Characterization of Ethylene–Propylene Rubber and Ethylene–Propylene–Diene Rubber Networks*

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Synopsis

The stress–strain (S/S) and the swelling equilibrium behavior in a series of ethylene propylene rubber (EPR) and ethylene propylene diene monomer (EPDM) networks were investigated and the results were employed to evaluate the effects of varying the cure conditions on the crosslinking efficiency in these networks. The S/S curve of completely swollen vulcanizates is in agreement with the predictions of rubber elasticity theory, while that of dry or partially swollen vulcanizates is fully described by the Mooney-Rivlin equation. χ values determined in benzene were found to vary linearly with v_r (v_r = equilibrium volume fraction of rubber in swollen sample). Crosslinking efficiency, moles of crosslinks produced per moles of crosslinking agent used, ranges from 3.7 in peroxide-cured EPDM (55% wt ethylene and 2.6% unsaturation) to 0.15 in similarly cured EPR (43% ethylene). Efficiency in the latter system improves to 0.6 by addition of a coagent (sulfur) to the cure formula. Crosslinking efficiency in EPDM (55% ethylene) was found to increase in the order: peroxide- > resin- > sulfur-cured. In the EPDM sulfur vulcanizates, changing the terpolymer in the cure formula resulted in significant changes in the crosslinking efficiency.

INTRODUCTION

Aside from recently developed vulcanizing agents,[1] peroxides are still the only known commercial means for vulcanizing the saturated ethylene–propylene rubbers (EPR).[2,3,4] Use of peroxides alone, however, results in a low degree of crosslinking in EPR, and several means, such as (1) use of a curing coagent[5,6] (2) modification of the polymer,[7,8] and (3) making of an ethylene–propylene terpolymer[9,10] using a diene monomer pendant to the ethylene–propylene polymer chain, have been devised to improve the peroxide crosslinking efficiency. The third method gives a partially unsaturated ethylene–propylene terpolymer (EPDM) which is easily curable by peroxides as well as by other conventional cure systems.[2,10,11] The crosslinking behavior in EPDM should depend on the degree and type of unsaturation, while the mechanical and elastic properties of the EPDM vulcanizates, as is the case in EPR, should depend on the polymer molecular structure, e.g., molecular weight, molecular weight distribution, ethylene-to-propylene ratios, etc. The purpose of this note is to examine the

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stress–strain (S/S) and the swelling equilibrium behavior in a series of EPR and EPDM vulcanizates and to determine the effects of various cure systems and cure conditions on the crosslinking behavior and crosslinking efficiencies in these vulcanizates.

EXPERIMENTAL

The various EPR and EPDM vulcanizates examined are shown in Tables I and II. The cure agents and coagents employed and their concentrations are shown in the same table. EPR and EPDM vulcanizates were prepared by curing commercial samples of ethylene–propylene copolymer, 43 wt-% ethylene, and EPDM terpolymer, 55 wt-% ethylene and 2.6 wt-% unsaturation.

TABLE I
Composition (phr) of EPR Vulcanizate

EPR[a]	Dicumyl peroxide	Peroxide S-890	Sulfur	Buton-150[b]	SR-206[c]
100	2	—	—	—	—
100	2	—	0.3	—	—
100	—	2	0.3	—	—
100	2	—	—	1	—
100	2	—	—	—	1

[a] Contains 43 wt-% ethylene.
[b] Butadiene polymer.
[c] A diethylene glycol dimethacrylate.

TABLE II
Composition (phr) of EPDM Vulcanizates

EPDM[a]	Dicumyl peroxide	Sulfur	Methyl zimate	Captax	Stearic acid	Resin SP-1055
100	2	0.3	—	—	—	—
100	—	1.5	1.5	0.5	1.0	—
100	—	—	—	—	1.0	12.0

[a] Contains 55 wt-% ethylene.

Cure temperature was maintained at 158°C. The samples were compressed into 0.2-cm thickness sheets. Dumbbell-shaped D specimens were cut from these using a standard 1.5-in. die (ASTM D599–61).

Characterization of networks was made as described earlier[12] from stress–strain measurements through the use of rubber elasticity theory and from swelling equilibrium measurements using the Flory-Rehner equation. Stress–strain measurements were performed first, followed by swelling equilibrium measurements and the determination of the solvent polymer interaction parameter, χ.

