoretical justifications if we assume that crosslinked polyethylene above the melting point of the polyethylene and disappearance of crystallinity can be considered thermodynamically analogous to vulcanized rubber. The basic concepts relating modulus to crosslinking density have been presented by Flory<sup>4</sup> and by Tobolsky<sup>5</sup> and may be roughly outlined as follows. There is a strong similarity between the thermodynamic properties of vulcanized rubber and an ideal gas, in that mechanical properties, such as compressibility, can be considered mainly a function of order and disorder and, in turn, of possible polymer configurations.

Tensile strength of a rubber, for instance, can be related to changes in internal energy  $U$  as a function of entropy  $S$  and changes in length  $L$  and volume  $V$  through the basic equation:

$$dU = TdS + XdL - pdV \quad (1)$$

where  $T$  is temperature,  $p$  is pressure, and  $X$  is tensile force.

Assuming that the forces in a rubber network are dominated by consideration of high entropy for a relaxed state and low entropy for an oriented state (because stretching reduces the number of possible configurations), an equation can be derived which now relates changes in tensile force  $X$  to the gas constant  $R$ , the number of molecules  $n$ , and changes in length  $L$ ,

$$F = X/A_u = nRT [(L/L_u) - (L_u/L)^2] \quad (2)$$

where  $A_u$  is the cross-sectional area prior to deformation,  $L$  is the length after deformation, and  $L_u$  the length prior to deformation. Against this background, another concept is introduced, namely, that the entropy change (and therefore indirectly changes in length and hence modulus) are dictated by the spacing between crosslinks. This is the same as saying that modulus will be related to the crosslinking density through an equation of this type:

$$E \text{ at low strains} = 3nRT \quad (3)$$

where  $E$  is Young's modulus (in dynes/square centimeter),  $n$  is the number of chains per unit volume,  $R$  is the gas constant, and  $T$  is the absolute temperature.

If  $n = 2c$ , where  $c$  is the moles of crosslinks per cubic centimeter assuming four chains terminate at each crosslink and where  $2c = d/M_c$ , where  $d$  is density and  $M_c$  is the number-average molecular weight of the network chain, eq. (3) becomes:

$$E \text{ at low strains} = 6cRT = 3dRT/M_c \quad (4)$$

Values for  $c$ , the theoretical number of moles of crosslinks per cubic centimeter calculated at 160°C. are included in the tables. These values can be compared to those obtained by Meltzer on natural and on styrene-butadiene rubber.<sup>6,7</sup>

In general, it appears that, while in rubber, higher crosslinking density can be achieved by increasing the amount of vulcanizing agent used,<sup>7</sup> this is not as easily done with polyolefins by the peroxide route alone.

It is probable that, aside from practical limitations of cost and peroxide odor, very high concentrations of peroxide degrade as well as crosslink the product.

Also, the data indicate that a crosslinked polyolefin which at room temperature seems like a rather strong, stiff rubber, is in actuality a very lightly crosslinked product. Its crosslinking density is much lower than that of a rubber of equivalent room temperature rigidity.

### Crosslinked Ethylene-Ethyl Acrylate Copolymer

Having explored the mechanical behavior of peroxide-crosslinked polyolefins of widely different degrees of crystallinity, attention was turned to a peroxide-crosslinked ethylene copolymer of low modulus (6000 psi). This material is a 6 melt index (18%) ethylene-ethyl acrylate copolymer (DPD-6169) previously described in the literature.<sup>8</sup> It is a flexible ther-

TABLE II  
Crosslinked, Unfilled Ethylene-Ethyl Acrylate Copolymer DPD-6169

DPD- 6169 <sup>a</sup>	Formulation		Tensile strength, psi		Elongation, %		Secant modulus, psi		Gel content, %	Cross- linking density factor $\rho$ , mole/cm. <sup>3</sup> $\times 10^{-3}$
	Dicumyl peroxide <sup>b</sup>	Coagent	23°C.	160°C.	23°C.	160°C.	23°C.	160°C.		
100	—	—	1910	Flows	980	Flows	5150	Flows	—	—
98.5	1.5	—	2980	—	870	—	4650	—	63.2	—
97.0	3.0	—	2980	50	670	36	3700	235	93.3	0.23
95.5	4.5	—	2170	—	620	—	3600	—	96.7	—
87.0	3.0	I, 10	1950	55	380	23	3800	302	—	0.29
87.0	3.0	II, 10	2840	—	570	—	3850	—	—	—
87.0	3.0	III, 10	2050	—	530	—	3300	—	—	—
87.0	3.0	IV, 10	2430	120	190	30	5090	487	98.0	0.47

<sup>a</sup> Ethylene-ethyl acrylate copolymer, melt index 6.

