

Vulcanization of Butyl Rubber by *p*-Quinone Dioxime Dibenzoate

L. M. GAN and C. H. CHEW, *Department of Chemistry, Nanyang University, Singapore*

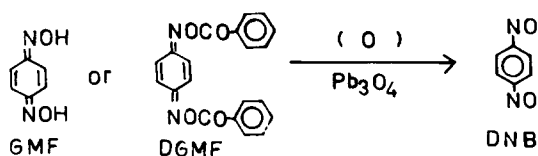
Synopsis

The maximum crosslink density for the dioxime-butyl vulcanizate was obtained at equimolar quantity of the dioxime and red lead. The formation of each quinoid crosslink required about 1.25 molecule of *p*-quinone dioxime dibenzoate. The vulcanizates consisted mainly of the anil-type crosslink. It was estimated that about 20% of the combined dinitro compounds was wasted in the form of the pendent groups. The vulcanization mechanisms are also discussed.

INTRODUCTION

Quinoid compounds such as *p*-dinitrosobenzene (DNB), *p*-quinone dioxime (GMF) and *p*-quinone dioxime dibenzoate (DGMF) are known to be able to crosslink unsaturated rubbers.¹⁻⁵ Both GMF⁶ and DGMF⁷ when activated by oxidizing agents are useful crosslinking agents for butyl rubber. The quinoid-cured butyl vulcanizates are noted for their excellent thermal stability. They have been used for wire insulation and tire curing bags.

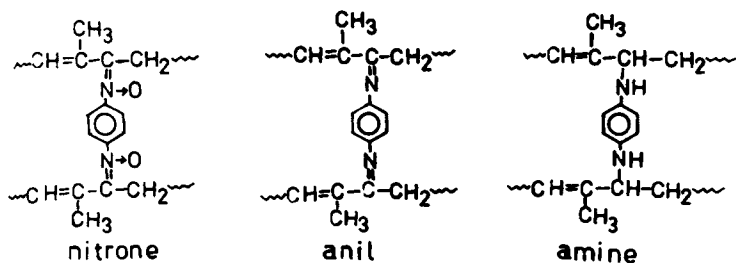
It is generally believed that DNB is the real crosslinking agent for quinoid vulcanization. DNB can readily be formed from GMF or DGMF by oxidation according to the Haworth's reaction scheme²:



The active DNB will then react with the olefin units of the rubber chains via an "ene" addition^{6,8} to form crosslinking intermediates. The stable quinoid crosslinks are subsequently produced through transformations of the intermediates.

The structure of the quinoid crosslink is yet to be fully understood. Rehner and Flory¹ first suggested that the quinoid crosslink is of the nitrone type. However, Yokose et al.⁹ inferred the presence of an anil-type crosslink. According to Knight and Peppers' nitrosoarene-olefin reaction scheme,⁸ a quinoid crosslink may either consist of a nitrone, an anil or an amine-type structure as

shown below:



From the recent study of the butyl vulcanization with GMF oxidized by red lead and/or chloranil, Gan et al.⁶ speculate that the anil-type crosslink is likely to prevail. This paper is the result of the continued study of quinoid-cured butyl vulcanization by DGMF.

EXPERIMENTAL

Materials

Butyl rubber of 1.6 mole % unsaturation (Polysar butyl 301) and red lead (Riedel-Dehaen) were used. DGMF was obtained from the Rubber Regeneration Co., U.K.

The purity of red lead was found to be 94.5% according to the standard method of chemical analysis.¹⁰ Based on nitrogen analysis, DGMF had a purity of 89.6%. These reagents were used without further purification. However, the weights of the reagents in the formulations were all based on 100% purity, i.e., the appropriate weights had been corrected for the impurity.

For infrared spectroscopic study, DGMF was recrystallized from methyl ethyl ketone. The chemical composition of the purified DGMF (C = 69.15%, H = 4.10%, N = 8.10%) agreed very well with the theoretical values (C = 69.36%, H = 4.07%, N = 8.09%).

Stoichiometric Considerations

Polysar butyl 301 of 1.6 mole % unsaturation is equivalent to 29×10^{-5} mole isoprene unit per gram butyl rubber (RH). In all formulations, DGMF was kept constant at 14.5×10^{-5} mole/g RH (or its active functional group of 29×10^{-5} mole/g RH) giving equal concentration to the isoprene unit. The amounts of the oxidizing agent (Pb_3O_4) were varied in such a way that the molar ratios of $\text{Pb}_3\text{O}_4/\text{DGMF}$ ranged from 0.25 to 2.0.

Preparation of Vulcanizates

Rubber compounding was done on a two-roll laboratory mill with water cooling of the rolls. The compounded stocks were cured in an electrically heated press at 130, 151, and 170°C for different cure times.

