

## Polymer-Solvent Interaction Parameters and Efficiency of Crosslinking of Ethylene-Propylene Copolymers

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### Synopsis

A study has been carried out of the vulcanization of ethylene-propylene copolymers having different propylene contents, by use of an organic peroxide. The polymer-solvent interaction parameter  $\mu$ , calculated by the Flory-Rehner equation from values of  $\nu_e$  and  $v_r$ , was found to be a linear function of  $v_r$  with benzene as the swelling agent. Values of  $\mu$  and their dependence upon  $v_r$  were independent of copolymer composition, at least within the limits of experimental error, for samples having a propylene content of 30-60 mole-%. The crosslinking efficiency of the peroxide used was found to depend considerably on copolymer composition, in agreement with the results found for dicumyl peroxide. Finally, sulfur as a crosslinking coagent was found to exert a large effect on the value of  $\nu_e$ , calculated from the equilibrium retractive force of benzene-swollen specimens.

### INTRODUCTION

Different methods exist for the determination of the degree of crosslinking of rubbery materials.

#### Swelling of the Crosslinked Material by Suitable Solvents

Under equilibrium conditions the Flory-Huggins<sup>1a</sup> relationship holds for swollen rubbers:

$$-\left[\ln(1 - v_r) + v_r + \mu v_r^2\right] = \nu_e V_1 (v_r^{1/3} - v_r/2) \quad (1)$$

where  $v_r$  is the volume fraction of polymer in the system,  $\mu$  is the polymer-solvent interaction coefficient,  $\nu_e$  is the number of elastically-active network chains per unit volume (expressed in moles/cm<sup>3</sup>), and  $V_1$  is the solvent molar volume.

$\nu_e$  may be deduced from eq. (1) by simple measurements of the degree of swelling, when the values of  $V_1$  and  $\mu$  are known. These values may be found in the literature, or may be obtained by simple chemical-physical measurements.<sup>2</sup>

#### Measurements of the Tensile Force of Swollen Test Pieces

The tensile force of swollen test pieces is connected with the crosslinking density by:<sup>1b</sup>

$$\sigma = \nu_e RT (\lambda - \lambda^{-2}) \nu_r^{-1/2} \quad (2)$$

where  $\sigma$  is the elastic force per unit cross-section of the unstretched and unswollen test piece,  $R$  is the gas constant,  $T$  is the absolute temperature, and  $\lambda$  is the extension ratio.

From eq. (2), by stress-strain measurements, knowing the degree of swelling, we may directly calculate  $\nu_e$  even when the value of  $\mu$  (which in some cases cannot easily be determined) is not known.

#### Determination of $c_1$

Determination of the  $C_1$  constant of the Mooney-Rivlin equation:<sup>3</sup>

$$\sigma/(\lambda - \lambda^{-2}) = 2[C_1 + (C_2/\lambda)] \quad (3)$$

where  $2C_1 = \nu_e RT$  and  $C_2$  is a constant, the physical meaning of which is not yet known, is a more rapid method than the second and does not require measurements of the degree of swelling.

When the value of  $\nu_e$  is known, we can calculate the number  $\nu$  of total chains per network unit volume, by the relationship:<sup>1b</sup>

$$\nu_e = \nu[1 - (KM_c/\bar{M}_n)] \quad (4)$$

where  $M_c$  is the average molecular weight of network chains,  $\bar{M}_n$  is the average molecular weight of the polymer before crosslinking, and  $K$  is a constant,<sup>4</sup> the value of which is about 2. By substituting in eq. (4) for  $M_c (= \rho/\nu)$  we obtain:

$$\nu = \nu_e + 2\rho/\bar{M}_n \quad (5)$$

where  $\rho$  is the specific gravity of the material.

If  $\nu$  is known, the crosslinking efficiency of the vulcanizing system may be checked by comparison with the theoretical number of crosslinks introduced into the polymer by the vulcanizing agent.

It is known that the crosslinking efficiency of organic peroxides in ethylene-propylene copolymers depends considerably on the composition of the copolymer. For example, the efficiency of dicumyl peroxide was found<sup>5</sup> to vary from 70% in samples containing 25 mole-% of propylene, to less than 10%, when the propylene content reaches 90%. In this paper we examine the crosslinking efficiency of  $\alpha, \alpha'$ -di(*tert*-butylperoxy)diisopropylbenzene,<sup>6</sup> in the vulcanization of ethylene-propylene copolymers having different compositions.

