

EFFECT OF RETARDERS ON CURE CHARACTERISTICS, KINETICS OF VULCANIZATION AND PHYSICAL PROPERTIES OF NATURAL RUBBER

Sara Chandy and Baby Kuriakose

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The effects of three retarders—benzoic acid, N-nitrosodiphenyl amine and N-(cyclohexylthio) phthalimide—on cure characteristics, kinetic parameters and physical properties of thiazole and sulphenamide accelerated natural rubber compounds were evaluated. The results indicated that the effect of the retarders depends on the type of accelerator used. The difference in the effect of the retarders on scorch and cure times of the compounds is explained based on kinetic parameters of the vulcanization reaction in the presence of the retarders. These observations agreed well with the already established reaction mechanisms of cure retardation.

Key words:— Natural rubber, Accelerators, Retarders, Scorch time, Cure time, Sulphur, Vulcanization kinetics.

Baby Kuriakose (for correspondence) and Sara Chandy, Rubber Research Institute of India, Kottayam-686 009, India.

INTRODUCTION

Vulcanization is the process by which chemical crosslinks are introduced between polymer chains, as a result of which the polymer attains higher strength and other elastomeric properties. For achieving high productivity, vulcanization time of the rubber compound should be as brief as possible and the use of ultra accelerators helps to attain shorter curing cycles. However, ultra accelerators adversely affect processing safety and storage life of the compounds. In the vulcanization of thick articles, the possibility of having uneven state of cure between the surface of the product and its core is very high because of very poor thermal conductivity of elastomers. Normally, in such cases, the surface will be overcured several fold while the core remains highly undercured. In order to make a balance between these

two states of cure and to ensure adequate processing safety, cure retarders are used in rubber compounds. Retarders prolong the induction period before the onset of vulcanization. An efficient retarder should influence the induction period, without affecting the actual curing time or the extent of vulcanization.

Different chemicals have been reported to function as cure retarders in rubber compounds (Trivette *et al.*, 1977). Carboxylic acids, anhydrides, nitroso compounds and N-substituted phthalimide derivatives have been widely used as cure retarders. Many of these retarders are highly effective in delaying the onset of vulcanization but have some undesired effects such as extending the vulcanization time, reducing crosslink density, discolouring the product or adversely affecting the activity of powerful antiozonants

such as p-phenylene diamines. The mechanism of cure retardation of N-(cyclohexylthio) phthalimide (CTP) had been studied in detail by different research groups (Son, 1973; Leib *et al.*, 1970; Datta *et al.*, 1986). The action of prevulcanization inhibitors such as N-thiosulphonamide and dithiotrichloromethane was reported by Hopper (1973). In this paper observations on the effects of three different types of cure retarders, namely, benzoic acid (BA), N-nitrosodiphenylamine (NDA) and N-(cyclohexylthio) phthalimide (CTP), on cure characteristics, kinetics of vulcanization and physical properties of natural rubber compounds containing a thiazole accelerator (Dibenzthiazyl disulphide-MBTS) and that containing a sulphenamide accelerator (N-Morpholinothio - 2 - benzothiazole - MOR) are described.

EXPERIMENTAL

Materials

Natural rubber (NR) used for the study was ISNR 3 (light colour) grade. Benzoic acid used was of laboratory reagent grade while NDA, CTP, MBTS, MOR and other ingredients used were of commercial grade. The formulations of the compounds are given in Tables 1 and 2. The dosage of MBTS and MOR was selected in such a way that their compounds have almost the same scorch and cure times. The dosage of retarders was varied from 0 to 0.6 phr in each case. The compounds were made from the same masterbatch consisting of rubber, zinc oxide, stearic acid and antioxidant, in a two-roll laboratory mill.