<sup>b</sup> Di-Cup R (Hercules Powder Co., all samples cured 15 min. at 160°C.



moplastic product superficially resembling a mechanical rubber or a plasticized vinyl. Actually it is a very different product and is mechanically more similar to a thermoplastic polyurethane.<sup>9</sup>

The effect of increasing the degree of crosslinking by increasing peroxide addition was investigated by adding 1.5, 3.0, and 4.5% dicumyl peroxide (Table II).

Stress-strain curves at 23°C. (Fig. 4) show a decrease in per cent elongation, an increase in tensile strength, and a decrease in modulus (Table II) with increasing peroxide content up to 3%. At 4.5%, there is a drop in properties.

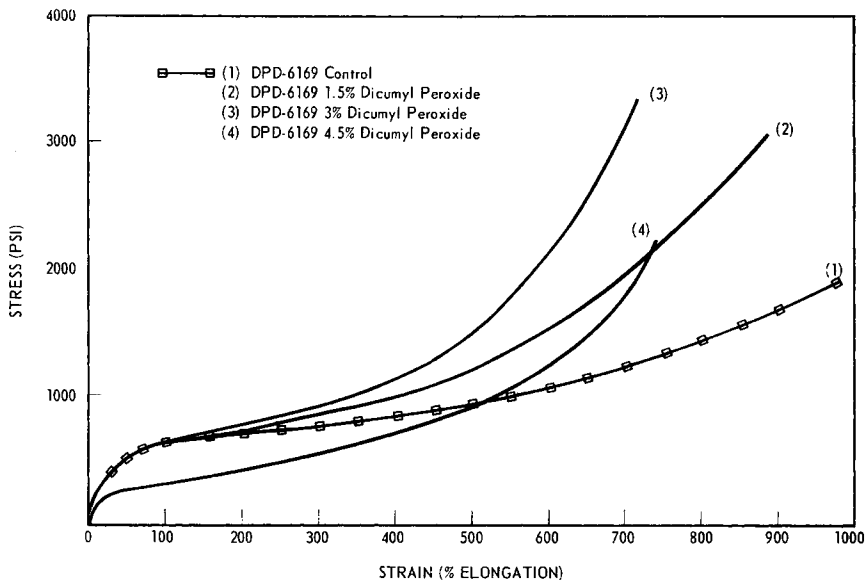


Fig. 4. Stress-strain curves at 23°C. of unfilled crosslinked acrylate copolymer DPD-6169: (1) DPD-6169, control; (2) DPD-6169, 1.5% dicumyl peroxide; (3) DPD-6169, 3% dicumyl peroxide; (4) DPD-6169, 4.5% dicumyl peroxide.

The modulus-temperature curve (Fig. 6) shows no rubbery plateau for 1.5% peroxide (63% gel), a plateau for 3% peroxide (93% gel) up to 175°C., which is higher than for the ethylene homopolymer DYNH, and a slightly higher plateau for the resin containing 4.5% peroxide (97% gel).

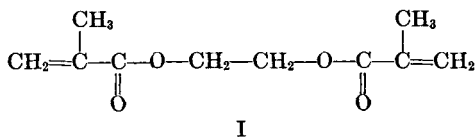
The increase in the level of the plateau with increasing amounts of crosslinking agent was interpreted to mean a greater number of effective crosslinking sites. This is in keeping with the kinetic theory of rubber elasticity previously mentioned and, apparently, also agrees fairly well with gel content determination.