## EXPERIMENTAL

### Materials

All copolymers were prepared by us by copolymerization of ethylene and propylene in different weight ratios. The composition was determined on each sample by infrared spectroscopy. The range of compositions studied varied from 32 to 62 mole-% of propylene.

TABLE I  
Properties of Ethylene-Propylene Copolymers of Different Compositions

Sample no.	Propylene content, mole-%	Intrinsic viscosity (in tetralin at 135°C)	Viscometric molecular weight $\times 10^{-3}$
1	27.0	2.92	200
2	31.5	3.80	303
3	38.0	2.65	226
4	45.5	3.27	290
5	48.5	2.70	230
6	50.0	2.58	216
7	50.5	3.12	275
8	53.0	2.48	212
9	58.5	2.34	210
10	62.0	1.73	143
11	64.5	1.30	100
12	66.3	1.69	145

Table I shows the compositions of the samples and the values of intrinsic viscosity in tetralin at 135°C; as may be seen, the propylene-richer samples exhibit lower viscosities. The samples having a propylene content of 60 mole-% or more also yielded very poor vulcanizates full of bubbles. The measurements of the degrees of swelling and of crosslinking of these samples were therefore very imprecise.

### Vulcanization of the Copolymers

Copolymers were crosslinked by two different vulcanization methods: one involved the use of organic peroxide only, the other a mixture of peroxide and sulfur in equimolecular ratios. The peroxide used in all runs was  $\alpha, \alpha'$ -di(*tert*-butylperoxy)diisopropylbenzene<sup>6</sup> with activated calcium carbonate, in the ratio of 1.5 part of carbonate per part of peroxide.

All mixtures were vulcanized under pressure in a parallel-plate metal mold at 165°C for 40 min.

### Determination of the Degrees of Swelling and of Crosslinking

The degree of swelling  $q_m = (v_1 + v_2)/v_2$  was determined as follows. The copolymer samples, previously weighed, were allowed to swell in benzene at 25°C until swelling equilibrium was reached, after which the test pieces were dried on the surface and rapidly weighed into stoppered bottles.

The samples were then dried in a vacuum oven at about 40–45°C to constant weight. The weight difference between the swollen and dry test piece gave the weight of the solvent, the value of which divided by the density gave  $v_1$ . In the same way,  $v_2$  was obtained from the weight and density of the dry test piece.

The swelling degree was also obtained from the ratio of the lengths

$l_{sw}$ ,  $l_0$  of the swollen and dry test pieces. In fact, if swelling is assumed to be isotropic, we may put:

$$v_{sw}/v_0 = (l_{sw}/l_0)^3$$

and as  $v_{sw} = v_1 + v_2$ , it follows that  $q_m = (l_{sw}/l_0)^3$ .

The degree of crosslinking was determined from eq. (2) by using the equilibrium tension in test pieces swollen in benzene, measured by a technique described elsewhere.<sup>7</sup> After measuring the equilibrium stress of these test pieces, we determined their degree of swelling, which was checked with that measured on other samples.

In general  $q_m$ , measured on stretched test pieces, was equal to the value obtained from unstretched test pieces. As the measurements were performed at rather low values of  $\lambda$ , in the range between 1.1 and 1.6, stretching probably did not exert a considerable effect on the swelling.

## RESULTS AND DISCUSSION

### Relationship between the Degrees of Swelling and of Crosslinking

The values of  $q_m$  and  $\nu_e$  obtained for two copolymers having different compositions are given in Tables II and III and in Figure 1.

It seems from Figure 1 that the same relationship holds between  $q_m$  and  $\nu_e$ , at least within the limits of error, for the two copolymers. Also, the curve of Figure 1 was found to be almost coincident with an analogous curve, obtained for a copolymer<sup>7</sup> having a composition intermediate be-

TABLE II  
Crosslinking Density and Degree of Swelling of an Ethylene-  
Propylene Copolymer Having a Propylene Content of 53 mole-%

