

Quinoid-Sulphur Vulcanisation of Natural Rubber

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Quinoid vulcanisation of natural rubber activated by zinc oxide was compared with lead oxide activation. Results revealed that activation by lead oxide caused an adverse effect on thermal ageing of the vulcanisates. On the other hand, zinc oxide-activated quinoid vulcanisates showed good scorch safety, excellent resistance to thermal ageing and thermal reversion during overcure. By incorporating the sulphenamide-accelerated sulphur system into the zinc oxide-activated quinoid cure, a higher level of technological properties coupled with excellent resistance to thermal ageing and overcure-reversion were obtained. These mixed quinoid-sulphur systems were also found to be suitable for use at high-temperature curing.

'Quinoid' vulcanisation refers to vulcanisation of rubbers by p-quinone dioxime (known as GMF) and its derivative such as p-quinone dioxime dibenzoate (DGMF). Quinoid compounds have been extensively used in the vulcanisation of butyl rubber giving excellent thermal and electrical properties^{1,2}. Quinoid-cured styrene-butadiene rubber was also reported to have good have resistance^{3,4}. Several papers⁵⁻⁸ have discussed the mechanism of quinoid vulcanisation of butyl rubber. It was proposed that the quinoid cross-linking reactions of natural rubber (NR) were similar to those of butyl rubber⁹. Unlike butyl rubber, quinoid vulcanisation of NR has not been used commercially. The disadvantages of using the quinoid-cure for NR are short scorch safety and inferior ageing properties. The conventional use of red lead (Pb_3O_4) as oxidant during crosslinking reactions may be responsible for the poor oxidative ageing. It is interesting to note that red lead can

be satisfactorily replaced by zinc oxide (ZnO) and litharge (PbO) for activating the quinoid cure of NR^{9,10}. The resulting vulcanisates exhibited good resistance to thermal ageing and overcure reversion. However, its tensile strength was poor¹⁰. Sulphur and organic accelerator such as benzothiazyl disulphide have been used in conjunction with quinoid cure of butyl rubber, NR, and NR/polybutadiene blend to achieve better tensile and ageing properties^{1,11-14}.

This paper has two objectives: to investigate the possibility of further improving the tensile and ageing properties of quinoid-vulcanisates of NR by incorporating the accelerated-sulphur cure system into the ZnO activated quinoid mixes; and to compare in greater detail ZnO and PbO in activating the quinoid cure of NR paying particular attention to the retention of tensile properties of quinoid vulcanisates after oxidative ageing at high temperature.

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EXPERIMENTAL

Materials

Natural rubber (SMR 5); PbO (Anchor Chemicals); ZnO (Durham); p-quinone dioxime dibenzoate (DGMF, Rubber Re-generation); dicumyl peroxide (Dicup R, Hercules); N-cyclohexyl-2-benzothiazole-sulphenamide (Santocure CBS, Monsanto); 2-mercaptobenzimidazole (Antioxidant MB, Bayer) and polymerised 2,2,4-trimethyl, 1,2-dihydro-quinoline (Permanex TQ, ICI) are commercial products which were used as received.

Preparation and Testing of Vulcanisates

The mixes were prepared on a two-roll laboratory mill at 70°C. Curing characteristics of thermal reversion during overcure of the mixes were examined by the Mooney scorch test and Monsanto rheometer. The mixes were subsequently vulcanised at 160°C in a steam-heated press until the maximum state of cure was attained. The tensile properties¹⁵, hardness¹⁶, resilience¹⁷ and compression set¹⁸ were determined using standard methods. Thermal-ageing of vulcanisates was carried out in a circulated air oven at 100°C.