#### Effect of Coagent Addition

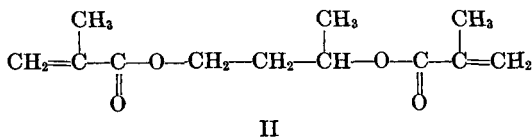
Assuming that crosslinking density could be measured by the relative height of the plateau on a modulus-temperature curve, attention was

turned to means of increasing this density without adding more peroxides. Work by Bartl<sup>10,11</sup> had indicated that low molecular weight materials having two or more reactive double bonds, such as triallyl cyanurate, might be considered as "grafting" reactive sites to aid in peroxide crosslinking. More recently, compounds that probably work on this principle have been suggested as coagents to improve the performance of peroxide-cured rubber.<sup>12,13</sup> Also, similar products have been found beneficial in the irradiation crosslinking of polyethylene.<sup>14</sup>

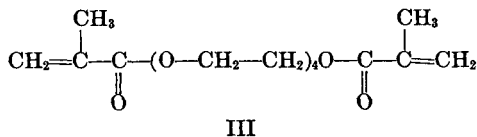
For our work (Table II) four coagents were used; these were ethylene glycol dimethacrylate (Sartomer SR 206) (I),



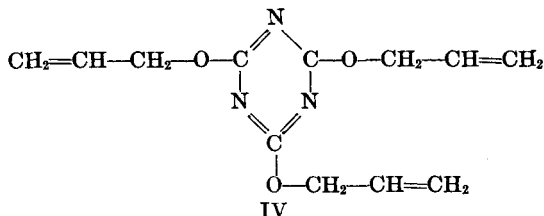
because it was a linear molecule with shortest spacing; 1,3-butylene glycol dimethacrylate (Sartomer SR 297) (II),



which had maximum compatibility and intermediate spacing; poly(ethylene glycol) dimethacrylate (Sartomer SR 210) (III),



which had maximum spacing between crosslinking sites; and triallyl cyanurate (American Cyanamid) (IV),



which is a trifunctional system, with maximum reactivity per mole and features the rigid triazine ring.

Table II and Figure 5 and 6 show the results of adding 10% of these coagents to our control formulation containing 3% dicumyl peroxide. The data may be interpreted as follows: (1) the coagents I, II, and IV react and increase the number of crosslinks as shown by reduction in elongation

at room temperature; (2) the most effective coagents were the ones with maximum functionality per unit weight; (3) there is some question as to the long-chained poly(ethylene glycol) dimethacrylate (III); it seems to yield lower crosslinking density (Fig. 6) and is weaker. The lower elongation (Table II) may not mean crosslinking; it may simply indicate early failure, as shown by Figure 5, due to incompatibility of the poly(ethylene oxide) backbone of the coagent.

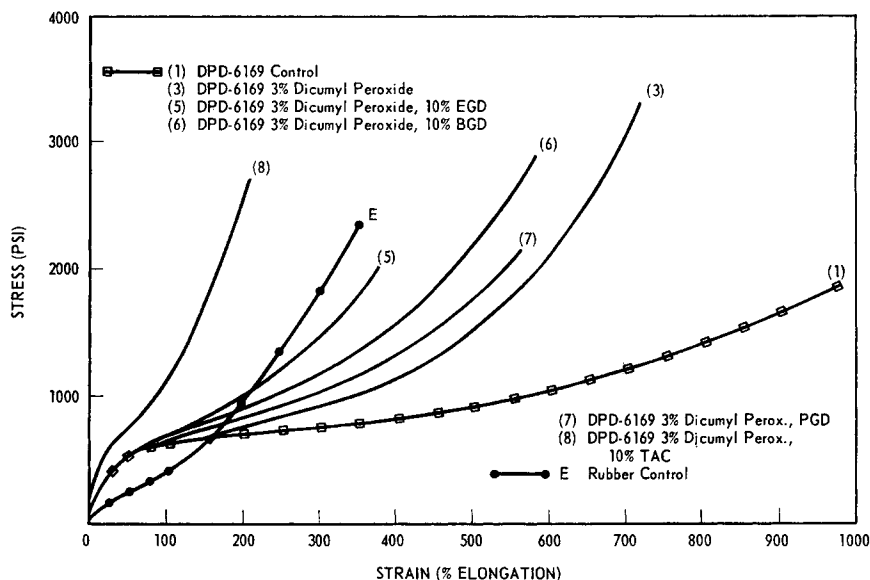


Fig. 5. Stress-strain curves at 23°C. of unfilled crosslinked acrylate copolymer DPD-6169: (1) DPD-6169, control; (3) DPD-6169, 3% dicumyl peroxide; (5) DPD-6169, 3% dicumyl peroxide, 10% I; (6) DPD-6169, 3% dicumyl peroxide, 10% II; (7) DPD-6169, 3% dicumyl peroxide, 10% III; (8) DPD-6169, 3% dicumyl peroxide, 10% IV; (E) rubber control.