$\nu_r$	$q_m$	$\nu_e \times 10^{-4}$ , mole/cm <sup>3</sup>
0.156	6.41	0.21
0.161	6.21	0.21
0.166	6.02	0.21
0.157	6.35	0.22
0.165	6.07	0.22
0.196	5.10	0.39
0.198	5.06	0.40
0.202	4.96	0.41
0.208	4.82	0.42
0.227	4.40	0.55
0.232	4.30	0.56
0.232	4.31	0.57
0.227	4.40	0.57
0.230	4.34	0.59
0.233	4.29	0.59
0.228	4.38	0.61
0.270	3.71	0.99
0.270	3.71	1.01
0.272	3.68	1.02

TABLE III  
 Crosslinking Density and Degree of Swelling of an Ethylene-  
 Propylene Copolymer Having a Propylene Content of 27 mole-%

$v_r$	$q_m$	$\nu_e \times 10^{-4}$ , mole/cm <sup>3</sup>
0.157	6.37	0.19
0.158	6.35	0.21
0.161	6.22	0.21
0.180	5.57	0.27
0.168	6.22	0.28
0.178	5.63	0.30
0.327	3.06	1.74
0.325	3.08	1.76
0.318	3.14	1.78
0.328	3.05	1.85
0.350	2.82	1.96
0.353	2.83	2.04
0.338	2.96	2.10
0.342	2.92	2.16
0.341	2.93	2.18

tween those considered here. This leads us to suppose that the relationship between degree of swelling and of crosslinking is independent of composition, at least in the range of compositions considered here. Since this relationship depends on the polymer-solvent interaction coefficient, the latter was calculated for all the samples examined.

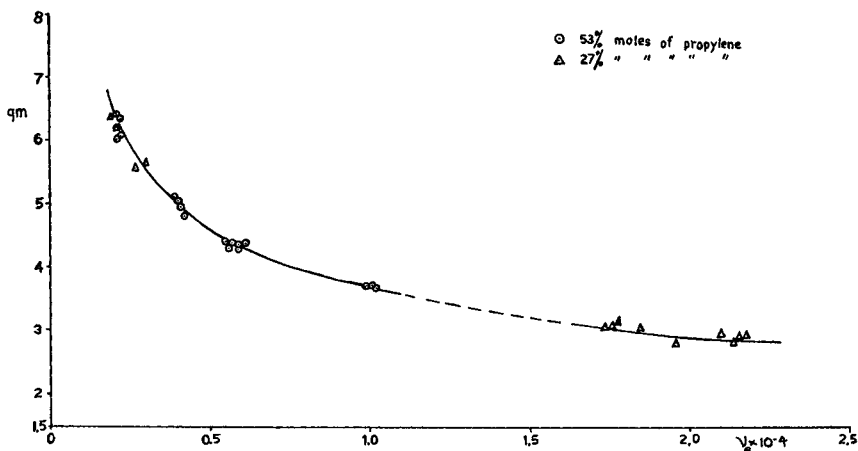


Fig. 1. Equilibrium degree of swelling in benzene vs. crosslink density of two ethylene-propylene copolymers with different composition.

### Polymer-Solvent Interaction Parameter

The parameter  $\mu$  was calculated from the values of  $\nu_e$  and  $v_r$  by using eq. (1). It was found that  $\mu$  depends on  $v_r$  according to a linear relationship expressed by the equation:

$$\mu = \mu_0 + \beta v_r \quad (6)$$

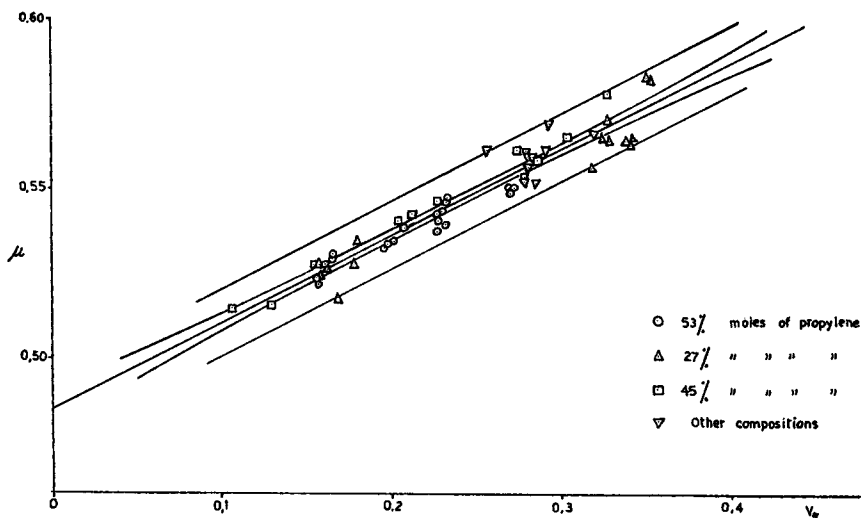


Fig. 2. Relationship between  $\mu$  and  $v_r$  for copolymers having different compositions.  $\mu = \mu_0 + \beta v_r$ , with  $\mu_0 = 0.485 \pm 0.005$  and  $\beta = 0.256 = 0.010$ .

