

Vulcanization of Butyl Rubber by *p*-Quinone Dioxime

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Synopsis

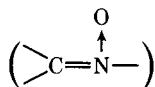
The vulcanization of butyl rubber by *p*-quinone dioxime oxidized by red lead and tetrachloroquinone was investigated. The maximum physical effective crosslinking density of the vulcanizates appeared to be when *p*-quinone dioxime and the oxidizing agent were equimolar. The formation of one physical effective crosslink required one molecule of *p*-quinone dioxime. Chemical reactions are suggested for the vulcanization steps.

INTRODUCTION

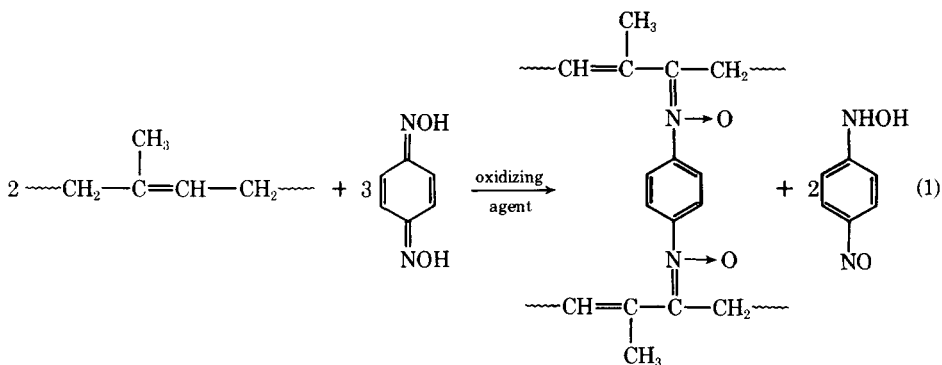
p-Quinone dioxime (GMF) and its esters when activated by oxidizing agents are known as crosslinking agents. They have invariably been used for vulcanization of butyl rubber compounds. The vulcanizates are noted for their excellent thermal stability.

It is generally accepted that the active agent involved in the GMF vulcanization reaction is *p*-dinitrosobenzene formed by oxidation of the dioxime.

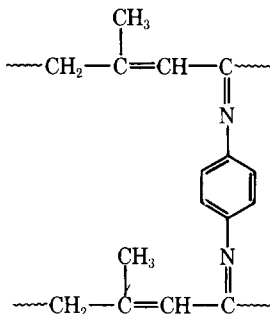
Based on Bruni-Geiger¹ reactions, Rehner and Flory² first proposed the vulcanization reactions of dioxime in butyl rubber. They postulated that each crosslink of nitrone



was produced at the expense of three molecules of *p*-quinone dioxime, as summarized in reaction eq. (1):



However, Yokose et al.³ later showed that only one molecule of *p*-quinone dioxime was sufficient to form one crosslink. The crosslink which they referred to was, in fact, a physical effective crosslink because they made no correction for entanglement contributions. They then inferred that the crosslink could not be nitron but consisted of an anil type ($>C=N-$) as



Cain et al.⁴ also reported that suitably substituted aromatic nitroso compounds could react with natural rubber to form network-bound *p*-phenylenediamines which act as antioxidants.

Based on the nitrosoarene-olefin reactions, Knight and Pepper⁵ suggested that in the case of olefin containing allylic hydrogen atom, the intermediate *N*-alkenyl-*N*-arylhydroxylamine is formed initially via an "ene" addition reaction. This active secondary hydroxylamine may either (1) attack the nitrosoarene to form an azoxyarene and a nitron, (2) decompose thermally to an *N*-alkenylaniline and a nitron, or (3) undergo dehydration to an anil.

Against this background, we had further investigated the vulcanization of butyl rubber by *p*-quinone dioxime.

EXPERIMENTAL

Materials

Butyl rubber of 1.6 mole % unsaturation (Polysar butyl 301); red lead (Riedel-Dehaven) were used. *p*-quinone dioxime (GMF) and tetrachloroquinone (chloranil) both were obtained from Tokyo Kasei TCI.

GMF had 92% purity based on nitrogen analysis. The reagent was used without further purification as employed by Yokose et al.³ However, the formulation of GMF was based on 100% purity. Thus, 2.174 parts of 92% GMF was actually used for 2 parts of GMF which appeared in the formulation.

