BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 2597—2603 (1967)

Dependence of the Crosslinking Efficiency on the Reaction Conditions in the Peroxide Crosslinking of Unsaturated Polyolefins

Nobuyuki Ashikari, Izumi Kawashima and Takehisa Kawashima

The Electrical Communication Laboratory, Nippon Telegraph and Telephone Public Corporation,
Musashino-shi, Tokyo

(Received April 10, 1967)

The crosslinking reactions of several unsaturated polyolefins with organic peroxides were carried out in an attempt to establish the dependence of the crosslinking efficiency on the reaction conditions, especially the reaction temperature and the peroxide concentration. Usually, the efficiency gradually increased up to a certain temperature and then decreased abruptly. This efficiency decrease can be considered to be due to (1) a decrease in the hydrogen abstraction, which is one reaction producing crosslinks, and (2) an increase in the termination rate in a chain reaction arising from opening up the double bond, which is another reaction producing crosslinks. Except for cases in which an extremely high temperature was employed or when a very high concentration of peroxide was used, the efficiency decrease by scission reaction upon an elevation of the temperature seems to be comparatively small.

The final objective of this study is to ascertain reaction conditions which make the reaction rate high without decreasing the crosslinking efficiency. Of course, the reaction rate becomes high when the reaction temperature is elevated or when the concentration of the crosslinking agent is increased. However, the crosslinking efficiency does not always increase upon the above procedures. In order to clarify this situation, the dependency of the crosslinking efficiency upon the reaction conditions should be investigated. Thus, this paper will report a study concerning the efficiency in crosslinking of several unsaturated polyolefins with various kinds of organic peroxide at various temperatures, including a rather high temperature.

In order to determine the exact efficiency, the chemical crosslink density should be isolated. For this purpose, several investigators[1-4] have proposed appropriate methods of separating the chemical crosslink density from the physically-determined crosslink density. Thus, the chemical crosslink density can be obtained by applying a suitable correction to the physically-determined crosslink density. However, when the crosslink density has a first-order dependency on the peroxide concentration, a very simplified technique can be applied to the determination of the efficiency,[2]

Since the present study has been undertaken to ascertain the variation in the efficiency when the reaction conditions are changed, the absolute value of the efficiency is not always necessary. Accordingly, in this paper, the apparent efficiency, as calculated from the physically-determined crosslink density, is used as a relative value when the first-order dependency is absent.

Experimental

Material. The polymers used were styrene-butadiene rubber (SBR), polybutadiene (PBd), and the ethylene-propylene terpolymer (EPT); their properties are shown in Table 1. SBR is a commercial substance, and EPT and PBd were prepared with a Ziegler catalyst and an organosodium catalyst respectively. These polymers were purified by reprecipitation.

TABLE 1. POLYMERS USED FOR CROSSLINKING REACTION

Polymer	Composition and microstructure	Molecular weight
SBR	St; 23.5 wt%	$\overline{M}_n$ 6.1×10^4 at 110°C, in tetralin
EPT	Et, 73.1; Pr, 25.3; dicyclopetadiene, 1.6 mol%	$[\eta]=1.10$ at 30°C, toluene
PBd	1.2-content;*3 more than 95%	$\overline{M}_v=3\times10^4$ in benzene, at 25°C*1 $\overline{M}_n=2.9\times10^5$ in tetralin, at 110°C*2

*1 Low molecular weight sample, which was prepared with organosodium catalyst.
*2 High molecular weight sample. Other catalyst than organosodium was used for preparing the polymer.
*3 Estimated by IR measurement.

Peroxides such as dicumyl peroxide (DCP) and dibenzoyl peroxide (BPO) were purified by recrystallization from methanol. The other peroxides, di-*t*-butyl

---

[1] For example, B. M. E. Van der Hoff, *I & EC Product Research and Development*, **2**, 273 (1963).
[2] L. D. Loan, *J. Polymer Sci.*, **7**, 2259 (1963).
[3] W. J. Bobear, *I & EC Product Research and Development*, **3**, No. 4, 277 (1964).
[4] L. Millins, *J. Appl. Polymer Sci.*, **2**, 1 (1959)

peroxide (DTBP) and di-butyl perbenzoate (DBPB) were used without any purification. Solvents such as benzene and *n*-heptane were purified by distillation after having been dried with sodium.