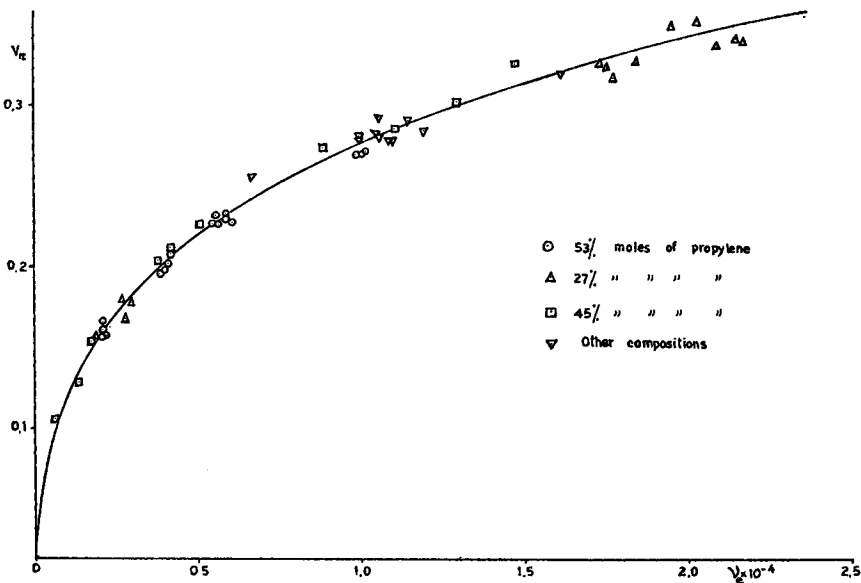


Fig. 3. Relationship between  $v_r$  and  $v_e$  drawn from the relationship of Fig. 2, by eq. (1).

The coefficients  $\mu_0$  and  $\beta$  of eq. (6) were found to be  $\mu_0 = 0.484 \pm 0.012$  and  $\beta = 0.253 \pm 0.042$  for the sample containing 27 mole-% of propylene, and  $\mu_0 = 0.491 \pm 0.008$  and  $\beta = 0.223 \pm 0.035$  for the sample containing 53 mole-% of propylene. Fairly similar values were also obtained for a copolymer with a propylene content of 45 mole-%<sup>7</sup> and for a terpolymer containing 47 mole-% of propylene.<sup>8</sup>

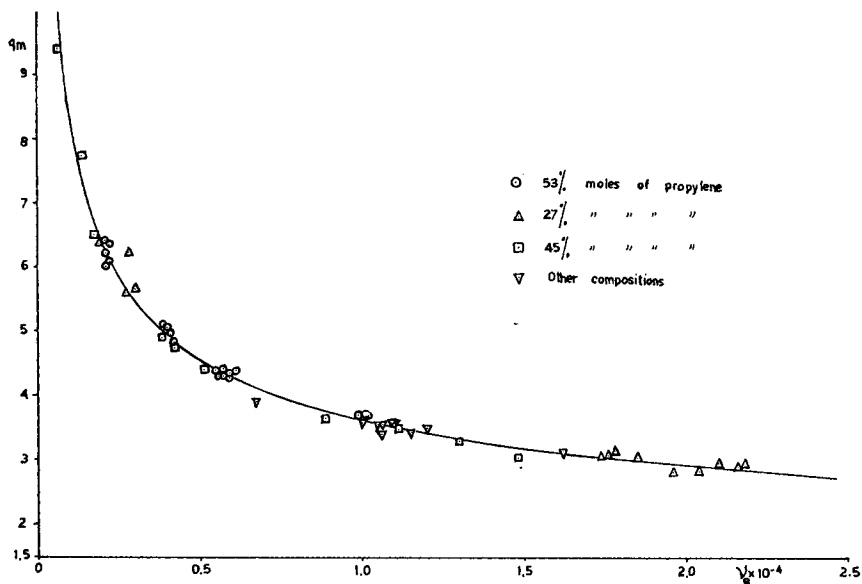


Fig. 4. Relationship between  $q_m$  and  $v_e$  drawn from the relationship of Fig. 2, by eq. (1).