On the basis of these data, the two best coagent systems, triallyl cyanurate and ethylene glycol dimethacrylate, were tested for strength and percent elongation at 160°C. Figure 7 shows that the coagents are helpful at this temperature, that the highly functional cyanurate is better than the ethylene glycol dimethacrylate, but that none of these systems are as good at elevated temperatures as a typical carbon-filled rubber composition.

Compared to low-density polyethylene, the copolymer shows slightly higher crosslinking density for equivalent peroxide used. This, coupled with the lower room temperature modulus, results in a flatter, more rubber-like, stiffness temperature behavior. It should be noted that with the help of coagents, respectable elevated temperature strengths and moduli were obtained without the need of reinforcing agents. Also, this was obtained without significantly stiffening the product at room temperature.

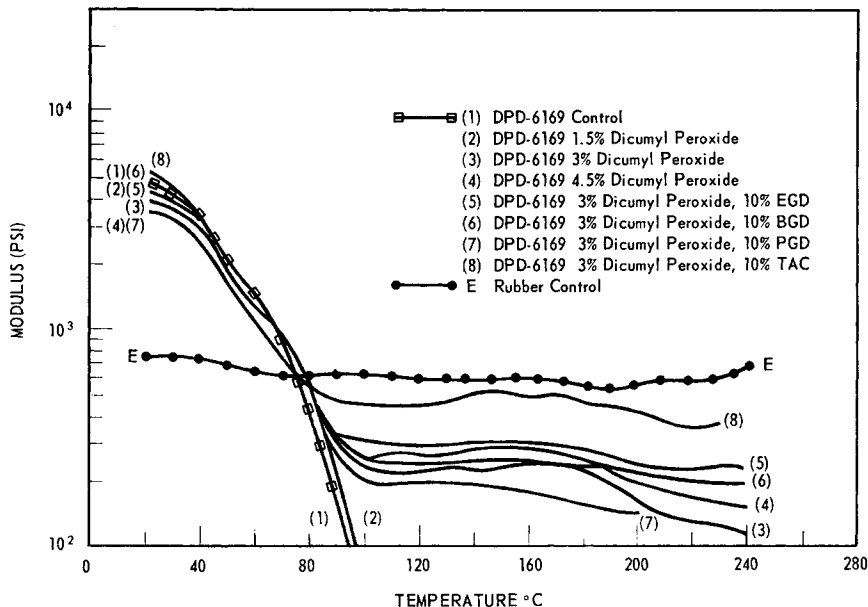


Fig. 6. Modulus vs. temperature for unfilled crosslinked acrylate copolymer DPD-6169: (1) DPD-6169, control; (2) DPD-6169, 1.5% dicumyl peroxide; (3) DPD-6169, 3% dicumyl peroxide; (4) DPD-6169, 4.5% dicumyl peroxide; (5) DPD-6169, 3% dicumyl peroxide, 10% I; (6) DPD-6169, 3% dicumyl peroxide, 10% II; (7) DPD-6169, 3% dicumyl peroxide, 10% III; (8) DPD-6169, 3% dicumyl peroxide, 10% IV; (E) rubber control.

### Low-Temperature Properties

The effect of crosslinking on modulus is shown in Figures 8 and 9. It appears that, unlike rubber, these crystalline products do not show a very sharp change in modulus at a particular temperature.<sup>6,7</sup> Instead, a gradual increase in stiffness is observed paralleling that of the uncrosslinked parent down to  $-80^{\circ}\text{C}$ . It is interesting to note that this polyethylenelike behavior dominates even the relatively highly crosslinked products where 3% peroxide and 10% triallyl cyanurate were used. X-ray diffraction showed polyethylenelike patterns even for those highly crosslinked products that appeared to be transparent and amorphous.

### Crystalline "Clutch" Mechanism

An interesting phenomenon observed with these crosslinked copolymers is that when warmed above the crystalline melting point they can be deformed, and if quenched in a new shape they will freeze in this shape. The reason for this is readily apparent by looking at any of the modulus-temperature curves. The crosslinked products may be considered as existing in two separate physical states. Above the crystalline melting point they appear to behave as relatively loose rubber networks. On the other hand, below the crystalline melting point, the crystalline forces dominate. These