Crosslink Density From Equilibrium Swelling in Benzene

The effective crosslink density of the vulcanizate was calculated by means of the modified Flory–Rehner equation with simple chain end correction¹¹:

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

where X = effective crosslink density (mole/g RH), ρ = density of dry rubber, V_r = volume fraction of rubber in swollen sample, μ = rubber–benzene interaction parameter (0.49)¹², V_s = molar volume of benzene at 25°C (89.3 ml), and \bar{M}_n = number-average molecular weight of butyl rubber (1.48×10^5 g/mole).¹³ Since the amount of entanglement contribution to equivalent chemical crosslink was uncertain, chemical crosslink density could not be calculated from this swelling measurement. Thus, the effective crosslink density is mainly used in this paper. However, the magnitude of the entanglement contribution is also discussed.

Determination of Combined Nitrogen

The vulcanizates were 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 subjected to digestion in a Kjeldahl flask until a clear solution was obtained. The digestion mixtures consisted of potassium sulfate, copper sulfate, selenium, and concentrated sulfuric acid. The analytical method was based on ASTM D1278-34.

The combined nitrogen in the vulcanizate was calculated from the following equation and expressed as the total amount of the chemically combined dinitro compounds in the vulcanizate (D):

$$D = \frac{NV}{2 \times 1000 \times W}$$

where D = mole of the combined dinitro compounds per gram rubber (mole/g

TABLE I
Structural Features of DGMF–Pb₃O₄ Butyl Vulcanizates^a

Molar ratio of Pb ₃ O ₄ /DGMF	Effective crosslink density from V_r , (mole/g RH) $\times 10^{-5}$	Combined dinitro compounds, (mole/g RH) $\times 10^{-5}$	No. of combined dinitro compounds per effective crosslink E
0.25	3.4	3.5	1.03
0.375	5.8	5.9	1.01
0.50	7.7	7.6	0.99
0.75	11.8	11.6	0.98
1.0	13.6	13.2	0.97
1.5	13.8	14.3	1.04
2.0	13.7	14.0	1.02

^a DGMF was kept constant at 5 parts (14.5×10^{-5} mole/g RH), but the amounts of Pb₃O₄ were varied in accordance with the molar ratios. At equimolar Pb₃O₄/DGMF, the system consisted of 5 phr DGMF and 10 phr Pb₃O₄. All the rubber compounds were cured at 151°C for 30 min to their respective optimum crosslink densities.

RH), V = volume of HCl used (ml) of 0.01*N* normality, and W = weight of rubber (g) which had been corrected from the weight of vulcanizate.

Infrared Spectroscopy

The infrared absorption and the attenuated total reflectance (ATR) spectra were obtained using a Perkin-Elmer 567 spectrophotometer. The ATR accessories were the Barnes VariMax Model ATR 3-131 and a 2-mm-thick KRS-5 (thallium bromide-iodide) prism with end faces cut at 45°.

The IR absorption spectra of pure DGMF and butyl rubber were obtained using films casted on a potassium bromide disk. However, the IR spectra of the extracted vulcanizates could only be obtained by ATR technique.

RESULTS AND DISCUSSION

Effect of Red Lead on Vulcanization

Throughout the study, 5 parts (14.5×10^{-5} mole/g RH) DGMF were used with different amounts of red lead. Theoretically, this quantity of DGMF could be fully converted to DNB by certain amount of red lead providing equimolar concentrations of the reactive nitroso group and isoprene unit in butyl rubber. Consequently, the maximum chemical crosslink density of 14.5×10^{-5} mole/g RH might be expected if all the nitroso groups reacted with the isoprene units at a one-to-one ratio. Since DGMF itself was unable to crosslink butyl rubber, the formation of crosslink would depend on the concentration of red lead for those systems with the molar ratios of Pb_3O_4 /DGMF less than 1.

Table I shows the structural features of the resulting quinoid vulcanizates. The effective crosslink density did increase linearly with the concentration of red lead up to near the equimolar ratio of Pb_3O_4 /DGMF. As plotted in Figure