RESULTS AND DISCUSSION

Gum Quinoid Semi-EV Mixes

Gum quinoid, semi-EV, and quinoid semi-EV systems are compared in *Table 1*. In accelerated-sulphur cure systems, the amount of sulphenamide accelerator, CBS, was fixed at 0.6 part per hundred of rubber (p.p.h.r.) and the sulphur ranged from 0.8 p.p.h.r. to 1.2 p.p.h.r. Within this range of CBS/sulphur ratios, the cure systems are generally known as semi-efficient vulcanisation or 'semi-EV' systems. Hence, the mixtures of quinoid and accelerated-sulphur systems in *Table 1* (*Mixes 3-8*) are now referred as 'Quinoid

semi-EV'. Since it has been established that 3 p.p.h.r. of DGMF was sufficient to produce the optimum properties of quinoid-NR vulcanisates¹⁹, this amount was used. The addition of 0.5 p.p.h.r. Dicup-R improved the tensile properties of metal oxide-activated quinoid-NR vulcanisates¹⁰. The levels of CBS accelerator (0.6 p.p.h.r.) and sulphur (0.8-1.2 p.p.h.r.) as used in the semi-EV systems were lower than those conventionally recommended. These levels were used so that the combination of quinoid and semi-EV systems could give an optimum level of chemical crosslinks sufficient to provide a good level of technological properties.

The technological properties as shown in *Table 1* clearly show that the addition of accelerated-sulphur system conferred a higher level of tensile strength. Lower compression set, higher modulus and higher resilience were also obtained. This better level of technological properties could be attributed to the higher degree of crosslinking as reflected by the increase in M300 values. It is expected that quinoid semi-EV vulcanisates consist of a mixture of quinoid and sulphidic crosslinks. With respect to scorch time, the use of accelerated-sulphur systems did not result in any increase in the scorch safety of quinoid semi-EV mixes. Data on tensile properties after ageing at 100°C for three days show that the addition of accelerated sulphur systems into the quinoid cure gave a higher retention of tensile strength after thermal ageing provided the lead oxide (PbO) was left out in the mix formulations. It is interesting to note that the use of PbO (*Mixes 4,6,8, Table 1*) seriously impaired the normally good ageing properties of quinoid semi-EV vulcanisates. After examining earlier published results¹⁰, it is realised that a similar adverse effect appeared in the PbO-DGMF-NR system. However, the adverse effect was more pronounced in

TABLE 1. TECHNOLOGICAL PROPERTIES OF GUM AND QUINOID SEMI-EV VULCANISATES

Property	Gum quinoid	Gum semi-EV	Quinoid semi-EV					
	1	2	3	4	5	6	7	8
SMR 5	100	100	100	100	100	100	100	100
DGMF	3		3	3	3	3	3	3
ZnO	5	3	3	3	3	3	3	3
PbO	3			4		4		4
Stearic acid	2	2	2	2	2	2	2	2
Dicup-R	0.5		0.5	0.5	0.5	0.5	0.5	0.5
CBS		0.6	0.6	0.6	0.6	0.6	0.6	0.6
Sulphur		1.0	0.8	0.8	1.0	1.0	1.2	1.2
Mooney scorch, T_5 at 120°C (min)	14.1	26.5	11.2	11.1	13.0	11.7	13.6	10.8
Rheometer cure rate at 160°C (min)	3	2.2	6.6	6.3	5.4	4.8	5.7	3.3
Maximum cure time at 160°C (min)	20	10	35	16	25	18	25	20
Tensile strength (MPa)	12.6	15.8	17.5	18.6	23.5	20.3	20.5	19.0
Elongation at break (%)	660	770	650	630	670	630	670	610
M300 (MPa)	1.3	1.2	1.8	1.9	2.0	2.0	2.1	2.1
Hardness (IRHD)	34.1	35.2	40.4	41.0	41.2	42.0	42.1	43.9
Resilience (%)	83.1	87.0	88.4	90.3	90.1	91.7	91.7	92.9
Compression set after 24 h at 70°C (%)	51.4	31.9	27.5	30.4	26.6	29.0	26.1	28.2
Aged 3 days at 100°C (% retention)								
Tensile strength	28.9	37.3	70.3	42.2	53.6	13.4	47.6	14.4
Elongation at break	78.8	77.9	84.6	82.5	82.1	55.6	74.6	57.4
M300	84.2	100	112	100	122	97	110	68