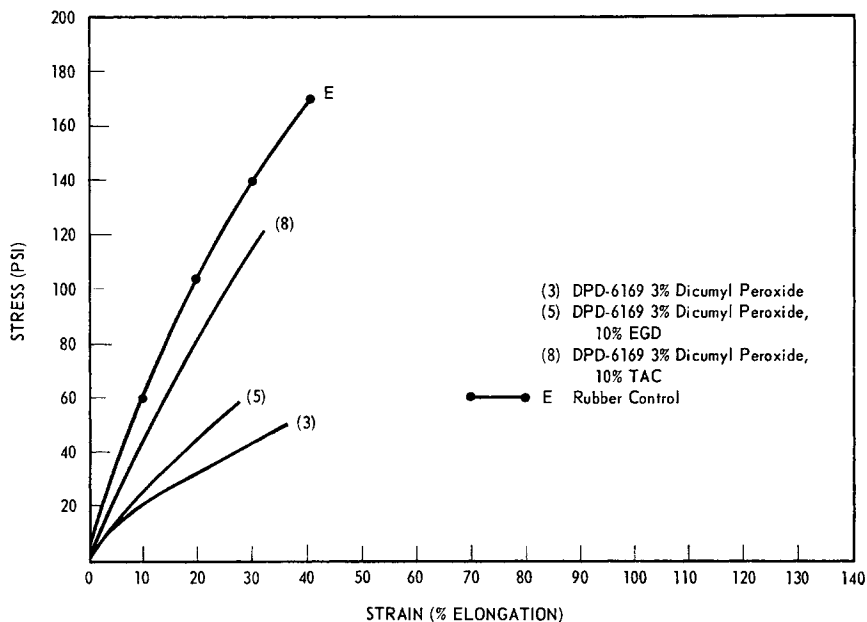


Fig. 7. Stress-strain curves at 160°C. of unfilled crosslinked acrylate copolymer DPD-6169: (3) DPD-6169, 3% dicumyl peroxide; (5) DPD-6169, 3% dicumyl peroxide, 10% I; (8) DPD-6169, 3% dicumyl peroxide, 10% IV; (E) rubber control.

forces introduce a restraining action which is so strong as to prevent the material from returning to the shape in which it was originally crosslinked. It should be noted that although "frozen" into the new shape, the product is still a low-modulus, rubbery material. Furthermore, as might be expected, the material will return to the original crosslinked shape when heated. This shaping process can be repeated at will provided the elevated temperature elastic limit of the particular crosslinked system is not exceeded. Otherwise the part will tear in shaping. The same phenomenon was observed in the case of irradiated polyethylene.<sup>14</sup>

## EXPERIMENTAL

### Tensile Strength, Elongation, Secant Modulus at 1% Elongation

These tests were conducted on an Instron tester, model TM (M-12). The specimens were 20 mils  $\times$   $\frac{1}{8}$   $\times$  2 in. span and the rate of loading was 2 in./min.

The 1% modulus versus temperature curves were obtained by deforming the sample to 1% elongation and immediately releasing the stress after having obtained it. This operation was repeated on the same sample every 5°C. The temperature in the test chamber was programmed to increase at a rate of 1.5°C./min.

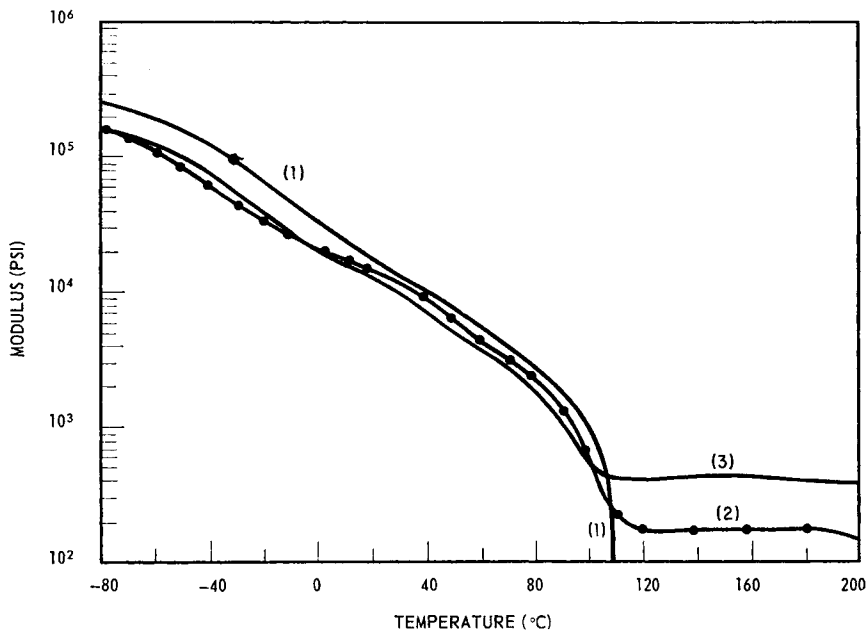


Fig. 8. Modulus vs. temperature for unfilled crosslinked low-density PE: (1) DYNH; (2) DYNH, 3% dicumyl peroxide; (3) DYNH, 3% dicumyl peroxide, 10% IV.