Stoichiometric Considerations

The formulations consisted of 100 parts butyl rubber, 2 parts pure GMF, and different amounts of oxidizing agent with a molar ratio of oxidizing agent/GMF varying from 0.25 to 2.5.

Polysar butyl 301 has 1.6 mole % isoprene units; this is equivalent to 2.9×10^{-4} mole isoprene unit per gram butyl rubber. On the other hand, the concentration of 2 parts GMF was 1.45×10^{-4} mole per gram butyl rubber. Since each molecule of GMF possesses two functional groups of $>C=N-OH$, the active functional

group of GMF was 2.9×10^{-5} mole/g RH. Therefore, the functionality of butyl rubber (isoprene unit) was equal to the functionality of GMF ($>C=N-OH$).

Preparation of Vulcanizates

Rubber compounding was done on a two-roll laboratory mill according to ASTM D15-70. Vulcanizations were carried out with the help of an electric heated press at 151°C for different cure times.

Crosslinking Density From Swelling Measurement

Equilibrium swelling of vulcanizates in benzene was obtained after six days of swelling at 25°C . The physical effective crosslinking density of the vulcanizate was calculated by means of the modified Flory-Rehner equation^{6,7} with simple chain end correction:⁸

$$X = -\frac{1}{2\rho V_s} \cdot \frac{\ln(1 - V_r) + V_r + \mu V_r^2}{V_r^{1/3} - (V_r/2)} + \frac{1}{\bar{M}_n}$$

where X = physical effective crosslinking density (mole/g rubber), ρ = density of dry rubber, V_r = volume fraction of rubber in swollen sample, μ = rubber-solvent interaction parameter (0.49)⁹, \bar{M}_n = number-average molecular weight of butyl rubber (1.48×10^5 g/mole)¹⁰, and V_s = molar volume of benzene at 25°C (89.3 ml).

Since the amount of entanglement contributing to effective crosslink was uncertain, no exact chemical crosslinking density could be estimated from this measurement. Nevertheless, physical effective crosslinking density was used with reservation for entanglement contribution.

Determination of Combined Nitrogen

The vulcanizate was extracted with a mixture of methyl ethyl ketone and benzene for six days at 70°C . About 2 g of the dried extracted vulcanizate was accurately weighed and subjected to digestion in a Kjeldahl flask until a clear solution was obtained. The digestion mixture consisted of potassium sulfate, copper sulfate, selenium, and concentrated sulfuric acid. The analytical method was based on ASTM D1278-34.

The chemically combined nitrogen was generally expressed as the amount of dinitro compound which was calculated by the following equation:

$$D = \frac{N \times V}{2 \times 1000 \times W}$$

where D = moles of dinitrocompound per gram rubber (moles/g RH), N = normality of HCl (0.01N), V = volume of HCl used (ml), and W = weight of vulcanizate used (g) which had been corrected for rubber.

RESULTS AND DISCUSSION

Butyl rubber had been vulcanized by *p*-quinone dioxime (GMF) either oxidized by tetrachloroquinone (chloranil) or red lead. Throughout the study, 2

TABLE I
Structural Features of GMF-Chloranil-Butyl Vulcanizates^a

Molar ratio of chloranil/GMF	Physical effective crosslinking density from V_r , (moles/g RH) $\times 10^{-5}$	Combined dinitro compound, (moles/g RH) $\times 10^{-5}$	No. of combined dinitro compounds per physical effective crosslink (X_D)
0.25	4.26 (4.0) ^b	3.99	0.97
0.375	5.27	5.28	1.00
0.50	7.26 (7.1)	7.24	0.99
1.00	8.56 (8.3)	9.07	1.06
1.50	8.06 (7.9)	9.26	1.14
2.00	8.56 (7.5)	12.42	1.44
2.50	8.56	12.82	1.49

^a GMF was kept constant at 14.5×10^{-5} mole/g RH, but the amount of chloranil was varied. All rubber compounds were cured at 151°C for 30 min to their optimum cures.