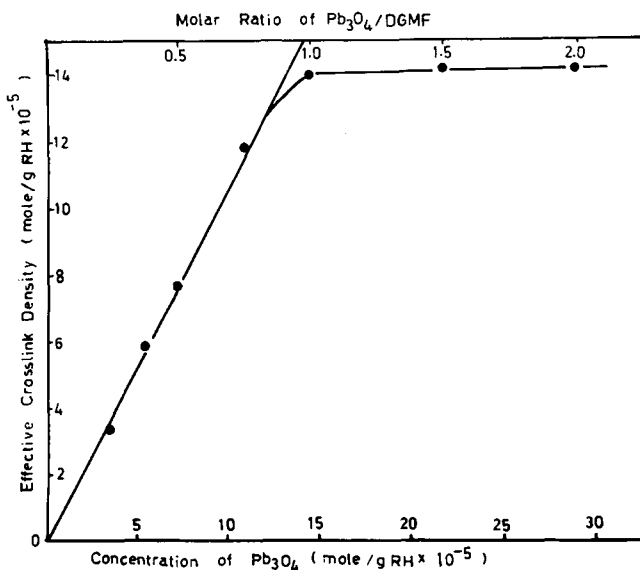


Fig. 1. Effect of red lead concentration on crosslink density.

1, the unit slope indicates that one molecule of red lead was required to react with DGMF in order to produce one quinoid crosslink. This might imply that each DNB was produced from the interaction of each Pb_3O_4 and DGMF. Subsequently, DNB reacted with two isoprene units to form one quinoid crosslink.

At equimolar ratio of Pb_3O_4 /DGMF, the effective crosslink density as high as 13.6×10^{-5} mole/g RH was obtained. This quantity was close to the theoretical value of 14.5×10^{-5} mole/g RH. It represented 94% of the added DGMF was in the form of the quinoid crosslinks. When the amount of the combined dinitro compounds was plotted against the effective crosslink density as shown in Figure 2, a slope E of unity was obtained. This indicates that the structure of the quinoid crosslink consisted of mainly simple dinitro compound.

For the systems with the molar ratio of Pb_3O_4 /DGMF greater than one, the increase in the concentration of red lead did not further affect the crosslink density. This was expected because neither DGMF nor red lead alone would be able to vulcanize the butyl rubber. However, inferior aging properties were observed for those vulcanizates containing excess red lead. This could be due to the effect of excess lead peroxide from red lead on aging.

Effect of Various Equimolar Pb_3O_4 /DGMF and Temperature

Further investigations were carried out on the systems containing an equimolar ratio but with various amounts of Pb_3O_4 and DGMF. The compounded stocks were cured at 130, 151, and 170°C with different times. Table II details the structural features of those systems. Most of the maximum effective crosslink densities obtained were about equal to the respective added DGMF concentrations for all the three curing temperatures. The facts suggested that high quinoid crosslinking efficiency could be achieved from any equimolar ratio of Pb_3O_4 /DGMF at an appropriate curing time. Each effective crosslink was produced

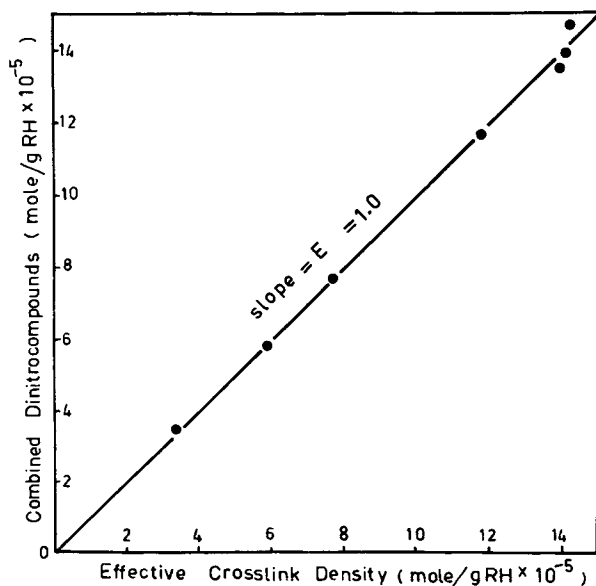


Fig. 2. Linear relationship between crosslink density and combined dinitro compounds.

TABLE II
Structural Features of Equimolar DGMF-Pb₃O₄ Butyl Vulcanizates

Equal concentrations of DGMF and Pb ₃ O ₄ , (mole/g RH) × 10 ⁻⁵	Cure temp. and time, °C/min	Effective crosslink density from <i>V_r</i> , (mole/g RH) × 10 ⁻⁵	Combined dinitro compounds (mole/g RH) × 10 ⁻⁵	No. of combined dinitro compounds per effective crosslink <i>E</i>
3.66	130/70	1.77	1.88	1.06
	151/20	3.20	3.10	0.97
	170/20	3.75	3.60	0.97
5.44	130/70	5.60	5.70	1.02
	151/20	5.85	5.88	1.00
	170/20	6.12	6.22	1.01
7.32	130/70	7.50	7.20	0.96
	151/20	7.60	7.70	1.01
	170/20	7.60	7.60	1.00
7.32	130/70	11.40	11.50	1.01
	151/20	12.00	11.60	0.96
	170/20	11.60	11.70	1.01
14.5	130/70	13.00	12.80	0.99
	151/20	12.90	12.70	0.98
	170/5	12.60	12.20	0.97
	170/20	10.60	12.80	1.20
29.0	130/70	17.62	17.90	1.01
	151/20	17.70	18.10	1.02
	170/5	17.30	18.10	1.04
	170/20	13.50	18.80	1.41