Crosslinking Reaction and Estimation of Crosslink Density. The polymer and the peroxide were mixed by either of two methods; one was the usual roll-mill method, and the other was the freeze-drying method. In the latter case, the two components (polymer and peroxide) were dissolved in benzene, and then dried under a frozen state. The crosslinking reaction was carried out by means of a press-cure or by a sealed-tube system. In the latter case, the compound was pressed at a comparatively low temperature for a short time (usually 140°C for 1 min) and then put in a nitrogen-replaced glass tube, which was set in an oil bath after having been sealed.

The cured sample, 10×25×1 mm or 20×50×1 mm, was immersed in the solvent for 3 days at 25°C, and the swelling value was measured. In this case, the weight of the absorbed solvent was obtained as the difference between the weight of the swollen and the dried samples. Drying was carried out at room temperature for about 30 hr under reduced pressure. Benzene was used as the solvent for SBR and PBd vulcanizates, and *n*-heptane, for EPT vulcanizate. From the swelling results, the crosslink density was calculated using the following equation⁵⁾:

$$[\nu] = -[\ln(1-v_2) + v_2 + \mu v_2^2]/2\rho V_1(v_2^{1/3} - v_2/2) \tag{1}$$

where μ: polymer-solvent interaction parameter, v_2: volume fraction of the polymer in the swollen gel, V_1: molar volume of the solvent, and ρ: density of the polymer vulcanizate. In the case of SBR vulcanizate, the literature values of μ⁶⁾ which are given by Eq. (2)⁷⁾ were used:

$$\mu = \mu_0 + \beta v_2 \tag{2}$$

$$\mu_0 = 0.33, \qquad \beta = 0.24$$

For PBd and EPT vulcanizates the values of 0.39¹⁾ and 0.44⁸⁾ were used respectively.

When the absolute value of the crosslink density was not necessary, the relative value represented by $(1/Q)^2$ was used; this had been introduced into natural rubber vulcanizate by Lorenz.⁹⁾ A linear relationship was observed between the crosslink density and $(1/Q)^2$ for SBR and EPT vulcanizates in the region of a comparatively low crosslink density. However, for PBd, a linear relationship was not obtained. These relationships are represented in Fig. 1. From Fig. 1, Eqs. 3 and 4 were obtained:

$$\text{for EPT, } [\nu]\times 10^4 = 0.15 + 3.83\ (1/Q)^2 \tag{3}$$

$$\text{for SBR, } [\nu]\times 10^4 = 0.75 + 7.30\ (1/Q)^2 \tag{4}$$

IR Measurement of the Decomposition Product of DCP. A sample cured with DCP in a sealed tube was immersed in chloroform for 2 days at room temperature. The polymer was then filtered off, and the filtrate was concentrated. A few drops of the concentrated solution were placed on a KBr plate. After the residual solvent had been vaporized, another KBr plate was placed on the first one and the IR measurement of the sample was performed. The ratio of acetophenone (CO) to cumyl alcohol (OH) was estimated using the calibration curve which had been prepared. In this case, the absorption bands around 1700 and 3500 cm⁻¹ were used for acetophenone and cumyl alcohol respectively.

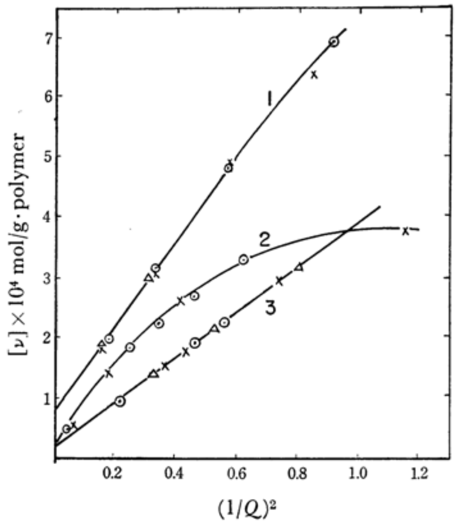

Fig. 1. Relation between $[\nu]$ and $(1/Q)^2$.