the quinoid semi-EV vulcanisates than in the quinoid-NR vulcanisates. To further investigate the adverse effect of using the oxidant PbO, mixes shown in *Table 2* were studied. Increasing amounts of PbO were added in the semi-EV and quinoid semi-EV mixes. Results on retention of tensile strength after ageing at 100°C show clearly that PbO brought about a rapid deterioration of tensile strength after ageing. Furthermore, results reveal that the deterioration of tensile strength was more serious in the semi-EV mixes than in the quinoid semi-EV mixes. These results confirm that the use of PbO

(or Pb_3O_4) in the quinoid cure is not desirable with respect to ageing properties even though the quinoid mix containing PbO gave excellent resistance to thermal reversion during overcure¹⁰. Therefore, to obtain the best resistance to thermal ageing, it is advisable to use ZnO to activate the quinoid cure of NR instead of a mixture of ZnO and PbO.

Filled Quinoid Semi-EV Mixes

The influence of HAF black and anti-oxidants on the ZnO activated quinoid semi-EV mixes are shown in *Table 3*.

TABLE 2. EFFECT OF LEAD OXIDE ON THE TECHNOLOGICAL PROPERTIES OF GUM SEMI-EV AND QUINOID SEMI-EV VULCANISATES

Property	Mix No.							
	1	2	3	4	5	6	7	8
SMR 5	5	100	100	100	100	100	100	100
ZnO	3	3	3	3	3	3	3	3
PbO	—	2	4	6	—	2	4	6
Stearic acid	2	2	2	2	2	2	2	2
CBS	1	1	1	1	1	1	1	1
Sulphur	1	1	1	1	1	1	1	1
DGMF	—	—	—	—	3	3	3	3
Mooney scorch, T ₅ at 120°C (min)	38.1	10.6	8.2	6.9	19.0	11.9	7.6	6.7
Maximum cure time at 160°C (min)	11	11	11	11	11	11	11	11
Tensile strength (MPa)	21.8	20.5	22.1	26.6	17.6	22.7	15.2	20.1
Elongation at break (%)	850	790	760	780	670	700	640	650
M300 (MPa)	1.1	1.3	1.4	1.5	1.7	1.8	1.8	1.9
Hardness (IRHD)	33.0	36.0	37.0	37.0	39.5	40.0	41.0	42.0
Resilience (%)	81.3	86.4	86.8	86.0	88.8	88.4	89.2	88.0
Compression set after 24 h at 70°C (%)	23.8	19.9	21.2	18.7	27.5	25.1	32.8	28.9
Percentage retention of tensile strength after ageing at 100°C for								
2 days	30.3	4.0	5.1	3.9	97.8	63.5	60.9	45.8
3 days	36.4	2.9	3.0	2.1	91.5	48.4	55.1	35.8
4 days	23.3	a	a	a	77.4	35.2	41.3	28.8

^aSamples were very sticky after ageing.

In comparison with the gum guinoid semi-EV vulcanisates (*Table 1*), these HAF-filled vulcanisates possessed a higher level of tensile strength, modulus and hardness. The scorch time was shortened to about 6.5 min. A variation of sulphur from 0.8 p.p.h.r. to 1.2 p.p.h.r. had negligible effect on the technological properties.