by every added DGMF for those vulcanizates containing DGMF up to about 13×10^{-5} mole/g RH, as shown in Figure 3. When DGMF was further increased to double the theoretical required quantity ($2 \times 14.5 \times 10^{-5}$ mole/g RH), effective crosslink density as high as 17.7×10^{-5} mole/g RH was obtained having exceeded the theoretical value by 3.2×10^{-5} mole/g RH. It was also noted that a much lower crosslink density resulted from those with a higher concentration of the curing agents and cured at 170°C for 20 min. This adverse effect could well be due to oxidative degradation of the rubber main chains accelerated by lead peroxide from red lead.

If each quinoid crosslink was bridged through two isoprene units, the maximum chemical crosslink density should be at most equal to 14.5×10^{-5} mole/g RH because of the limited isoprene unit concentration (29×10^{-5} mole/g RH) in butyl rubber. The excess 3.2×10^{-5} mole/g RH effective crosslink density or 22% of the total crosslink density could be due to the entanglement contribution to equivalent chemical crosslink. Moore and Watson¹⁴ had estimated that entanglement could contribute to about 3×10^{-5} mole of equivalent chemical crosslink per gram of natural rubber. If this correction factor is valid, the chemical crosslink density may be calculated from the effective crosslink density by multiplying by factor of 0.78 for those with high crosslink density.

A good linear relationship between the effective crosslink density and the combined dinitro compounds is again shown in Figure 4. A slope of 1 ($E = 1$) indicates that only one dinitro compound was combined in each effective

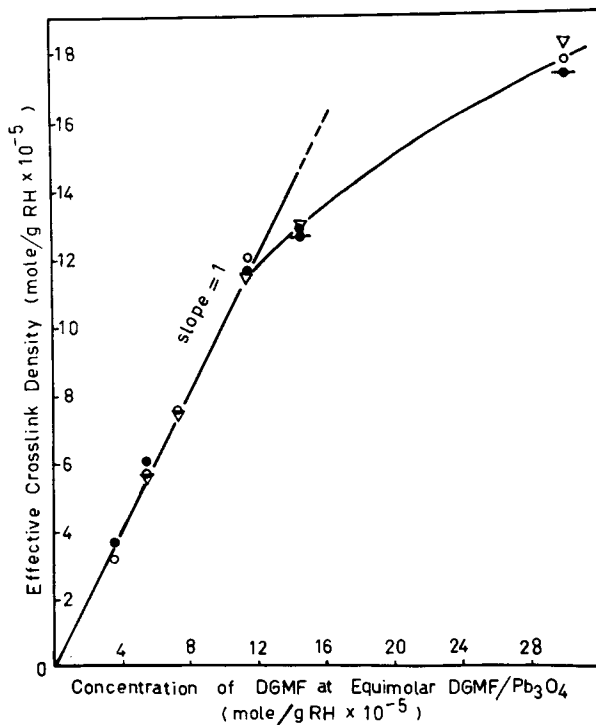


Fig. 3. Effect of DGMF concentration on crosslink density at different cure temperatures and times: (▽) 130°C, 70 min; (○) 151°C, 20 min; (●) 170°C, 20 min; (◐) 170°C, 5 min.

crosslink. But if the effective crosslink was corrected for the chemical crosslink as mentioned above, there would be about 1.25 molecule of the combined dinitro compounds per chemical crosslink for most of the DGMF-Pb₃O₄ vulcanizates. The major portion of the combined dinitro compounds was envisaged to be in the simple quinoid crosslinks. Others might be in the form of pendent groups and/or crosslinks with azoxy units. However, it has been shown⁶ that a crosslink with an azoxy unit would be unlikely to occur in the system containing sufficient amount of oxidizing agent such as red lead. It is therefore believed that the quinoid crosslinks of the DGMF-Pb₃O₄ vulcanizates consisted mainly of one dinitro compound and that about 20% combined dinitro compounds were in the form of pendent groups.