No. 1 SBR-TBPB system
⊙ 1PHR, × 2PHR, △ 3PHR (parts of peroxide per 100 parts by weight of polymer)
Temp. 150°C, Time 60 min
No. 2 PBd-DCP system
In this case, ordinate; $[\nu]\times 10^3$, not but $[\nu]\times 10$
⊙ 140°C (120—220 min)
× 150°C (10—160 min); [DCP], 0.4PHR
No. 3 EPT-DTBP system
DTBP; 2, 3, 4PHR
⊙ 150°C △ 160°C × 170°C

Results

Preliminary Test as to the Cure Time. SBR was cured with DCP in an attempt to find the appropriate cure time. The results are shown in Fig. 2. Since the half-lives of DCP are about 40, 17, 6, 2.3 and 1 min at temperatures of 150, 160, 170 and 180°C, respectively,¹⁰⁾ one can see that the optimum cure is obtained at any temperature within ten times the half-life of the peroxide. The optimum cure time changes, of course, according to the sort of polymer-peroxide system. However, in the following experiments, about ten times the

---

5) P. J. Flory and J. Rehner, Jr., *J. Chem. Phys.*, **11**, 512 (1943); P. J. Flory, *ibid.*, **18**, 108 (1950).

6) T. J. Dudek, *J. Appl. Polymer Sci.*, **8**, 555 (1964).

7) G. Kraus, *Rubber World*, **135**, 67 254 (1956).

8) T. J. Dudek and F. Bueche, *J. Polymer Sci., Part A*, **2**, 811 (1964).

9) O. Lorenz and C. R. Parks, *J. Polymer Sci.*, **50**, 299 (1961).

10) E. M. Dannenberg, M. E. Jordan and H. M. Cole, *ibid.*, **31**, 127 (1958); M. S. Kharasch, A. Fono and W. Nudenberg, *J. Org. Chem.*, **16**, 105 (1951).

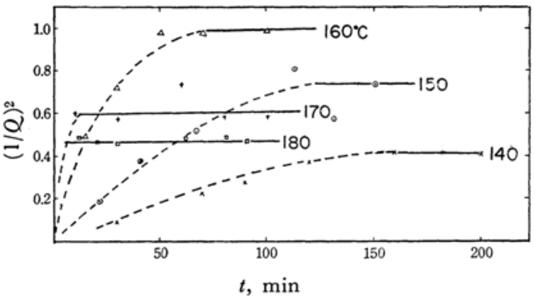

Fig. 2. Rate and state of cure at various temperatures.
System: SBR-DCP (2PHR)

half-life of the peroxide was used as the standard time, referring to the results of the preliminary test.

Dependency of the Crosslink Density on the Reaction Temperature. As is clear from Fig. 2, the crosslink density of the optimum cure state increased with an increase in the temperature (from 140°C to 160°C), while it decreased beyond 160°C. In this system, 160°C is the highest temperature that gives the highest crosslinking efficiency. The same phenomena have often been observed in other systems also. In this paper, the highest temperature giving the highest crosslinking efficiency is called HET, meaning the temperature of the highest efficiency. The HET changes according to the sort of polymer-peroxide system, while it does not change even if the peroxide concentration changes under any given polymer-peroxide system. The efficiency decrease can be seen from Figs. 3—5, in which the EPT-DCP, SBR-TBPIP, and SBR-DCP systems are represented respectively. Here, TBPIP denotes *t*-butylperoxy-isopropylate.