With respect to ageing, the unprotected vulcanisates (*Mixes 1, 3, 5, Table 3*) still had about 40% of the original tensile strength after ageing at 100°C for three days. A significant improvement on this thermal ageing property was achieved

by using a mixture of antioxidants, Permanax TQ and Vulcanox MB. In cases of protected vulcanisates, the retention of tensile strength after ageing was around 85%. Another benefit of using these antioxidants was that the scorch time was increased from about 6.5 min to about 10 min. On the other hand, the use of antioxidants decreased slightly the unaged tensile strength, resilience and increased the compression set and heat build-up. This is related to the fact that the antioxidants could have undergone reaction with some of the curatives. This results in the loss of chemical cross-

TABLE 3. TECHNOLOGICAL PROPERTIES OF FILLED QUINOID SEMI-EV VULCANISATES

Property	Mix No.					
	1	2	3	4	5	6
SMR 5	100	100	100	100	100	100
ZnO	3	3	3	3	3	3
Stearic acid	2	2	2	2	2	2
DGMF	3	3	3	3	3	3
Dicup-R	0.5	0.5	0.5	0.5	0.5	0.5
HAF black	50	50	50	50	50	50
Dutrex R	5	5	5	5	5	5
Santocure CBS	0.6	0.6	0.6	0.6	0.6	0.6
Sulphur	0.8	0.8	1.0	1.0	1.2	1.2
Permanax TQ	—	1	—	1	—	1
Vulkanox MB	—	1	—	1	—	1
Mooney scorch at 120°C, T ₅ (min)	6.3	10.6	6.9	10.0	6.6	10.0
Rheometer cure rate at 160°C (min)	5.9	6.6	6.0	7.1	6.0	6.6
Maximum cure time at 160°C (min)	15	15	15	15	15	15
Tensile strength (MPa)	30.1	27.8	29.4	26.8	29.3	27.4
Elongation at break (%)	550	520	530	520	500	550
M300 (MPa)	14.8	11.8	14.1	11.2	15.0	12.1
Hardness (IRHD)	66.4	67.8	66.7	69.3	68.8	70.2
Resilience (%)	62.9	59.1	62.9	57.4	65.0	58.4
Compression set after 24 h at 70°C (%)	33.3	43.2	33.3	43.9	33.1	41.9
Aged 3 days at 100°C (% retention)						
Tensile strength	41.5	87.6	43.9	84.5	41.0	84.5
Elongation at break	56.4	86.5	56.6	80.8	56.0	74.5
M300	79.7	122.0	91.3	140.0	—	138.0
Heat build-up after 25 min at 100°C (°C) (0.44 cm stroke, 16.4 kg load)	28	51	24	48	25	36

links as reflected by the decrease in M300 when the antioxidants were used. This statement is also supported by the lower rheometer torque modulus of black-filled quinoid semi-EV mix when the antioxidants were used (*Mixes 3 and 4 in Figure 1*).

Thermal Reversion during Overcure

The Monsanto rheographs at 190°C for gum ZnO-quinoid, gum quinoid

semi-EV, filled quinoid semi-EV and protected quinoid semi-EV compounds (*Formulations 1-4 respectively in Table 4*) are shown in *Figure 1*. Even at a high cure temperature of 190°C, both gum ZnO-quinoid and gum quinoid semi-EV mixes gave excellent resistance to reversion during overcure. In the presence of black and antioxidants, the resistance to overcure reversion was slightly inferior to that of the gum mix.

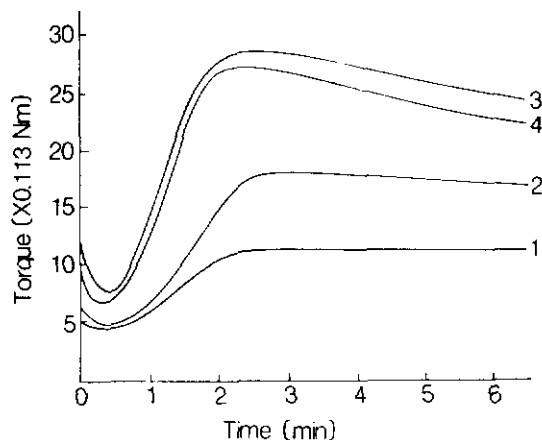


Figure 1. Monsanto rheograph for mixes shown in Table 4 at 190°C.