RESULTS AND DISCUSSION

Stress–Strain Results

According to the Mooney-Rivlin equation, the stress–strain behavior of dry and swollen networks can be described by the relationship[13,14]

$$\phi = \tfrac{1}{2}fA_0^{-1}v_r^{1/3}(\alpha - \alpha^{-2})^{-1} = C_1 + C_2\alpha^{-1} \tag{1}$$

where C_1 and C_2 are constants. A plot of ϕ versus α^{-1} should give a straight line with an intercept of C_1 and a slope of C_2. The intercept C_1 has been identified with the function

$$C_1 = \tfrac{1}{2}\rho RT(\bar{M}_c)^{-1} = \tfrac{1}{2}\nu kT. \tag{2}$$

In the above equations, f is the force; A_0 is the cross-sectional area of the unstrained sample; T is the absolute temperature; k is the Boltzmann constant; $\alpha = L/L_0$, with L the elongation at $f \neq 0$ and L_0 the initial length of the sample at $f = 0$; ν is the number of elastically active network chains per unit volume; $\bar{M}_c$ is the molecular weight between the crosslinks; v_r is the volume fraction of rubber in the swollen sample; and ρ is the elastomer density.

Typical stress–strain curves obtained for dry and completely swollen EPDM vulcanizates in which ϕ is plotted versus α^{-1} are shown in Figure 1. Similar results with lower C_1 values were obtained from the EPR vulcanizates. The straight line plot with a slope of C_2 and intercept of C_1 is in agreement with the theoretical results, eq. (1), the Mooney-Rivlin equation. Furthermore, all of the experimental results established by this procedure up to $\alpha^{-1} = 0.95$ are seen to fall on this straight line. The slope, C_2, is seen to be zero when the stress–strain measurements are performed in completely swollen vulcanizates, which means that the final term in eq. (1), $C_2\alpha^{-1}$, is zero. Under such conditions of complete network swelling, eq. (1) reduces to

$$C_1(\text{swollen}) = \tfrac{1}{2}fA_0^{-1}v_r^{1/3}(\alpha - \alpha^{-2})^{-1} = \tfrac{1}{2}\nu kT \tag{3}$$

and the stress–strain of completely swollen EPR and EPDM is in accord with the prediction of the simple rubber elasticity theory.[15] This behavior was shown to exist also for the swollen NBR[12] as well as for other systems.[16]
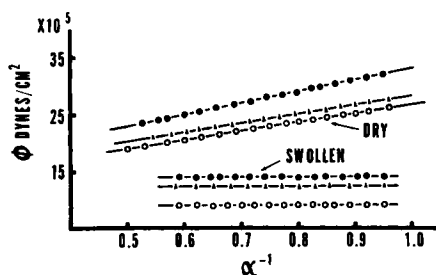

Fig. 1. Stress–strain in EPDM vulcanizates cured with: (▲) peroxide; (O) sulfur; (●) resin (SP-1055).

For the dry EPR and EPDM vulcanizates, the slopes are positive (Fig. 1), and the stress–strain curves in these systems are better described by the Mooney-Rivlin equation. Typical C_2 values obtained from stress–strain in dry EPR and EPDM vulcanizates are shown in Table III. For the EPDM vulcanizates, C_2 is larger than C_2 obtained for EPR networks. The large difference in C_2 between the two systems is perhaps due mainly to the large differences in their crosslink densities. Below a certain crosslink density ($>20 \times 10^{18}$ crosslinks/cc), C_2 appears to be dependent on the crosslink density of the network. This condition was observed in the NBR–peroxide vulcanizates[12] and seems to hold for the present EPR networks where C_2 values are seen to increase as the EPR crosslink density is increased, as shown in Table III. At a crosslink density of $\sim 20 \times 10^{18}$, C_2 for EPR vulcanizates is expected to approach $\sim 16 \times 10^5$ dynes/cm, the C_2 value for peroxide-cured EPDM. The C_2 values obtained for EPDM ($C_2 \simeq 18 \times 10^5$ dynes/cm^2) are much larger than those for natural rubber[16] ($C_2 \simeq 10^5$ dynes/cm^2). Bueche[17] suggested that these abnormally large C_2 values may be due to the large number of chain entanglements which are found in EPDM and EPR elastomers.