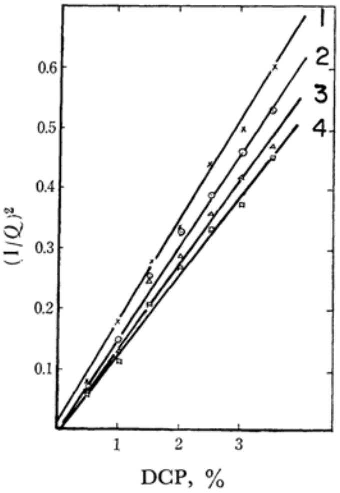

Fig. 3. Relation between $(1/Q)^2$ and the peroxide concentration in EPT-DCP system.
1 150°C 2 160°C 3 170°C 4 180°C

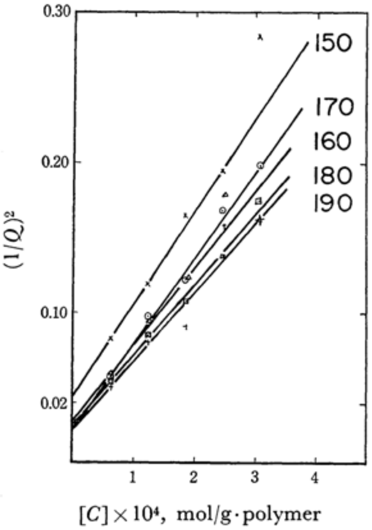

Fig. 4. Relation between $(1/Q)^2$ and the peroxide concentration in SBR-TBPIP system.
—×— 150°C —△— 160°C —⊙— 170°C
—⊡— 180°C —+— 190°C

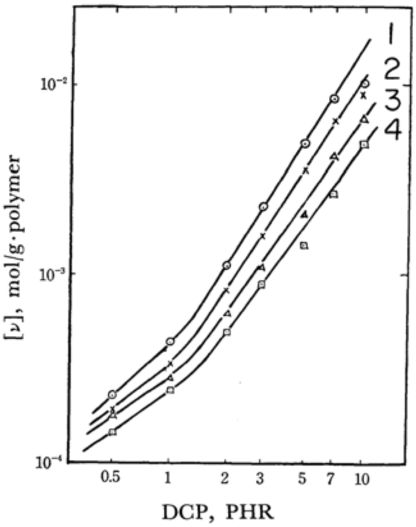

Fig. 5. Relation between crosslink density and the peroxide concentration for SBR-DCP system.
1 160°C 2 170°C 3 180°C 4 190°C

Crosslinking Efficiency. In order to determine the efficiency, the relations between the crosslink density and the peroxide concentration were obtained for various combinations of polymer and peroxide. The crosslink density often had a first-order dependence with respect to the peroxide concentration, as may be seen in Figs. 3 and 4. In these cases, the slopes of the lines show the crosslinking efficiencies.

Figure 5 shows a different type of relationship between the crosslink density and the peroxide concentration. In this case, linear lines were obtained by log-log plots.

Therefore, the linear portions of the lines at comparatively high peroxide concentrations can be written as Eq. (5). Here, $[C]$ is the concentration of peroxide.

$$[\nu] = a[C]^{\alpha} \tag{5}$$

So long as the α value is unity, the efficiency does not change even if the peroxide concentration changes. However, if the α value is not unity, the efficiency changes according to the change in the peroxide concentration. Therefore, in such a case, the efficiency comparison should be made at a certain peroxide concentration. In this case, the crosslink density at the peroxide concentration of 1×10^{-4} mol/g·polymer was used as the value of efficiency. This peroxide concentration corresponds to about 3 wt% when DCP is used. In the region of low peroxide concentrations, there are cases where the α value is unity, as has been reported by another investigator.2)

The crosslinking efficiency changes, then, according to the change in temperature. Therefore, the efficiency comparison should be performed at the HET. Table 2 shows the efficiencies of various polymer-peroxide systems. The lowest temperature in the same series of a given polymer-peroxide system in Table 2 shows the HET.

TABLE 2. CROSSLINKING EFFICIENCIES OF VARIOUS POLYMER-PEROXIDE SYSTEMS

Polymer	Peroxide	T, °C	Eff. (α)
SBR	DCP	160	19.5 (1.70)
		170	14.3 (1.71)
		180	10.3 (1.63)
		190	8.2 (1.50)
	DBPIP	150	0.45
		160	0.38
		170	0.42
		180	0.34
		190	0.33
	BPO	170	0.37
	TBPB	180	2.50
EPT	DCP	150	1.82
		160	1.64
		170	1.52
		180	1.41
	DTBP	160	0.87

Value in bracket shows α.
With respect to the high molecular weight 1.2-PBd-DCP system, extremely high value of efficiency was obtained (*i. e*, apparent value more than one hundred), at 160°C with $\alpha=1.3$.
TBPIP denotes *t*-butylperoxy-isopropylate.