TABLE 4. MIX FORMULATIONS FOR CURING BEHAVIOUR SHOWN IN FIGURE 1

Compound	Mix No.			
	1	2	3	4
SMR 5	100	100	100	100
DGMF	3	3	3	3
ZnO	5	3	3	3
Dicup-R	0.5	0.5	0.5	0.5
Stearic acid	2	2	2	2
Santocure CBS	—	0.6	0.6	0.6
Sulphur	—	1.0	1.0	1.0
HAF black	—	—	50	50
Dutrex R	—	—	5	5
Permanax TQ	—	—	—	1
Vulkanox MB	—	—	—	1

High Temperature Curing of Quinoid Semi-EV Mixes

The excellent resistance to overcure reversion at 190°C for quinoid semi-EV mixes indicates that these mixes could be suitable for use at high temperature curing. To investigate this possibility, technological properties of some gum and HAF-filled quinoid semi-EV mixes (Table 5) vulcanised at 160°C and at 180°C were examined. Cure time corresponding to the maximum state of cross-

linking was chosen for each mix. The results as shown in Table 5 showed that there was little loss of technological properties as cure temperature was raised from 160°C to 180°C. This result coupled with the excellent resistance to overcure reversion indicate that the quinoid semi-EV mixes could meet the requirements for high temperature curing of rubber articles. In contrast, when the accelerated-sulphur NR mixes were subjected to high temperature curing, a lower level of technological properties was invariably obtained²⁰

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REFERENCES

1. SMITH, W.C. (1964) The Vulcanisation of Butyl, Chlorobutyl and Bromobutyl Rubber. *Vulcanisation of Elastomers (Alli ger, G. and Sjothun, I.J., ed)*, pp. 245-248. New York: Reinhold.
2. HAWORTH, J.P. (1948) Vulcanisation of Butyl Rubber with p-Quinone Dioxime and Its Derivatives. *Ind. Engng Chem.*, 40, 2314.
3. ANTONOV, B.N. AND ZHAVORONOK, S.G. (1970) Chemical Stress Relaxation in Vulcanisates Obtained with p-Quinone Dioxime. *Soviet Rubb. Technol.*, 29(9), 19.

TABLE 5. EFFECT OF CURE TEMPERATURE ON THE TECHNOLOGICAL PROPERTIES
OF QUINOID SEMI-EV VULCANISATES

Property	Quinoid semi-EV vulcanisate											
	1		2		3		4		5		6	
SMR 5	100		100		100		100		100		100	
DGMF	3		3		3		3		3		3	
ZnO	3		3		3		3		3		3	
Stearic acid	2		2		2		2		2		2	
Sulphur	1		1		1		1		1		1	
Santocure CBS	0.9		1.2		1.5		0.9		1.2		1.5	
Dutrex R							5		5		5	
HAF black							50		50		50	
Cure temperature (°C)	160	180	160	180	160	180	160	180	160	180	160	180
Cure time (min)	15	5	15	5	15	5	12	4	12	4	12	4
Tensile strength (MPa)	17.9	18.1	20.7	19.7	19.7	17.5	28.9	33.4	29.9	33.5	31.4	32.5
Elongation at break (%)	700	750	705	700	685	700	510	490	490	490	470	480
M300 (MPa)	1.5	1.4	1.5	1.5	1.6	1.4	14.6	16.7	14.7	16.5	16.3	16.4
Aged 3 days at 100°C (% retention)												
Tensile strength	39.9	42.5	44.1	30.9	40.9	55.3	61.6	62.3	64.4	65.7	57.4	69.8
Elongation at break	72.9	62.7	73.8	71.4	68.6	65.7	62.7	65.3	65.3	65.3	59.6	64.6
M300	116	173	148	125	171	204	111	114	111	121	—	—
Hardness (IRHD)	39.4	37.5	39.5	38.5	40.4	39.2	68.4	66.7	67.6	65.2	69.7	67.7
Resilience (%)	88.4	86.8	87.6	87.2	88.0	86.8	63.9	63.9	65.3	63.9	62.0	65.0
Compression set after 1 day at 70°C (%)	29.7	35.1	27.8	34.2	26.1	30.1	32.3	36.6	40.5	37.3	32.5	35.6
Heat build-up after 25 min at 100°C (°C) (0.44 cm stroke, 16.4 kg load)	—		—		—		22	24	21	22	21	21