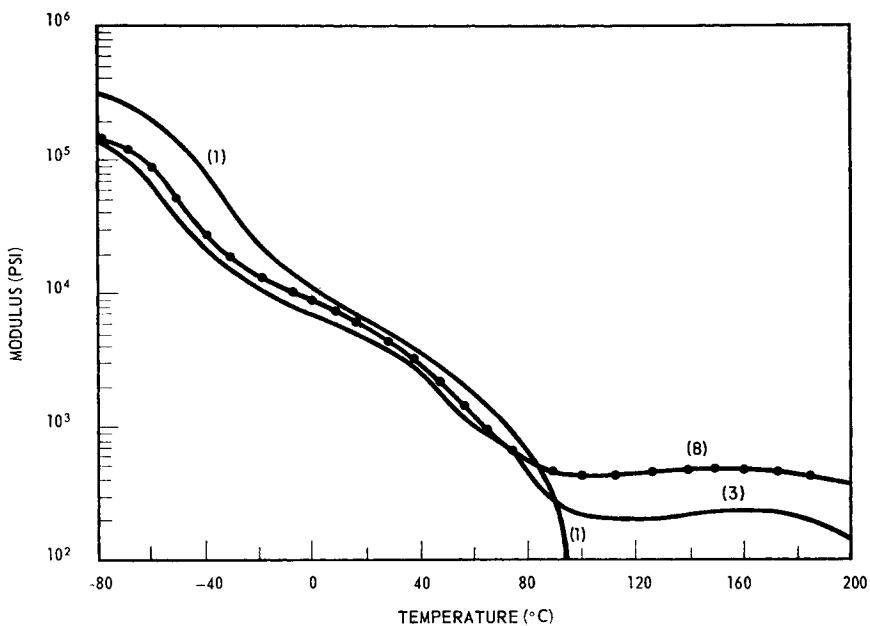


Fig. 9. Modulus vs. temperature for unfilled crosslinked acrylate copolymer DPD-6169: (1) DPD-6169; (3) DPD-6169, 3% dicumyl peroxide; (8) DPD-6169, 3% dicumyl peroxide 10% IV.

### Per Cent Gel

About 0.3 g. of crosslinked material in a 100-mesh screen cage was placed in a flask containing 50 ml. of refluxing ethylbenzene (140°C.) for 16 hr. After air drying for 1/2 hr., the sample was further dried in an air circulating oven at 120°C. for 4 hr. and then allowed to come to room temperature. The per cent gel is the weight of undissolved polymer:

$$\% \text{ gel} = (W_1/W_0) \times 100$$

where  $W_0$  = original weight and  $W_1$  = final weight.

### Crosslinking Density Factor

The crosslinking density factor  $c$  at 160°C. was defined by

$$G = 2cRT$$

or

$$c = G/2RT$$

where  $c$  is in moles per cubic centimeter and  $R = 8.3156 \times 10^7$  ergs/degree mole,  $G$  is in units of dynes/square centimeter (or psi  $\times 6.894 \times 10^6$ ), and  $T = 433.15^\circ\text{K}$ .

### CONCLUSIONS

Crosslinked polyethylene may be envisioned as a rubber network of relatively low crosslinking density which at ambient temperatures is reinforced by polyethylene crystals.

The performance of crosslinked polyethylene at elevated temperatures depends on crosslinking density, while at lower temperatures it is dominated by polyethylene crystalline morphology. This latter factor makes crosslinked polyethylene at ambient temperature a completely different product from vulcanized rubber. It also means that a crosslinked polyethylene will have lower crosslinking density than most rubber compositions of equivalent room temperature stiffness. A good indication of crosslinking density of crystalline polyolefins may be obtained by measuring mechanical properties such as modulus at elevated temperatures.