The fact that the efficiency for the SBR-DCP system is rather higher than the literature value2) is due to the higher peroxide concentration.

Decomposition of DCP in Various Polymers. A polymer containing a desired amount of peroxide was cured in a sealed tube, and the ratio of acetophenone to cumyl alcohol was examined by the method described above. The results are shown in Fig 6.

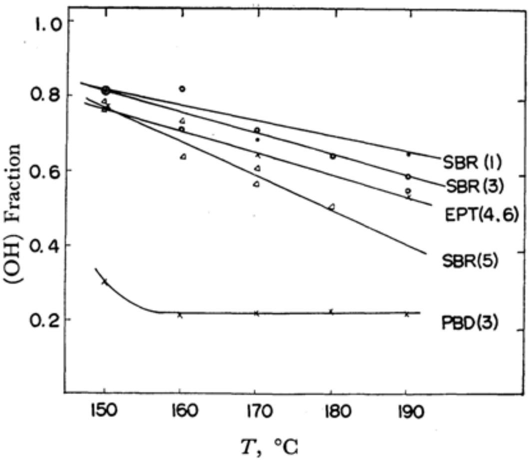

Fig. 6. Relation between (OH) fraction and temperature.
Number in bracket shows DCP concentration.

It is clear from Fig. 6 that the fraction of cumyl alcohol decreased with a rise in the temperature except for the case of PBd. Especially in the same series, as the concentration of peroxide increases, the OH fraction decreases. Of course, the (CO)/(OH) ratio shows the difference in the reactivity of the cumyloxy radical to hydrogen in the polymer, and corresponds to the ratio of the two rate constants,11) k_2/k_1.

Employing Additives and Stabilizers with the SBR-DCP System. In order to examine the influence of some additives9,12,13) or some stabilizers,14) several substances which had been known to be useful in increasing the crosslink density of propylene-containing polymers were used in the SBR-DCP system. The results are shown in Figs. 7 and 8. In Fig. 7, such additives as squalene, diallyl phthalate, quinone dioxime, triallyl cyanurate, and 1.2-PBd of a low molecular weight are used. In every case, the additive/peroxide ratio was four. Figure 7 shows that none of the additives except for PBd have any effect in inhibiting the decrease in efficiency. PBd is, moreover, not a true additive because the polymer itself can be crosslinked highly with the peroxide. In Fig. 8, two stabilizers, mercaptobenzoimidazol (MB) and zinc salt of mercaptobenzoimidazol (MBZ), are used.

---

11) H. C. Bailey and G. W. Godin, *Trans. Faraday Soc.*, **52**, 68 (1956).
12) J. V. Fusco, *Rubber World*, **147**, 48 (1963).
13) A. E. Robinson, J. V. Marra and L. O. Amberg, *I & EC Product Research and Development*, **1**, No. 2, 78 (1962).
14) J. Lacombe and W. Wrobel, *Wire and Wire Products*, **38**, 670 (1963).

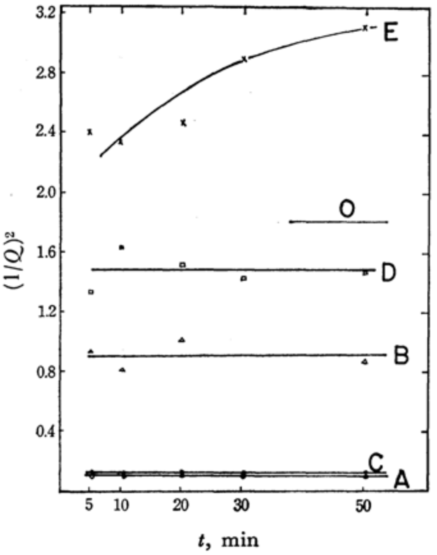

Fig. 7. Effect of ADD on $(1/Q)^2$.