Testing

Scorch time of the compounds was determined at 120°C using a Mooney viscometer. Cure characteristics and kinetic parameters were evaluated using a Monsanto Rheometer

100. The range of temperatures selected for kinetic studies was 140°C to 170°C. The angle of oscillation of the rotor was 3° and the frequency 100 cycles per min. Compounds were moulded in a steam heated hydraulic press to their respective curing time to get different test samples. The moulded samples were tested for tensile properties as per ASTM D 412.

A general equation for the kinetics of a first order chemical reaction can be written as

$$\ln(a-x) = -kt + \ln a \quad \dots\dots (1)$$

where, a = initial reactant concentration,
 x = reacted quantity at time 't', and
 k = first order reaction rate constant

For the vulcanization reaction of rubber, the rate of crosslink formation is usually monitored by measuring the torque developed during its course by using a curometer and the torque values thus obtained are proportional to the modulus of the vulcanizate. Hence if a physical property such as modulus is being measured rather than the change in reactant concentration, then the following substitutions can be made

$$(a-x) = (M_{\alpha} - M) \quad \dots\dots (2)$$

$$a = (M_{\alpha} - M_0) \quad \dots\dots (3)$$

where, M_{α} = the maximum modulus,
 M_0 = the minimum modulus
 and M = the modulus at time 't'.

Substituting torque values for modulus, we get

$$(a-x) = (M_h - M_t) \quad \dots\dots (4)$$

where, M_h = the maximum torque developed, and
 M_t = the torque at time 't'.

Table 1. Formulation of MBTS based compounds

[illegible]

Table 2. Formulation of MOR based compounds

[illegible]

If the reaction is of first order, a plot of $\ln(M_h - M_t)$ against 't' should give a straight line whose slope will be the specific reaction rate constant 'k'.

To find out the activation energy of the vulcanization reaction, modified Arrhenius equation is used

$$t_{90} = Ae^{E/RT} \quad \dots\dots (5)$$

$$\log t_{90} = \log A + \frac{E}{2.303 RT} \quad \dots\dots (6)$$

where, E = activation energy

t_{90} = time in min to attain 90 per cent of maximum torque

T = absolute temperature °K

A plot of $\log t_{90}$ vs $1/T$ gives a straight line, from the slope of which E is calculated.

RESULTS AND DISCUSSION

Scorch time

Figure 1 shows the effect of three different retarders on scorch time. In the compound

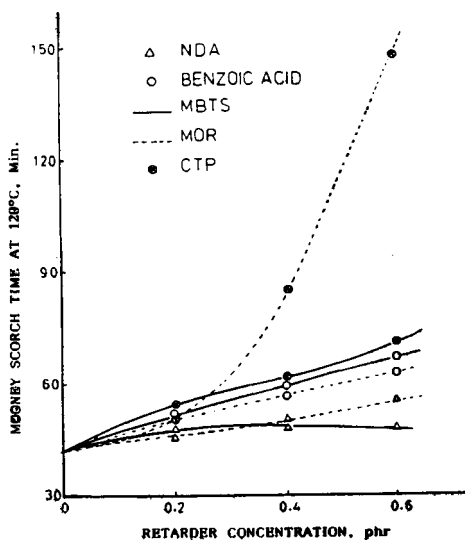
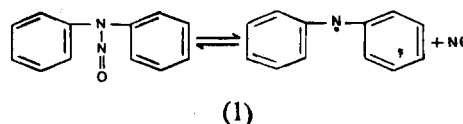


Fig. 1. Effect of type of retarder and dosage on scorch time at 120°C

containing MBTS, both benzoic acid and CTP showed a steady increase in scorch time with increase in concentration of retarders. However, this effect was only marginal with NDA in the MBTS accelerated compound. It can also be noted that the difference between the performance of BA and CTP in improving scorch safety of the MBTS based compound was only marginal. The effect of NDA on scorch time of the MOR based compound was slightly better than its effect in MBTS accelerated compounds especially at a higher dosage. But, the effect of BA in this case was inferior to its effect in the MBTS accelerated compound. In the case of NDA, the retardation effect is due to its dissociation products. On heating above 100°C, NDA dissociates according to the following scheme.