Since propylene-rich samples yield values of  $\mu_0$  identical with, and values of  $\beta$  very similar to, those of the samples considered above, we conclude that the experimental errors are higher than possible differences due to the different composition of the samples.

In order to establish whether the composition of the copolymer affects the relationship between degree of swelling, and degree of crosslinking or not, it would be necessary to perform a more accurate study based on a much larger number of measurements. On the basis of the results obtained, all the values found for  $\mu$  were considered as belonging to the same relationship, represented in Figure 2.

In this relationship, the coefficients  $\mu_0$  and  $\beta$ , calculated by the least-squares method with 95% confidence limits are  $\mu_0 = 0.485 \pm 0.005$  and  $\beta = 0.256 \pm 0.010$ . In Figure 2 the two symmetrical curves close to the central straight line represent the 95% confidence limits, whereas the two external curves represent the same limits for the single values.

The value  $\mu_0 = 0.48$  agrees perfectly with the values 0.48 and 0.49 found by other authors,<sup>7,8</sup> whereas for  $\beta$  the agreement is not so good, in that the value of 0.25 found by us is considerably lower than those of 0.29 and 0.33 found by the quoted authors.<sup>7,8</sup>

These values of the interaction coefficient  $\mu$  differ from those for the polyethylene and polypropylene homopolymers. Two different values (0.27 at 94°C<sup>9</sup> and 0.42 at 80°C<sup>10</sup>) were found for the polyethylene-benzene system, and for polypropylene the value of 0.497 at 25°C was found.<sup>11</sup> However, a comparison between these results and those obtained by us is not very appropriate, due to the different operating conditions.