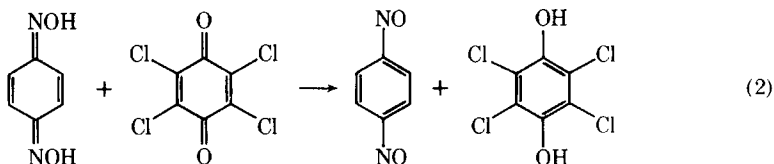
^b Figures in parentheses are quoted from Yokose et al.³

parts (14.6×10^{-5} mole/g RH) GMF was used with varying amounts of the oxidizing agents.

GMF Oxidized by Chloranil

Unlike in natural rubber, chloranil itself was unable to vulcanize butyl rubber.³ Similarly, no vulcanization was observed in butyl rubber when GMF was used alone. On the other hand, butyl rubber containing chloranil and GMF with a molar ratio ranging from 0.25 to 2.5 cured readily at 151°C . Table I shows the structural features of the vulcanizates at their optimum cures. Physical effective crosslinking densities reported by Yokose et al.³ are also shown for comparison.

The maximum physical effective crosslinking density of 8.56×10^{-5} mole/g RH was obtained at equimolar of chloranil and GMF. The corresponding concentration of dinitro compound was 9.07×10^{-5} mole/gRH, which represented 62% GMF combined in rubber network. Thereafter, the crosslinking density remained virtually constant even when the molar ratio of chloranil/GMF was progressively increased to 2.50. This was in accordance with GMF being oxidized by chloranil at equimolar to dinitrosobenzene according to eq. (2):



Since dinitrosobenzene is believed to be the only active crosslinking agent, the crosslinking reaction would therefore depend solely upon its formation. An excess of chloranil to GMF might only enhance the rate of dinitrosobenzene formation and hence the rate of vulcanization without affecting the amount of crosslink.

The physical effective crosslinking density was linearly proportional to the concentration of chloranil up to about 8×10^{-5} mole/g RH, as shown in Figure

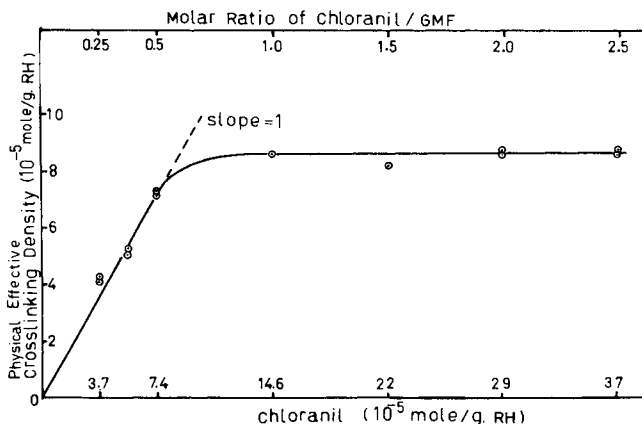


Fig. 1. Effect of chloranil on crosslinking density.

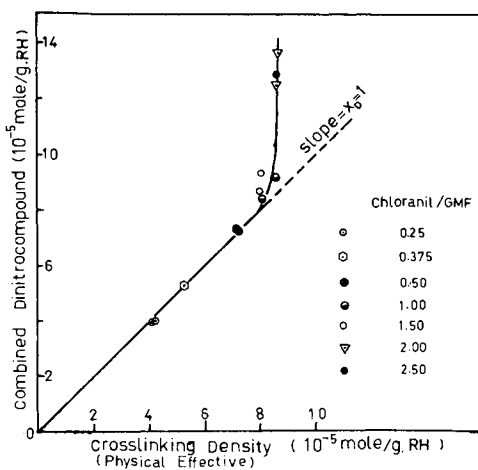


Fig. 2. Crosslinking density and combined dinitro' compound for the chloranil/GMF system.

1. This critical concentration nearly coincided with the maximum crosslinking density. The unity slope of the linear portion could be interpreted as follows: each physical effective crosslink was produced at the expense of one molecule of GMF and chloranil. GMF was presumably first oxidized by chloranil in a one-to-one ratio to dinitrosobenzene which subsequently reacted with the rubber molecules to produce one physical effective crosslink. Since the type of quinoid crosslinks could not be ascertained, the amount of combined nitrogen was generally expressed in terms of dinitro compound. Figure 2 shows the plot of physical effective crosslinking density against combined dinitro compound, and the slope is equal to the crosslinking efficiency, i.e., the number of dinitro compound per physical effective crosslink (X_D). The slope was unity up to the maximum physical effective crosslinking density. This clearly indicates that each physical effective crosslink consisted of only one dinitro compound.