TABLE III
C_2 in EPR and EPDM Vulcanizates

Cure system	Cure time, min	Crosslink density, crosslinks/cc $\times 10^{-18}$	C_2, dynes/cm^2 $\times 10^{-5}$
A. Peroxide-Cured EPR			
no coagent	10	5.8	8.7
Buton 150, 1 phr	10	6.5	8.9
SR-206, 1 phr	10	9.2	10.5
sulfur, 0.3 phr	10	11.0	11.9
B. EPDM Vulcanizates			
sulfur-cured	30	22.3	18
resin-cured	30	33.3	20
peroxide-cured	5	31.0	16

Swelling Equilibrium Results

According to the Flory-Rehner[18,19] equation,

$$-\ln (1 - v_r) - v_r - \chi v_r^2 = \rho v_0 \bar{M}_c^{-1} [v_r^{1/3} - (v_r/2)], \qquad (4)$$

$\bar{M}_c$ can be determined from swelling equilibrium measurements if χ for the polymer–solvent system is known. In the present investigation, χ values for EPR– and EPDM–benzene were established using $\bar{M}_c$ determined from stress–strain measurements made on swollen networks, and v_r was obtained from swelling equilibrium measurements; v_r was determined by swelling the sample in benzene for 120 hr and changing the solvent every 24 hr. No change in v_r was noticed on extended swelling of the samples beyond this
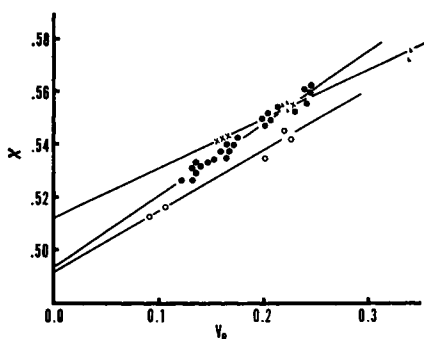
Fig. 2. Plots of χ vs. v_r in benzene for: (●) EPR; (▲) peroxide-cured EPDM; (×) sulfur-cured EPDM; (○) resin-cured EPDM.

period. All v_r values were corrected for the benzene-soluble noncrosslinked polymer which was collected and dried in a vacuum oven at 80°C to a constant weight. χ Values obtained through eq. (4) for the EPR and EPDM vulcanizates are plotted versus v_r in Figure 2. A linear relationship of the form $\chi = \chi_0 + \gamma\, v_r$ is seen to exist between χ and v_r. χ Values determined by this method were as follows: $\chi_{EPR} = 0.493 + 0.26 v_r$; $\chi_{EPDM} = 0.513 + 0.18 v_r$ for peroxide- or sulfur-cured vulcanizates and $0.492 + 0.23 v_r$ for the resin-cured EPDM vulcanizates. Small differences in χ are noticed to arise upon changing the cure conditions, e.g., compare χ for resin (12 phr) and peroxide-cured EPDM, and the polymer composition, e.g., compared χ for peroxide-cured EPR which contains 43 wt-% ethylene and χ for peroxide-cured EPDM which contains 55 wt-% ethylene.

χ Values of $0.493 + 0.26 v_r$ obtained for the present EPR (53 mol-% ethylene) compare with $\chi = 0.48 + 0.29 v_r$ for an EPR examined by Natta.[7] χ Values of $0.513 \pm 0.18 v_r$ for the EPDM (65 mole-% ethylene) are slightly different from $\chi = 0.49 + 0.33 v_r$ reported by Bueche[17] for an EPDM containing 53 mole-% ethylene. The differences may be due to the difference in the ethylene content of the two terpolymers employed.

Effect of Cure Condition on Crosslink Density in EPR and EPDM Vulcanizates

Figure 3 shows the effects of changing the cure time on crosslink density $\nu/2$ for EPR vulcanizates, while Figures 4 and 5 show respectively the changes in v_r and $\nu/2$ with cure time for EPDM vulcanizates. All $\nu/2$ values were obtained from swelling equilibrium measurements through eq. (4) using the χ values shown above. In all cases, $\nu/2$ (and v_r) increases with cure time and also with cure agent or coagent concentration.