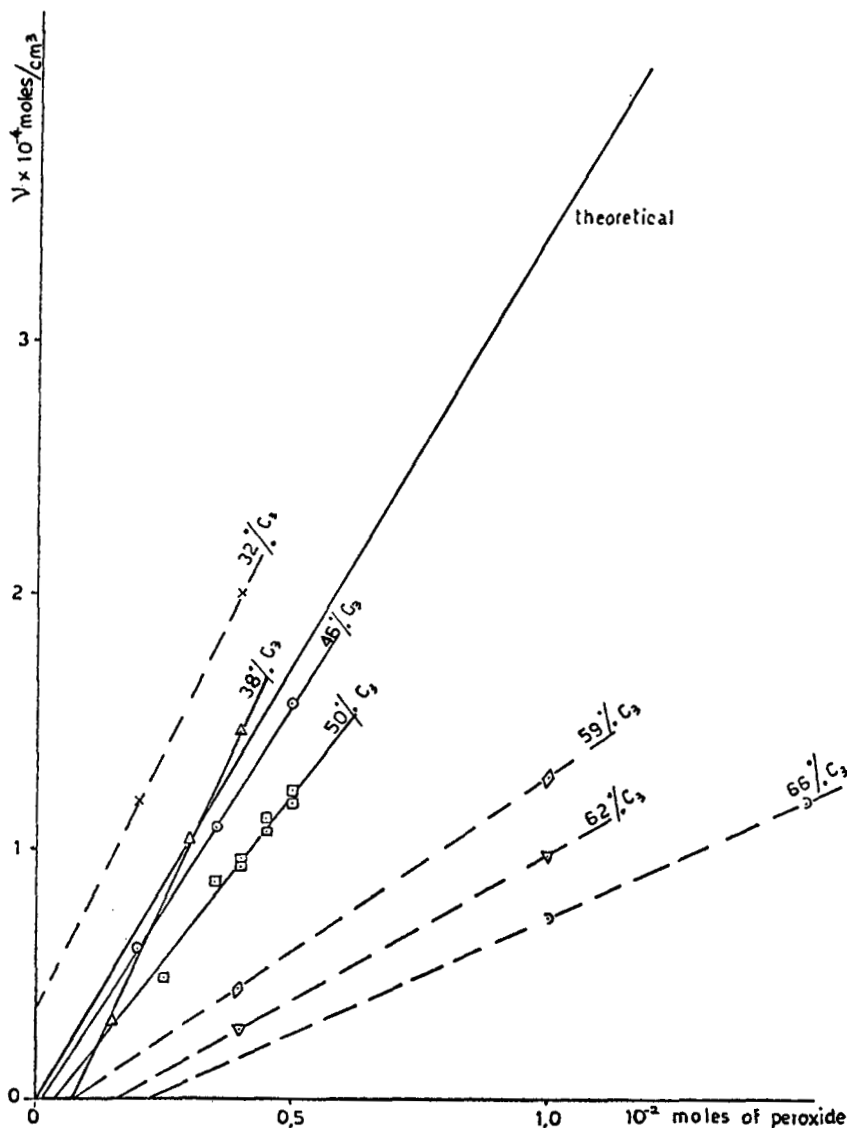


Fig. 5. Degree of crosslinking  $\nu$  vs. the amount of peroxide used. Theoretical straight line and experimental values.

Relationships similar to eq. (6) were obtained by Gent and Vickroy<sup>12</sup> for polyethylene swollen in different solvents at high temperatures; also in this case, however, the data cannot be compared with ours, the solvent and temperature conditions being different.

From the relation shown in Figure 2 we calculated relationships between  $\nu_r$  and  $\nu_e$ , and between  $q_m$  and  $\nu_e$ , which are plotted in Figures 3 and 4, respectively. These relationships enable us to determine the crosslinking



density from the degree of swelling for copolymers having compositions ranging from 30 to 60 mole-% of propylene.

### Crosslinking Efficiency of Peroxide

Some copolymer samples were vulcanized with different amounts of  $\alpha, \alpha'$ -di(*tert*-butylperoxy)diisopropylbenzene. The degree of crosslinking was measured on the vulcanizates thus obtained and the results are shown in Figure 5. The theoretical line of Figure 5 was calculated by assuming that each molecule of peroxide gives two crosslinks, that is, four network chains.

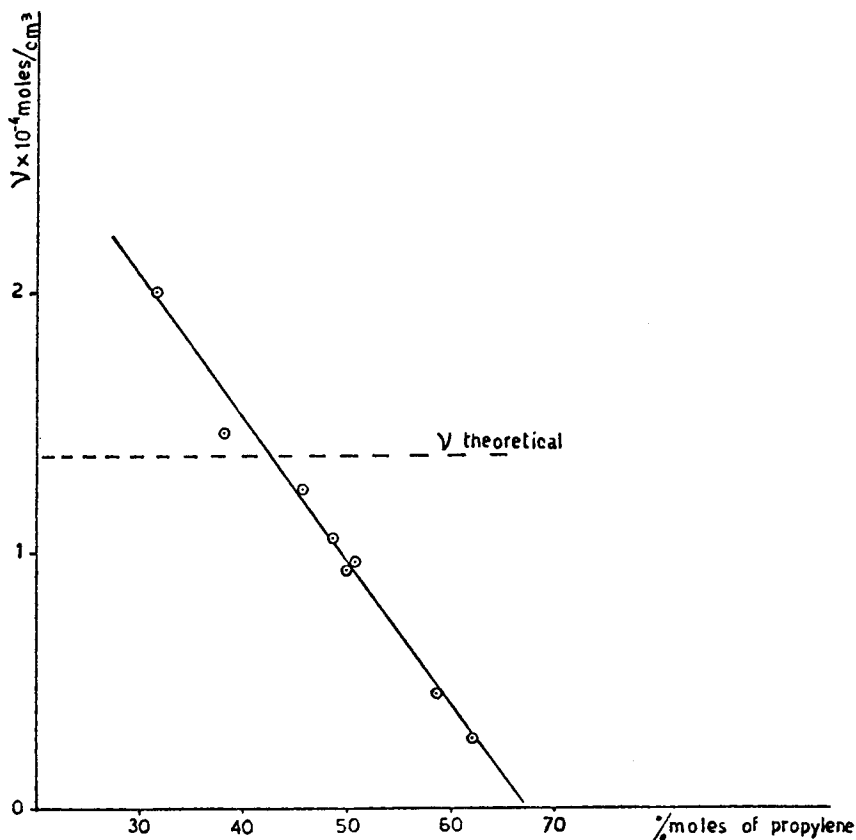


Fig. 6. Dependence of  $\nu$  on the composition for crosslinked samples with the same amount of peroxide: 0.4 centimole/100 g rubber.