When chloranil was in excess to GMF, X_D increased steadily to about 1.5. But their physical properties such as modulus, tensile strength, and elongation appeared to be unaffected by the change in X_D value.

TABLE II
Structural Features of GMF-Pb₃O₄-Butyl Vulcanizates^a

Molar ratio of Pb ₃ O ₄ /GMF	Physical effective crosslinking density from V_r , (moles/g RH) $\times 10^{-5}$	Combined dinitro compound, (moles/g RH) $\times 10^{-5}$	No. of combined dinitro compounds per physical effective crosslink (X_D)
0.25	3.20	3.21	1.00
0.375	4.71	4.70	1.00
0.50	7.35	7.40	1.01
0.75	9.81	9.98	1.02
1.0	11.92	12.01	1.00
1.5	11.80	11.81	1.00
2.0	11.91	11.92	1.00
2.5	11.87	11.60	0.98

^a GMF was kept constant at 14.5×10^{-5} mole/g RH, but the amount of Pb₃O₄ was varied. All rubber compounds were cured at 151°C for 30 min to their optimum cures.

GMF Oxidized by Red Lead

Lead tetraoxide (red lead) had been used to oxidize GMF, although the actual oxidizing agent was lead dioxide. The use of lead dioxide alone would be too severe,¹¹ resulting in actual oxidation of dinitrosobenzene to unreactive dinitrobenzene.

The formulations were similar to the previous system, except that chloranil was replaced by Pb₃O₄. Table II shows the structural features of the vulcanizates. The maximum physical effective crosslinking density of 11.92×10^{-5} mole/g RH also appeared at equimolar concentrations of Pb₃O₄ and GMF. This maximum crosslinking density was about 40% higher than that of the GMF-chloranil vulcanizate. Obviously, Pb₃O₄ was a better oxidant for GMF in producing quinoid crosslinks.

When the concentration of Pb₃O₄ was plotted against physical effective crosslinking density, a linear relationship was again obtained. The linearity extended up to the maximum physical effective crosslinking density or to equimolar Pb₃O₄/GMF, as shown in Figure 3. As in the chloranil-GMF system, the slope was equal to one indicating that one physical effective crosslink was produced by using one molecule of GMF and one of Pb₃O₄. In addition, Figure 4 shows that the average number of combined dinitro compound per physical effective crosslink (X_D) was also equal to one, irrespective of Pb₃O₄/GMF ratios. The experimental results again implied that GMF was oxidized by Pb₃O₄ at a 1:1 ratio to dinitrosobenzene which subsequently reacted with rubber chains to produce one physical effective crosslink. Unlike the chloranil/GMF system, the network structure of Pb₃O₄/GMF vulcanizate appeared to be simpler.

GMF Oxidized by Mixed Chloranil and Red Lead

As shown previously, GMF oxidized by Pb₃O₄ seemed to yield higher crosslinking efficiency than that oxidized by chloranil. Further verification was done by vulcanizing GMF with a mixture of chloranil and Pb₃O₄. Table III shows

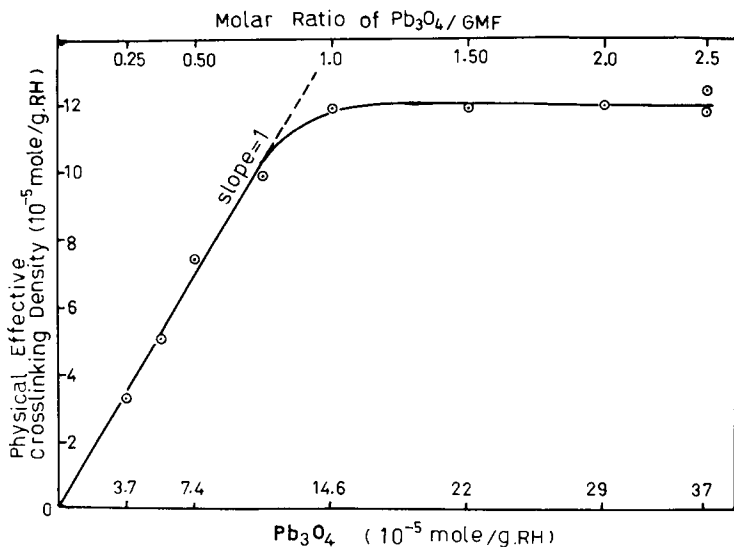


Fig. 3. Effect of red lead on crosslinking density.