Infrared Spectroscopy

The infrared absorption spectra of butyl rubber and *p*-quinone dioxime di-benzoate (DGMF) are shown in Figure 5. DGMF shows five characteristic absorption bands at 1755, 1650, 1256, and 922 cm⁻¹ and a doublet at 1545 and 1520 cm⁻¹. The first band of 1755 cm⁻¹ is clearly due to —COO absorption. The 1650 cm⁻¹ absorption band is assigned to —C=N stretching which is comparable to 1640 cm⁻¹ for oximes in the solid state.^{15a} The doublet at 1545 and 1520 cm⁻¹ is attributed to symmetrical stretching frequency of the conjugated system —C=C—C=N— which is expected^{15b} to be near 1570 cm⁻¹. The N—O stretching is believed to be responsible for the absorption bands at 1256 and 922

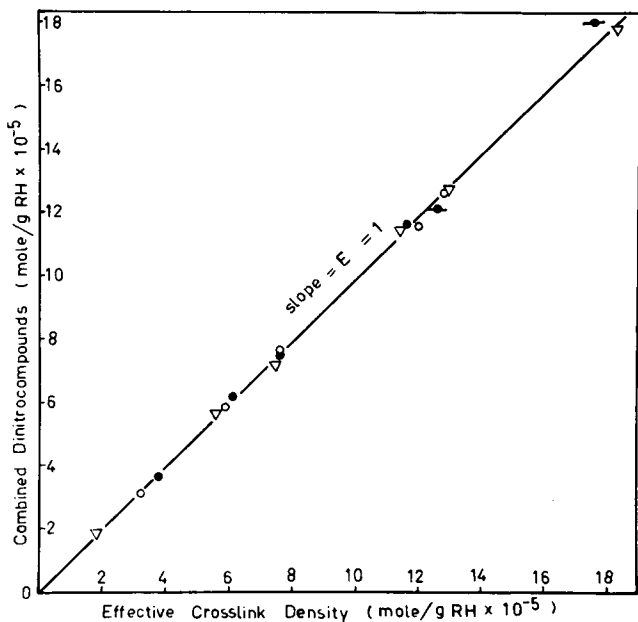
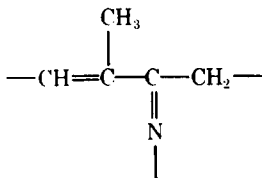


Fig. 4. Linear relationship between crosslink density and combined dinitro compounds for equimolar $\text{Pb}_3\text{O}_4/\text{DGMF}$ vulcanizates: (▽) 130°C, 70 min; (○) 151°C, 20 min; (●) 170°C, 20 min; (●) 170°C, 5 min.

cm^{-1} for they normally appear in the regions^{16a} of 1300–1200 and 960–930 cm^{-1} .

The ATR spectrum of an equimolar $\text{DGMF}/\text{Pb}_3\text{O}_4$ butyl vulcanizate is recorded in Figure 6. A small new band appeared at 1627 cm^{-1} amidst a broad band around 1650 cm^{-1} . Nakanishi^{16b} assigned 1690–1640 cm^{-1} absorption to $\text{C}=\text{N}$ stretching, which was shifted lower to 1627 cm^{-1} by conjugation in benzylideneaniline. Hence, the ATR absorption band at 1627 cm^{-1} for the vulcanizate is assigned to $\text{C}=\text{N}$ stretching of an anil group with conjugation as



Three other new absorption bands at 1535, 1262, and 1014 cm^{-1} may arise from nitroso (---C---N=O) which might be present as a pendent group in the vulcanizate. It is known^{16a} that absorption band of aromatic nitroso (---C---N=O) due to bond stretching of ---N=O occurs around 1500 cm^{-1} . The absorption band in the region of 1300–1250 cm^{-1} is most likely to be associated with the aromatic C---N stretching.^{15c} In addition, the Russian workers¹⁷ had assigned the absorption band at 1262 cm^{-1} to vibrations of the ---C---N=O group in *N*,4-dinitroso-*N*-methylaniline. The rather strong and diffuse absorption band around 1014 cm^{-1} may be attributed to the combination effect of C---N