Use of a coagent increases crosslink density in peroxide-cured EPR, with maximum crosslink density obtained by the use of 0.3 to 0.6 phr sulfur with dicumyl peroxide or Hercules Peroxide S-890. The use of the latter peroxide with the coagent sulfur minimizes the odor produced from dicumyl peroxide–sulfur-cured EPR networks.

The degree of crosslinking in EPDM vulcanizates is much greater than in similarly treated EPR vulcanizates, and, as shown in Figure 5, it depends largely on the type of crosslinking agent employed. Thus, use of dicumyl peroxide results in highly crosslinked vulcanizates, while the use of the
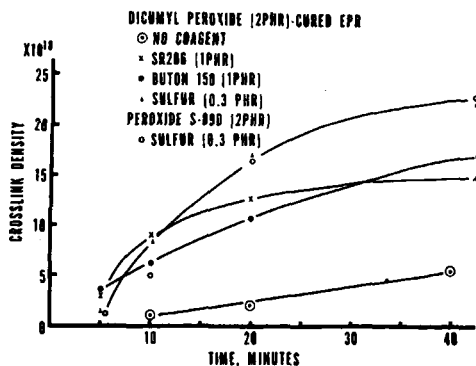

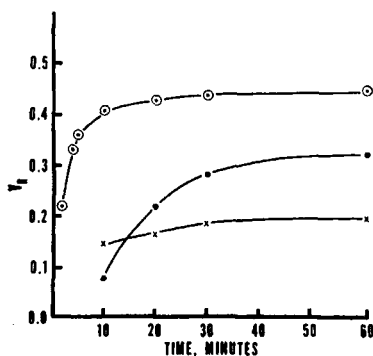Fig. 3. Crosslink density vs. cure time in EPR vulcanizates.

Fig. 4. Plot of v_r vs. cure time in EPDM vulcanizates: (⊙) peroxide-cured; (●) resin-cured; (✕) sulfur-cured.
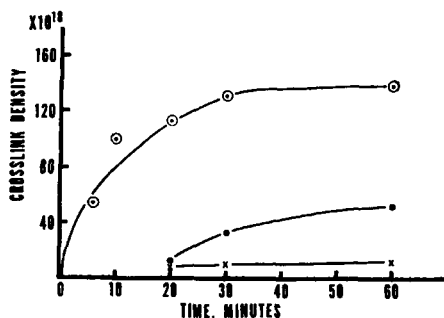

Fig. 5. Crosslink density vs. cure time in EPDM vulcanizates: (⊙) dicumyl peroxide-cured (2 phr); (●) resin (SP-1055)-cured (12 phr); (✕) sulfur (1.5 phr)–methyl zimate (1.5 phr)-cured.

resin or sulfur methyl zimate produces respectively a moderately or lightly crosslinked EPDM vulcanizate.

Crosslinking Efficiency in EPR and EPDM Vulcanizates

The crosslinking efficiency of EPR and EPDM vulcanizates was calculated as per cent (moles of crosslinks produced per gram rubber/mole of crosslinking agent used in the formula per gram rubber). The moles of crosslinks per gram rubber, which is equal to $\nu/2\rho N$, was computed from the measured quantities $\nu/2$ and ρ. Tables IV through VII show moles of crosslinks per gram rubber and per cent crosslinking efficiencies for the various vulcanizates examined. Addition of a coagent to the EPR peroxide-cure formula improved efficiency from 15% without coagent to a maximum of 59% ($\sim$0.6 crosslink/one peroxide molecule) with 0.3 phr sulfur. The addition of diethylene glycol dimethacrylate (SR 206) and the butadiene polymer in which the ratio of 1,2 and 1,4 unsaturation is 3:1 (Buton 1 50) resulted in a similar crosslinking, e.g, the efficiency is $\sim$43%, Table IV. With the exception of the coagent, sulfur cure efficiency also increases with cure coagent concentration, Table V. Sulfur shows maximum efficiency at 0.3 to 0.6 phr. Beyond this level, crosslinking efficiency decreases.

The improvement of cure efficiency with the addition of a coagent to EPR peroxide cures can be explained in terms of the peroxide crosslinking mech-

TABLE IV
Crosslinking Efficiency in Dicumyl Peroxide-Cured EPR[a]

Coagent added	Crosslinks, moles/g rubber	Efficiency, %
None	1.121×10^{-5}	15
SR-206, 1 phr	2.993×10^{-5}	41
Buton-150, 1 phr	3.281×10^{-5}	44
Sulfur, 0.3 phr	4.358×10^{-5}	59

[a] Cure, 40 min; 2 phr dicumyl peroxide.