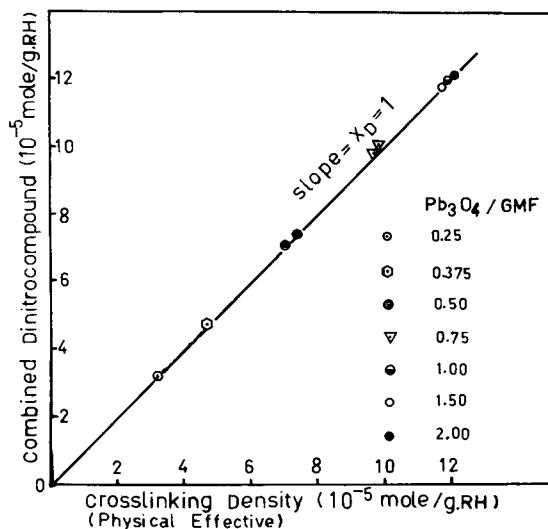


Fig. 4. Crosslinking density and combined dinitro compound for the Pb_3O_4 /GMF system.

the formulations together with the structural features of the resulting vulcanizates.

The maximum physical effective crosslinking density was markedly increased from 8.56 to 12.45×10^{-5} mole/g RH when some Pb_3O_4 was added to the system containing chloranil/GMF having a molar ratio of 2. This new maximum crosslinking density could not be attained by the effect of either one of the oxidizing agents at those concentrations. Not only crosslinking density but also crosslinking efficiency was substantially improved by the effect of Pb_3O_4 . The evidence was an appreciable decrease of X_D from 1.44 to about 1, which seemed to be the lower limit.

TABLE III
Structural Features of GMF-Chloranil-Pb₃O₄-Butyl Vulcanizates

Compound	Cure time at 151°C, min	Physical effective cross-linking density from V_r , (moles/g RH) $\times 10^{-5}$	Combined dinitro compound, (moles/g RH) $\times 10^{-5}$	No. of combined dinitro compounds per physical effective cross-link (X_D)
A	10	10.57	10.30	0.97
	15	11.27	11.03	0.98
B	10	12.05	12.10	1.0
	15	12.25	12.12	0.99
C	10	12.45	12.35	0.99
	15	11.99	12.64	1.05
D	30	8.56	12.42	1.44

Formulations:

Compound	Butyl 301	GMF	Chloranil	Pb ₃ O ₄	Molar ratio of chloranil/GMF	Molar ratio of Pb ₃ O ₄ /GMF
A	100	2.0	7.2	3.73	2.0	0.375
B	100	2.0	7.2	4.98	2.0	0.50
C	100	2.0	7.2	7.47	2.0	0.75
D	100	2.0	7.2	—	2.0	—

The lower crosslinking efficiency for chloranil/GMF could be due to some of the side-crosslinking reactions which might not be favourably formed in Pb₃O₄/GMF system. The effect of Pb₃O₄ in the chloranil/GMF system was to suppress the side-crosslinking reaction. The possible side reactions will be discussed in the next section.