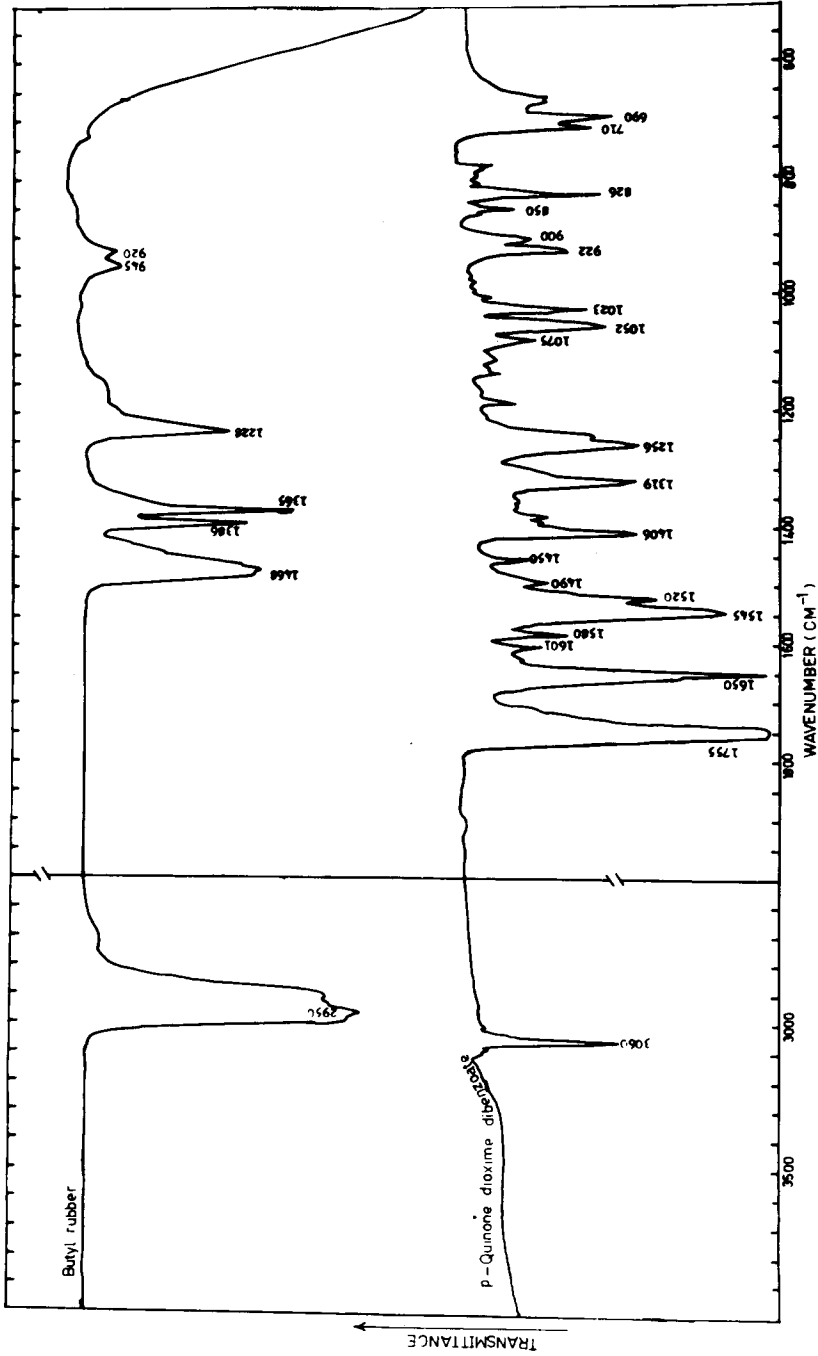


Fig. 5. Infrared spectra of butyl rubber and DGMF.