A Squalene, B Diallyl phthalate
C Quinone dioxime, D Triallyl cyanurate
E 1.2-PBd, O Original (without additive)
[DCP] 3 PHR

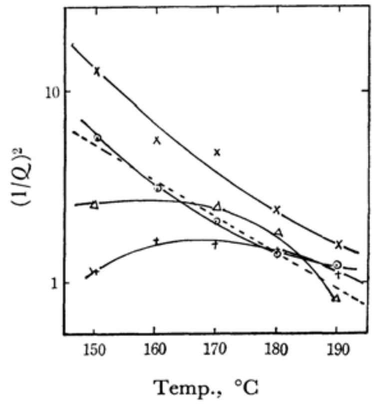

Fig. 8. Effect of MB and MBZ on crosslinking of SBR.

—×— DCP-MBZ —⊙— DCP-MB
—△— DTBP-MB —+— DTBP-MBZ
------ Original
MB Mercaptobenzimidazol
MBZ Zn-salt of MB

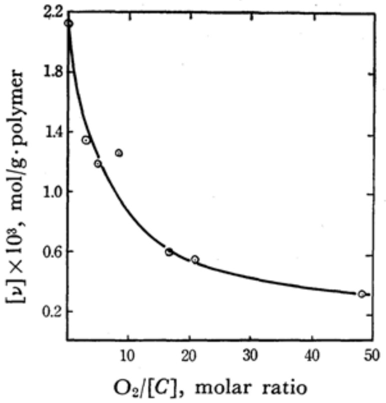

Fig. 9. Efficiency decrease of SBR-DCP system with increasing the amount of oxygen.
[DCP] 3 PHR, Temp. 160°C

Efficiency in the Presence of Oxygen. An SBR piece containing 3 PHR DCP was put in a glass tube which had been connected to a vacuum apparatus. The tube was then cooled by dry ice-methanol, and any air present was eliminated. A desired amount of oxygen was introduced into the tube, and it was immersed in an oil bath after being sealed. Then, the reaction was carried out at 160°C for 2 hr. The crosslink density decreased abruptly with an increase in the amount of oxygen, as may be seen in Fig. 9. In this case, the vulcanizate having low crosslink density was deeply colored. The efficiency decrease at a comparatively high temperature is likely to be due to oxidative degradation alone, not to any decrease in the effective primary radical occurring through interaction between the primary radical and oxygen. The explanation[15] that a polymer-producing tertiary peroxy radical easily undergoes oxidative degradation may be applied to the SBR-DCP system, which shows a rapid decrease in efficiency in the presence of oxygen. At any rate, from the above reason, the efficiency decrease in this case differs substantially from the case where oxygen is absent.

Discussion

Various different tendencies have been observed by several investigators[1,16-18] with respect to the dependency of the crosslinking efficiency on the

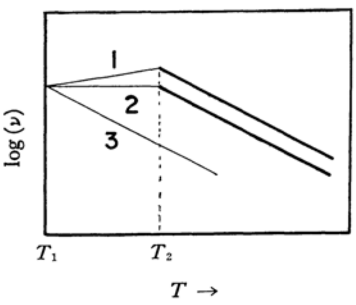

Fig. 10. Model lines showing the variation of efficiency.

---

15) A. V. Tobolsky and P. M. Norling, *J. Polymer Sci, Part A*, **3**, 1435 (1965).

16) W. Scheele, *Rubber Chem. and Technol.*, **34**, 1306 (1961).

17) H. Ushio and M. Yoshikawa, *Journal of the Society of Rubber Industry, Japan*, **31**, 276 (1958).

18) K. Hummel and G. Kaiser, *Rubber Chem. and Technol.*, **38**, 581 (1964).

reaction temperature. Figure 10 is a model showing these tendencies. Generally, the temperature dependency of the efficiency can be represented as an exponential form. There is no special meaning in the magnitude of the slope of each line. First, let us discuss the slender lines.