Crosslinked, partly crystalline ethylene copolymers such as ethylene-ethyl acrylate show the same pattern as found in polyethylene. However, they appear much more rubberlike, due to the lower initial modulus (due to lower crystallinity) and a somewhat higher crosslinking density for equivalent peroxide used.

Use of reactive coagents is effective in raising crosslinking density to the point where fairly good elevated temperature properties are obtained without increasing the room temperature rigidity.

The combination of relatively strong crystalline forces at room temperature and an adequate crosslinked structure at elevated temperatures gives

rise to thermosetting structures that can be shaped to a limited degree at elevated temperatures and set by quenching. These structures when heated above the crystalline melting point, show a strong elastic memory and return to the original crosslinked shape.

Finally, it is probable that most of these observations will apply equally well to any other crosslinked ethylene copolymer having a substantial degree of residual polyethylene crystallinity.

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### Résumé

Des courbes tension-élongation à diverses températures et des courbes du module en fonction de la température ont été utilisées pour l'étude des différences existantes entre le polyéthylène ponté au peroxyde et le caoutchouc vulcanisé. Une série d'hypothèses concernant la densité de pontage et la cristallinité est proposée en vue de visualiser les différences entre le polyéthylène ponté et le caoutchouc traité. Les mêmes techniques ont été utilisées pour étudier la nature de copolymères pontés d'éthylène et acrylate d'éthyle. Ces copolymères, étant beaucoup plus flexibles que le polyéthylène, apparaissent semblables au "caoutchouc mécanique" en particulier après pontage. Des expériences récentes, toutefois, indiquent qu'il existe de profondes différences. Les propriétés du polyéthylène ponté et des copolymères d'éthylène à températures élevées dépendent de la densité de pontage, tandis qu'à températures plus basses elles sont dominées par la morphologie cristalline du polyéthylène. Ce dernier facteur rend à température ambiante le polyéthylène ponté un matériau complètement différent du caoutchouc vulcanisé. Cela signifie également qu'un polyéthylène ponté aura une densité de pontage plus faible que la plupart des caoutchoucs pour une rigidité équivalente déterminée à température de chambre. Une bonne indication de la densité de pontage de



polyoléfines cristallines peut être obtenue en mesurant les propriétés mécaniques ainsi le module à température élevée. L'emploi de coréactifs est efficace pour augmenter la densité de pontage jusqu'au point où les propriétés à température élevée sont bonnes sans toutefois accroître la rigidité à température de chambre.

### Zusammenfassung

Spannungs-Dehnungskurven bei verschiedener Temperatur und Sekantenmodul gegen Temperaturkurven wurden zur Untersuchung des zwischen peroxydvernetztem Polyäthylen und vulkanisiertem Kautschuk vorhandenen Unterschieds verwendet. Eine Reihe von Hypothesen über Vernetzungsdichte und Kristallinität wird zur Veranschaulichung des Unterschieds zwischen vernetztem Polyäthylen und vulkanisiertem Kautschuk herangezogen. Die gleichen Methoden wurden zur Untersuchung der Natur vernetzter Äthylen-Äthylacrylatcopolymerer verwendet. Diese Copolymeren sind biegsamer als Polyäthylen und dem "mechanischen Kautschuk" besonders nach der Vernetzung, ähnlich. Neuere Versuche zeigen jedoch, dass tiefgreifende Unterschiede bestehen. Das Verhalten von vernetztem Polyäthylen und von Äthylencopolymeren hängt bei erhöhter Temperatur von der Vernetzungsdichte ab, während es bei niedrigerer Temperatur durch die Kristallmorphologie des Polyäthylens bestimmt wird. Letzterer Faktor macht vernetztes Polyäthylen bei Raumtemperatur zu einem von vulkanisiertem Kautschuk vollständig verschiedenen Produkt. Er bedeutet weiterhin, dass vernetztes Polyäthylen eine niedrigerer Vernetzungsdichte besitzt als die besten Kautschukmischungen von gleicher Steifigkeit bei Raumtemperatur. Ein gutes Mass für die Vernetzungsdichte von kristallinen Polyolefinen kann durch die Messung mechanischer Eigenschaften, z.B. Modul bei erhöhter Temperatur, erhalten werden. Die Verwendung reaktionsfähiger Hilfsstoffe ist zur Erhöhung der Vernetzungsdichte bis zu dem Punkt wirksam, wo recht gute Eigenschaften bei erhöhter Temperatur ohne Anwachsen der Steifigkeit bei Raumtemperatur erhalten werden.

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