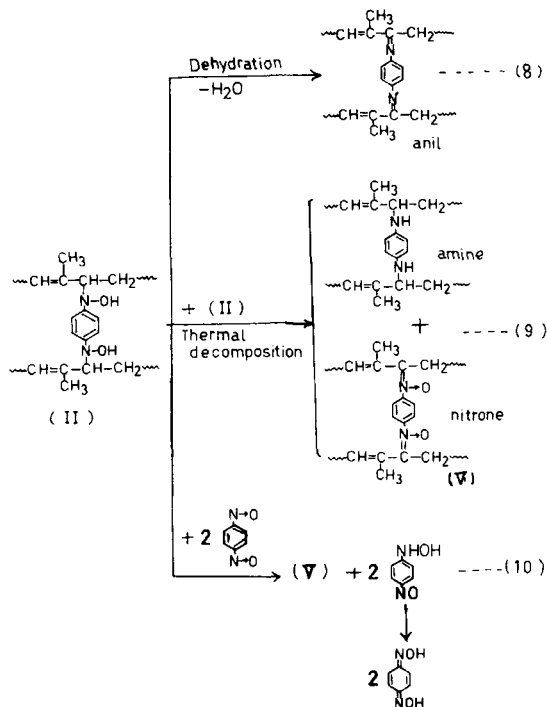
Vulcanization Mechanism

Since no suitable equation is available for calculating chemical crosslinking density for butyl rubber, physical effective crosslinking density is reported in this study with reservation for entanglement contributions. The presence of physical entanglements between chains could have the same effect as genuine chemical crosslinks. Entanglement contributions to equivalent chemical crosslink could be very important, especially at low extents of chemical crosslinking. Moore and Watson¹² estimated that entanglement could contribute to about 3×10^{-5} mole of equivalent chemical crosslink per gram natural rubber. Kramer et al.¹³ also reported recently that as much as about 50% equivalent chemical crosslinks was derived from entanglements for 1,2-polybutadiene cured by irradiation.

If physical effective crosslinking density was corrected for entanglement contributions by the same factor as that for natural rubber, the number of combined dinitro compounds per chemical crosslink became larger than one for all the vulcanizates studied. For instance, vulcanizates of equimolar Pb₃O₄/GMF as well as for those from the mixed oxidizing system would consist of about 1.3 molecule of combined dinitro compound per chemical crosslink. On the other

similar to the nitrosoarene-olefin system⁵ are envisaged for these intermediate crosslink transformations which are shown in reaction scheme II.

REACTION SCHEME II
TRANSFORMATIONS OF INTERMEDIATE CROSSLINK



It seems that reaction eq. (10) is less likely to occur because it would require three moles of oxidizing agent instead of one, as found experimentally for producing maximum crosslinking density. The probability for bimolecular reaction according to reaction eq. (9) may also be very small due to possible low instantaneous concentration of intermediate crosslink (II) and its restricted mobility in vulcanizate.

Pendent hydroxylamine (III) and intermediate crosslink of azoxy units (IV) may further be transformed to other stable forms without affecting the amount of combined nitrogen. Their presence can be responsible for a larger number of combined dinitro compound per physical effective crosslink (X_D) or per chemical crosslink (E) of chloranil-GMF vulcanizates. When excess of chloranil to GMF was used, X_D or E was found to increase substantially. This could be due to rapid formation of dinitrosobenzene resulting in instantaneous accumulation of intermediate (I) as well as tetrachlorohydroquinone. Consequently, the formed tetrachlorohydroquinone might favorably reduce intermediate (I) to pendent hydroxylamine (III) according to reaction eq. (6). Subsequent reaction of the formed pendent hydroxylamine (III) with dinitrosobenzene and isoprene units would produce crosslinks with azoxy units by following reaction eq. (7).

When various amounts of Pb_3O_4 were added to the system containing chloranil/GMF at a molar ratio of 2, the value of E was reduced to a minimum, i.e., from 1.8 to 1.3. For equimolar Pb_3O_4 /GMF vulcanizate, E was also found to be

about 1.3. This shows that Pb_3O_4 could minimize the formation of pendent hydroxylamine (III) by interacting with reducing agent, such as the formed tetrachlorohydroquinone in the chloranil/GMF system. Hence, the occurrence of the side reactions according to eqs. (6) and (7) may be negligible in the presence of sufficient amount of Pb_3O_4 in the quinoid-cured system.

It is envisaged that not all the intermediate (I) might have a chance to further react with the limited number of isoprene units of butyl rubber, especially at the latter stage of vulcanization. The vulcanizate might consist of a certain amount of the half-crosslinked pendent group of intermediate (I) or its other stable form. This could be one of the main reasons for the difference between the theoretical E value of 1.0 and the experimental E value of 1.3.

With the above consideration, we believe that vulcanization of butyl rubber by GMF/ Pb_3O_4 may proceed mainly via the reaction sequences represented by eqs. (3), (4), (5), and (8). Consequently, an anil-type crosslink may prevail in the quinoid vulcanizate.

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