T_1 is a certain temperature at which the peroxide can decompose, and T_2 is HET. Of course, when the HET is extremely low, it becomes type 3. When a crosslink formation occurs through hydrogen abstraction alone, types 2 and 3 seem probable. In view of the temperature dependence of (CO)/(OH), type 3 seems most probable. Since natural rubber is crosslinked with DCP through hydrogen abstraction, type 1 is not probable in this system. Nevertheless, such a case has been found; it has been explanined as being due to nonrubber constituents, such as an impurity.[19)]

When a crosslink formation occurs not only by hydrogen abstraction, but also by a polymerization-type reaction, it is not clear whether or not an impurity is the only factor causing the tendency toward type 1, because the HET varies according to the sort of peroxide, even if the same series of polymer is used.

As a whole, when a peroxide showing weak activity with regard to crosslink formation is used, HET is likely to shift to the right of the abscissa.

Next, let us consider the portion of the bold line. The efficiency decrease can be considered to be due to one or more of the following reasons:

1) Decrease in hydrogen abstraction, which is the one reaction producing crosslinks.

2) Increase in the termination rate in the chain reaction arising from opening up the double bond; this is another reaction producing crosslinks.

3) Increase in scission efficiency.

4) Thermal decomposition of the main chain.

In these processes, of course, thermal decomposition occurs at extremely high temperatures. However, within the temperature region of the present study, the contribution of No. 4 seems to be small. The results of Fig. 2 show no reversion. The fact that the additives and the stabilizers have no apparent effect in reducing the efficiency decrease, as may be seen in Figs. 7 and 8, may suggest, in return, that the thermal decomposition is negligible. In Figs. 7 and 8, there is one exceptional example, the MBZ-DCP system. MBZ seems to have a little effect, for it elevates the temperature at which the same crosslinking efficiency can be obtained by about 15°C. However, the effect will not be substantial because the MBZ-DCP line runs parallel with the original line. Other combinations where MB or MBZ is used have no effect in inhibiting the decrease in efficiency.

With respect to the second reason, there should indeed be a chain reaction (polymerization), because the crosslinking efficiency is larger than unity, at least in the cases where SBR and PBd are used in combination with DCP. Generally, the chance of collision between the primary radical and the polymer radical will become higher with an elevation of the temperature. Therefore, even when the hydrogen abstraction is the only reaction producing the crosslinks, the efficiency should decrease. Especially when the chain reaction on the double bond is also the reaction producing the crosslinks, the efficiency decrease arising from the increase in the termination rate will become much more apparent. Here there are two cases in the chain reaction; one is a cross polymerization[2)] through the main-chain double bonds, and the other is a polymerization through the pendant double bonds. Thus, the contribution of No. 2 can be considered to be large.

Bristow[19)] studied the peroxide crosslinking of natural rubber to find the temperature dependence of the scission efficiency; he concluded that the temperature dependence was absent. The present authors' experiment concerning the EPT vulcanizate also showed that the temperature dependence of scission efficiency was small. Thus, it can be said that the contribution of No. 3 is comparatively small.

It is obvious that No. 1 is a factor in reducing the crosslinking efficiency. The effect of No. 1 should be more apparent when the hydrogen abstraction is the only reaction producing the crosslinks. The effect of No. 1 can be recognized by comparing Fig. 6 with the figures showing the decrease in efficiency with an increase in the temperature; one can find a close resemblance between Fig. 6 and the above figures with respect to the decrease in efficiency and the (OH) fraction.

The reaction between a polymer and DCP proceeds as in Eqs. (7)—(11),[13,20,21)] which show the crosslink formation through hydrogen abstraction. Furthermore, it has been reported that the amount of ethane was larger than that of methane when DTBP was decomposed in natural rubber.[20)]

$$\mathrm{DCP} \overset{k_d}{\rightarrow} 2\phi\mathrm{C(CH_3)_2\dot{O}} \qquad (7)$$

$$\phi\mathrm{C(CH_3)_2\dot{O}} + \mathrm{RH} \overset{k_1}{\rightarrow} \phi\mathrm{C(CH_3)_2OH} + \mathrm{\dot{R}} \qquad (8)$$

$$\phi\mathrm{C(CH_3)_2\dot{O}} \overset{k_2}{\rightarrow} \phi\mathrm{COCH_3} + \mathrm{\dot{C}H_3} \qquad (9)$$

$$\mathrm{RH} + \mathrm{\dot{C}H_3} \overset{k_3}{\rightarrow} \mathrm{\dot{R}} + \mathrm{CH_4} \qquad (10)$$

$$\mathrm{\dot{C}H_3} + \mathrm{\dot{C}H_3} \overset{k_4}{\rightarrow} \mathrm{C_2H_6} \qquad (11)$$

The decomposition aspect of DCP will be almost the same as that of DTBP. Thus, the reaction

---

19) G. M. Bristow, *J. Appl. Polymer Sci.*, **9**, 3255 (1965).