TABLE V
Crosslinking Efficiency versus Cure-Coagent Concentration in Peroxide-Cured EPR[a]

| Coagent, phr | Crosslinking efficiency with the coagent, % | | |
	SR-206	Buton-150	Sufur
0.0	sol.	sol.	sol.
0.3	—	—	17.8
0.5	19	11	—
0.6	—	—	17.5
1.0	24	16	—
1.2	—	—	10
2.0	27	24	—
5.0	31	35	—

[a] Cure, 10 min; 2 phr peroxide.

anism.[2,5,6] On heating, the peroxide yields free radicals which induce radicals in the EPR chains. These radicals could combine with other radicals introduced similarly along other rubber chains, thus leading to the formation of a carbon–carbon crosslinking bond; or, alternatively, the radical may be neutralized by the removal of a tertiary H from the chain (in the propylene segment), leading to a chain scission. The two reactions are competitive, with the chain scission reaction increasing in magnitude as the propylene content in the EPR polymer is increased. In the presence of a coagent, it is suggested that the coagent reacts with the radical formed on the chain of the elastomer, by a rapid addition, thus forming a radical of intermediate stability. In this way the chain scission reaction is reduced considerably and the crosslinking reaction is thus favored. The results shown in Figure 3 seem to support this conclusion. Replacement of dicumyl peroxide with Hercules Peroxide S-890 in the EPR cure formula containing 0.3 phr sulfur did not change the EPR crosslink density significantly. The stabilization of the radical on the elastomer chain by sulfur rather than the number and the stability of the peroxide radicals produced from the two different peroxides seem to determine the number of crosslinks produced in EPR vulcanizates.

The crosslinking efficiency in peroxide-cured EPDM, 55 wt-% ethylene, increases with cure time, reaching 370% at 60 min and 158°C but seems to decrease with cure agent concentration, as shown in Table VI. The changes in peroxide efficiency during cure are interesting. Further investigation of these systems, possibly using ESR technique, may lead to the understanding of their crosslinking mechanism. These efficiencies, attributed to the higher degree of unsaturation in EPDM (2.6 wt-%, or $\simeq 100 \times 10^{-5}$ mole —C=C—/g rubber), are much higher in EPDM peroxide vulcanizates than those in similarly cured EPR vulcanizates prepared from the saturated ethylene–propylene copolymer, and also higher than those for similarly cured NBR vulcanizates[12] (see Table VII). Peroxide seems to be the most effective crosslinking agent for this EPDM terpolymer. For example, the crosslink densities $\nu/2$ obtained from 60-min EPDM (55 wt-% ethylene and 2.6% unsaturation) vulcanizates are:

TABLE VI
Crosslinking Efficiency in Peroxide-Cured EPDM

Cure time, min	Peroxide, phr	Crosslinks, moles/g rubber	Crosslinking efficiency, %
5	2	10.47×10^{-5}	140
10	2	18.81×10^{-5}	254
20	2	21.80×10^{-5}	290
30	2	25.55×10^{-5}	345
60	2	27.88×10^{-5}	370
10	2	18.81×10^{-5}	254
10	3	26.42×10^{-5}	238
10	4	33.31×10^{-5}	225

TABLE VII
Crosslinking Efficiency in Peroxide-Cured EPR, EPDM, and NBR

Cure system	Cure time, min	Crosslinks, moles/g rubber	Efficiency, %
EPR	40	1.34×10^{-5}	15
EPDM	60	27.58×10^{-5}	370
NBR	60	12.37×10^{-5}	215

143×10^{18} crosslinks/cc (370% efficiency) using dicumyl peroxide, 53×10^{18} crosslinks/cc with the resin as a crosslinking agent; and only 7×10^{18} crosslinks/cc (24% crosslinking efficiency) using the cure agent sulfur–methyl zimate.

Finally, similarly cured EPDM–sulfur vulcanizates of various commercial EPDM terpolymers show significant differences in their crosslinking efficiency. The results which will not be described here indicate that the degree of crosslinking produced in these networks depends on the nature and on the structure of the terpolymer employed in their preparation.

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