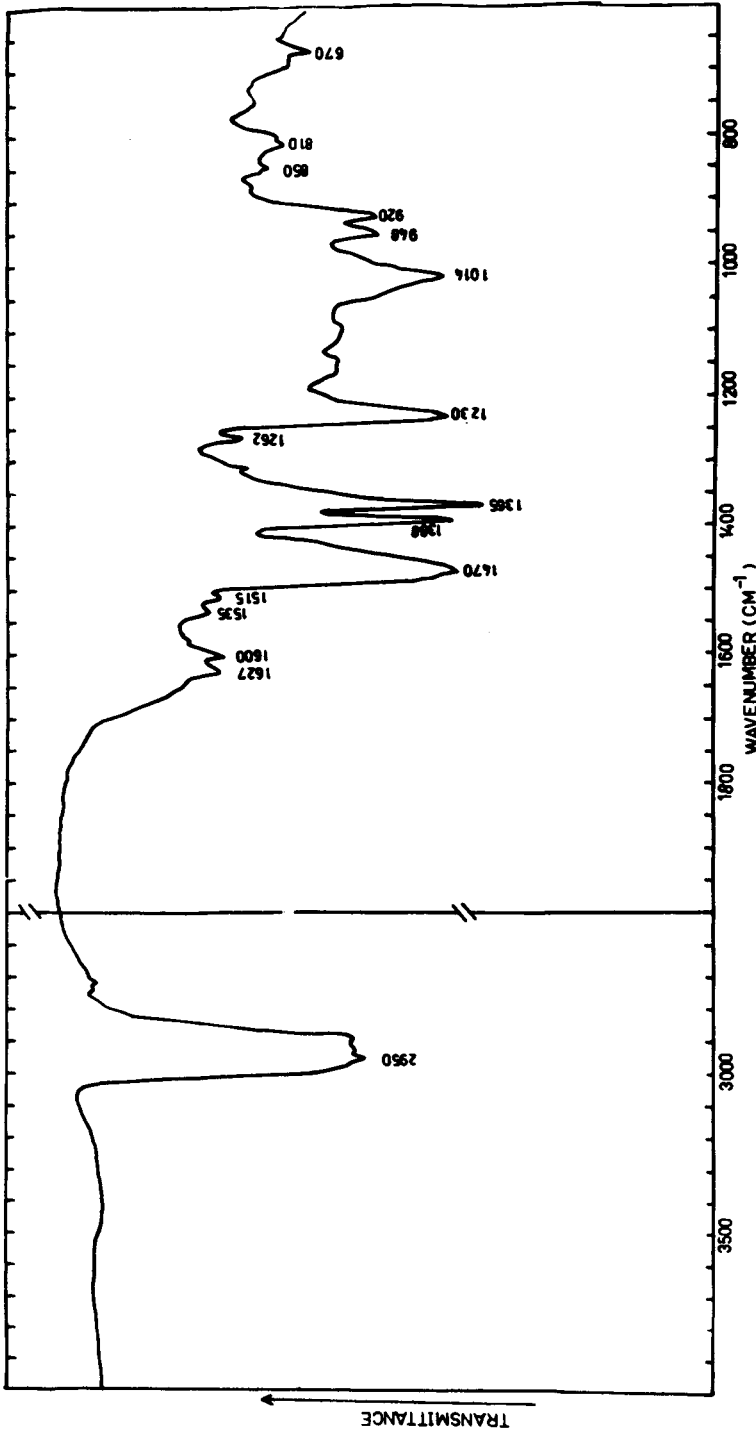
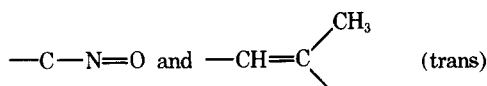
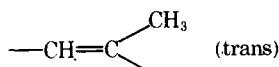


Fig. 6. ATR spectrum of equimolar DGMF/Pb₃O₄ butyl vulcanizate.

stretching in

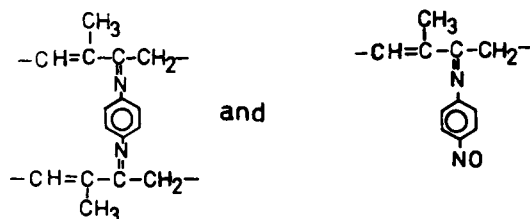


The contribution of C—N stretching has been associated with a strong diffuse band^{15d} near 1100 cm^{-1} , which is distinctively shown together with a smaller band around 1010 cm^{-1} in the spectrum¹⁸ of *p*-dinitrosobenzene. Moreover, a band in the region of $1000\text{--}980 \text{ cm}^{-1}$ which has been identified with the group^{15e}



also appears clearly in the spectra¹⁷ of squalene (985 cm^{-1}) and 2-methylpent-2-ene (990 cm^{-1}). Such a trisubstituted vinyl group is expected to be present in the vulcanizate. Hence, the assignment of band 1014 cm^{-1} due to the above combination effect seems to be reasonable.

Though Morita¹⁹ showed a strong —NH absorption band at 3360 cm^{-1} for the reaction of *N*,4-dinitroso-*N*-methylaniline and squalene, no clear indication of an —NH absorption band around 3400 cm^{-1} was observed for the quinoid vulcanizates. It is thus believed that the equimolar DGMF/ Pb_3O_4 butyl vulcanizates consisted mainly of the following characteristic structures:



Vulcanization Mechanism

The proposed vulcanization mechanism for the oxidized DGMF-butyl system is presented in the reaction scheme of Figure 7. It is envisaged that *p*-dinitrosobenzene (DNB) is first produced from the oxidation of DGMF by red lead at an equimolar ratio. The newly formed DNB reacts instantaneously with isoprene unit via “ene” addition to form a semicrosslink (I). Such an intermediate can further react with another isoprene unit to produce an initial crosslink of alkenylhydroxylamine (II). This initial crosslink is most likely to dehydrate eventually to a stable anil-type crosslink (IV).