20) C. G. Moore and W. F. Watson, *J. Polymer Sci.*, **19**, 237 (1956).

21) W. Scheele, *Kautschuk und Gummi*, **15**, WT 482 (1962).

producing acetophenone does not contribute to the crosslink formation very much, while the reaction producing cumyl alcohol contributes greatly to the crosslink formation. Therefore, it can be said that the larger the (OH) fraction, the higher the crosslink density. In the above equations, RH denotes a polymer, and a crosslink formation occurs through the coupling of two polymer radicals.

With respect to the relation between the crosslinking efficiency and the peroxide concentration, there are two cases; one is the case where the crosslinking efficiency is not affected by the peroxide concentration, and the other is the case in which the efficiency is affected. In the latter case, there are also two examples; one is the example in which the efficiency increases with an increase in the peroxide concentration, and the other is the reverse. These facts mean that the efficiency increases up to a certain concentration of peroxide, and that beyond that the efficiency decreases.

Now, let us discuss individual case. In the SBR-DCP system, the dependency of the crosslink density on the peroxide concentration is different from those of the other systems; that is, the crosslink density of this system is proportional to $[C]^{a}$. Therefore, in this case, a direct comparison of the efficiency with those of the other systems is rather difficult. However, that the efficiency is high can easily be seen. The fact that the value obtained here is slightly higher than the reported value (12.5) may be due to a higher region of the peroxide concentration.

It may be supposed that the hydrogen abstraction of 1.2-PBd will be easy because of the existence of tertiary hydrogen atoms. However, this is not true, because the (OH) fraction is very low. That a high crosslinking efficiency is obtained in spite of the low hydrogen abstraction can be considered to be due, to a large extent, to a chain reaction on the double-bond cleavage.

It has been reported[13) that the crosslinking efficiency of a polymer containing propylene units is generally low. However, the EPT-DCP system has a comparatively high efficiency, as may be seen in Table 2. The fact that the efficiency exceeded unity could not have been easily anticipated. The efficiency[13,22) for ethylene-propylene rubber (EPR) decreases from 1 to about 0.05 as the ethylene content decreases from 100% to 0%. The values for the EPR[23) containing 58 mol% of ethylene and 65 mol% of ethylene are 0.34 and 0.40 respectively. Although it can easily be recognized that the efficiency for the EPT used in the present study becomes higher than the values mentioned above, it is difficult to explain the fact that the efficiency exceeds unity, for the content of the T-component is very low. At any rate, the influence of the T-component will be very great.

Conclusion

Several unsaturated polyolefins were crosslinked with various kinds of peroxide in an attempt to find the dependency of the crosslinking efficiency on the reaction conditions. The reactions were carried out in the presence or absence of oxygen, and also in the presence of a third component, such as an additive or a stabilizer. Since the efficiency decrease in the presence of oxygen was considered to be due to thermal oxidative degradation, which is, of course, different from the other cases, the case was not discussed.

The third component has no appreciable effect in stopping the efficiency decrease with an increase in the temperature.

The increase and decrease in efficiency which appeared upon an elevation of the reaction temperature were also discussed; the phenomena were interpreted as follows. With respect to the increase in efficiency, it is not clear whether the phenomenon is due to the impurity alone or not. The decrease in efficiency can be considered to be due to a decrease in the hydrogen abstraction and to an increase in the termination rate.

From the point of view of crosslinking efficiency, the activity of peroxide itself is in the following order: DCP>DTBP>TBPB>TBPIP>BPO.

---

22) A. A. Miller, *J. Polymer Sci.*, **42**, 441 (1960).
23) L. D. Loan, *ibid.*, **2**, 3053 (1964).