As may be seen in Figure 5, the crosslinking efficiency of the peroxide used is close to the theoretical value in ethylene-rich samples, whereas it is considerably reduced with increasing propylene content. The dependence of crosslinking efficiency on composition is shown in Figure 6, where values of  $\nu$ , all obtained with the same amount of peroxide, i.e., 0.4 centimole per

100 g of rubber, are plotted versus the percentage of propylene in the samples.

An analogous decrease in crosslinking efficiency with composition was previously found by other authors;<sup>5</sup> however, our data do not agree well with theirs. The authors quoted find, for a sample containing 33 mole-% of propylene, a yield of 65%, whereas the efficiency found by us for an analogous sample was about 100%. This considerably higher value is probably due to the method used for the calculation of  $\nu$ ; our method of measuring equilibrium moduli of swollen test pieces may give values of  $\nu$  in excess, especially in highly crosslinked samples.

The range of compositions studied by us has been limited by the requirement of an amorphous copolymer easily vulcanizable with peroxides.

### Effect of Sulfur as Vulcanization Coagent

Different samples of copolymers were vulcanized with a mixture of peroxide and sulfur in equivalent amounts. One mole of peroxide is considered equivalent to two moles of sulfur, as it contains two peroxidic groups. The degree of crosslinking measured on the vulcanizates thus obtained was compared with that of the samples crosslinked with peroxide alone in equivalent amount. The results reported in Table IV show that, when half the amount of peroxide is replaced by an equivalent amount of sulfur, the value of  $\nu_0$  is considerably increased.

In previous papers<sup>5,13,14</sup> it was reported that the use of sulfur as coagent in crosslinking with dicumyl peroxide causes a negligible increase in the degree of crosslinking of unfilled vulcanizates, although the tensile strength was considerably increased.

TABLE IV  
Effect of Sulfur on the Crosslinking Efficiency of Peroxide

Sample no.	Propylene content, mole-%	Peroxide, centimole/100 g rubber	Sulfur, centimole/100 g rubber	$\nu_0 \times 10^{-4}$ , mole/cm <sup>3</sup>
2	31.5	0.20		1.14
"	"	0.10	0.20	1.28
3	38.0	0.30		0.95
"	"	0.15	0.30	1.19
4	45.5	0.50		1.52
"	"	0.25	0.50	1.75
"	"	0.35		1.05
"	"	0.15	0.30	1.10
5	48.5	0.35		0.87
"	"	0.15	0.30	1.13
6	50.0	0.35		0.79
"	"	0.15	0.30	0.92
7	50.5	0.40		0.91
"	"	0.15	0.30	1.16
9	58.5	1.00		1.21
"	"	0.50	1.00	1.60

## CONCLUSIONS

As shown in this work, when the degree of crosslinking is determined by measuring the equilibrium swelling of vulcanizates, the experimental values are very uncertain, especially in highly crosslinked samples. Such an uncertainty did not allow us to establish whether the polymer-solvent interaction coefficient for ethylene-propylene copolymers and benzene depends on the copolymer composition in the range of compositions studied or not. From the experimental values, a unique relationship between  $q_m$  and  $\nu_c$  was calculated, comprising all values in the range of composition studied.

From the values of the degree of crosslinking obtained by this general relationship, we determined the crosslinking efficiency as a function of composition (see Fig. 6). The efficiency of  $\alpha, \alpha'$ -di(*tert*-butylperoxy)-diisopropylbenzene is high in ethylene-rich samples and shows a dependence on the copolymer composition similar to that of dicumyl peroxide.<sup>5</sup>

In Figure 6 the horizontal dashed line represents the  $\nu$  calculated theoretically by assuming that each peroxidic group gives one crosslink. The very high value of  $\nu$  for the sample richest in ethylene may be due to the contribution of entanglements, which in the measurements performed by us act as real crosslinks.<sup>3</sup>

With regard to the effect of sulfur on the crosslinking efficiency of organic peroxide, it was found that sulfur, in equimolecular ratio with the peroxidic group, generally causes an increase in the crosslinking density of the vulcanizate by more than 100%.

This result is unexpected, since Loan<sup>14</sup> found that sulfur, in almost equimolecular amounts with dicumyl peroxide, has only a very slight effect upon the crosslink density of gum vulcanizates.

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