Some of the nitroso group of the semicrosslink (I) might not have a chance to consecutively react with the limited number of isoprene units in butyl rubber. Consequently, the vulcanizate might consist of some unreacted nitroso pendent group in the form of III as revealed by the ATR spectrum. The presence of nitroso pendent groups is also reflected in the chemical crosslink efficiency, i.e., $E = 1.25$. It was estimated from the E value that about 20% of the combined dinitro compound was in the form of semicrosslinks (III). This estimation was

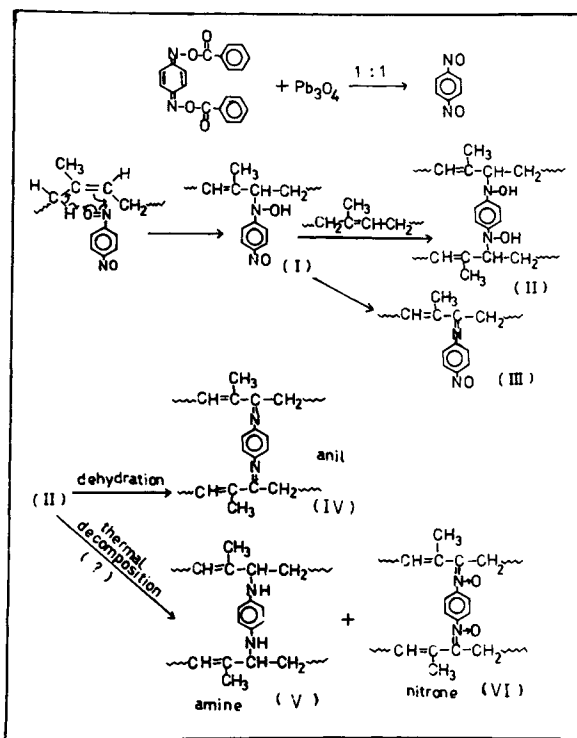


Fig. 7. Reaction scheme of crosslinking reactions for DGMF-Pb₃O₄ butyl system.

based on the assumption that no or only a negligible amount of azoxy-type crosslinks existed in the red lead-oxidized system.⁶

Though the presence of amine-type crosslinks (V) and nitro-type crosslinks (VI) via thermal decomposition of two initial crosslinks (II) might also be possible, the probability for such bimolecular reaction seemed to be extremely small due to the low instantaneous concentration and the restricted mobility of the initial crosslinks (II). Such speculation was substantiated by the ATR spectrum, which shows no amine absorption.

In conclusion, an anil-type crosslink prevailed in the quinoid butyl vulcanizate which also consisted of a sizable amount of pendent groups.

References

1. J. Rehner, Jr. and P. J. Flory, *Ind. Eng. Chem.*, **38**, 500 (1964).
2. J. P. Haworth, *Ind. Eng. Chem.*, **40**, 2314 (1948).
3. W. Hofmann, *Vulcanization and Vulcanizing Agents*, Maclaren, London, 1967, pp. 293-300.
4. L. E. Lim, M.Sc. Thesis, Nanyang University, Singapore, 1976.
5. L. M. Gan and L. E. Lim, *Bull. Singapore Natl. Inst. Chem.*, **4**, 91 (1976).
6. L. M. Gan, G. B. Soh, and K. L. Ong, *J. Appl. Poly. Sci.*, **21**, 1771 (1977); *Rubber Chem. Technol.*, **51**, 267 (1978).
7. G. Alliger and I. J. Sjothun, Eds. *Vulcanization of Elastomers*, Reinhold, New York, 1964, pp. 246-248.
8. G. T. Knight and B. Pepper, *Tetrahedron*, **27**, 6201 (1971).
9. K. Yokose, T. Arai, and T. Shiga, *J. Soc. Rubber Ind. Jpn.*, **33**, 513 (1960).
10. W. Wilfred and D. Scott, *Standard Method of Chemical Analysis*, Vol. 1, The Technical Press, London, 1939.

11. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, 1953, p. 579.
12. T. C. Ang and L. M. Gan, unpublished results.
13. G. J. Wilson, Polysar Ltd., Sarnia, Canada, private communication.
14. C. G. Moore and W. F. Watson, *J. Polym. Sci.*, **19**, 237 (1956).
15. L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Wiley, New York, 1964, (a) p. 269, (b) p. 271, (c) pp. 304 and 308, (d) p. 307, (e) p. 52.
16. K. Nakanishi, *Infrared Absorption Spectroscopy—Practical*, Holden-Day, San Francisco, 1962, (a) p. 50, (b) p. 222.
17. L. S. Zhrebkova, A. S. Shashkov, T. N. Dynmayeva, E. Ya. Devirts, and F. A. Galil-Ogly, *Vysokomol. Soedin., Ser. A*, **11**(1), 227 (1969).
18. Infra-Red Spectrogram 15431, Sadtler Standard Spectra, Sadtler Research Laboratories, Pennsylvania.
19. E. Morita, *Rubber Chem. Technol.*, **49**, 1019 (1976).

Received November 20, 1978