4. GHATGE, N.D. AND MALDAR, N.N. (1979) The Vulcanisation of Styrene Butadiene Rubber with 2-Pentadecyl-Benzoquinone Dioxime. *Rubb. Chem. Technol.*, **52**(2), 353.
5. REHNER, J. JR. AND FLORY, P.J. (1946) Vulcanisation Reactions in Butyl Rubber. *Ind. Engng Chem.*, **38**, 500.
6. YOKOSE, K., ARAI, T. AND SHIGA, T. (1960) Mechanism of the Vulcanisation of Butyl Rubber by Quinone Dioxime. *J. Soc. Rubb. Ind. Japan*, **33**, 513.
7. GAN, L.M., SOH, G.B. AND ONG, K.L. (1977) Vulcanisation of Butyl Rubber by p-Quinone Dioxime. *J. appl. Polym. Sci.*, **21**, 1771.
8. GAN, L.M. AND CHEW, C.H. (1979) Vulcanisation of Butyl Rubber by p-Quinone Dioxime Dibenzoate. *J. appl. Polym. Sci.*, **24**, 371.
9. GAN, L.M., CHEW, C.H. AND LIM, L.E. (1978) Quinoid Vulcanisation of Natural Rubber. *J. Rubb. Res. Inst. Malaysia*, **26**(2), 33.
10. CHEW, C.H., GAN, L.M. AND LOO, C.T. (1980) Vulcanisation of Natural Rubber by p-Quinone Dioxime Dibenzoate. *J. Rubb. Res. Inst. Malaysia*, **28**(3), 138.
11. METZELER AKTIENGESELLSCHAFT (1966) Method for Improving the Chemico-Physical Properties of Blends Consisting of Natural Rubber and cis-1,4-Polybutadiene. *Germ. Pat. No. 1 051 333*.
12. ONG, K.L., LAWSON, D. AND GAN, L.M. (1972) Aspects of the Vulcanisation Mechanism of Quinone Dioxime System. *J.I.R.I.*, **6**(1), 16.
13. GAN, L.M. AND LIM, L.E. (1976) Some Aspects of Sulfur-Quinoid Cured Natural Rubber. *Singapore Natn. Inst. Chem. Bull.* **4**, 91.
14. GHATGE, N.D. AND MALDAR, N.N. (1981) Vulcanisation of Butyl Rubber: Curative Effects of 2-Pentadecylbenzoquinone Dioxime. *Rubb. Chem. Technol.*, **54**(4), 692.
15. INTERNATIONAL STANDARDS ORGANISATION (1976) Determination of Tensile Stress-Strain Properties of Vulcanized Rubbers. *ISO 37*.
16. INTERNATIONAL STANDARDS ORGANISATION (1975) Vulcanized Rubbers - Determination of Hardness (Hardness between 30 and 85 IRHD). *ISO 48*.
17. BRITISH STANDARD INSTITUTION (1963) Determination of Rebound Resilience. *BS 903 Part A8*.
18. INTERNATIONAL STANDARD ORGANISATION (1972) Vulcanized Rubber - Determination of Compression Set under Constant Deflection at Normal and High Temperatures. *ISO 815*.
19. ONG, K.L., LAWSON, D. AND GAN, L.M. (1971) Vulcanisation Studies of Natural Rubber Cured with Quinone Dioxime Dibenzoate. *Rubb. J.*, **49**.
20. LOO, C.T. (1975) Studies on Sulphenamide-accelerated Sulphur Systems for High Temperature Vulcanization of Natural Rubber. *Proc. Int. Rubb. Conf. Kuala Lumpur 1975*, **5**, 31.