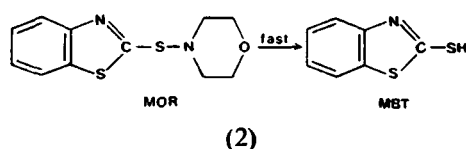


The liberated nitric oxide is reported to affect the reaction of both sulphur and accelerator with rubber (Dibbo *et al.*, 1963). This results in scorch delay in compounds containing NDA. Organic acids are known to react with basic ingredients in the formulation which would otherwise accelerate the onset of cure. However, the effect of BA on the MOR accelerated compound is found to be less than its effect on the MBTS accelerated compound because of the chemical incompatibility between the acidic retarder and the amine derived sulphenamide accelerator as reported by Luecken and Harold (1977).

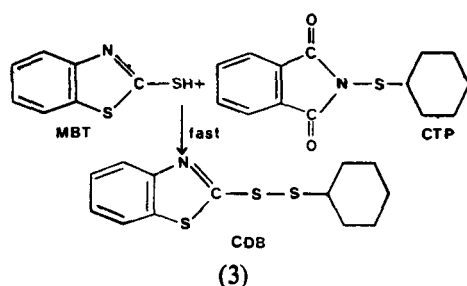
CTP improved the scorch safety of the MOR based compound to a very great extent and this effect was much higher than its effect on the MBTS based compound. This marked difference in the behaviour of CTP towards MBTS and MOR accelerated compounds

can be explained based on the mechanism of retardation by CTP.

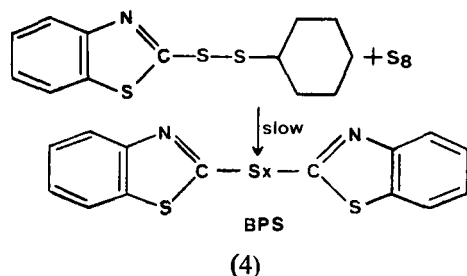
In the presence of rubber and activators, both MBTS and MOR generate MBT and this decomposition is very rapid in the case of MOR (Datta *et al.*, 1986).



The MBT thus formed reacts very rapidly with CTP to form 2-cyclohexyl dithiobenzothiazole (CDB).



This autocatalytic reaction continues until all the MOR is converted into CDB. Sulphur reacts with CDB to form bis (2-benzothiazyl) polysulphide (BPS) which is a crosslink precursor.

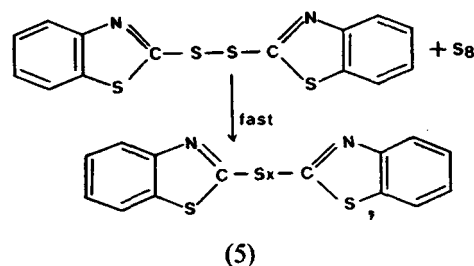


Thus, in the presence of CTP, MOR reacts with sulphur and rubber through BPS to form the crosslinks.

In the case of MBTS it takes two routes to form the crosslinks. (1) In the presence of CTP, it can follow the same route as in the case of MOR.



(2) MBTS can react directly with sulphur to form 2,2'-polythiobis (benzothiazole) very rapidly, which is again a crosslink precursor (Campbell and Wise, 1964a, 1964b).



Thus in the case of MBTS, CTP is less effective in prolonging the induction period compared to its effect in the MOR accelerated compound.

Cure time

Figure 2 shows the effect of retarders on the cure time (t_{90}) of MBTS and MOR accelerated NR compound at 150°C. In both these compounds, NDA had the least effect, and CTP the maximum, in extending the cure time of compounds. At lower dosages BA showed comparatively less effect in the MBTS accelerated compound than in the MOR based compound. However, this trend was reversed at a higher dosage of BA. This behaviour was expected because all acidic materials slow down the vulcanization reaction which is mainly electrophilic in nature. The increase in cure times of both MBTS and MOR accelerated compounds

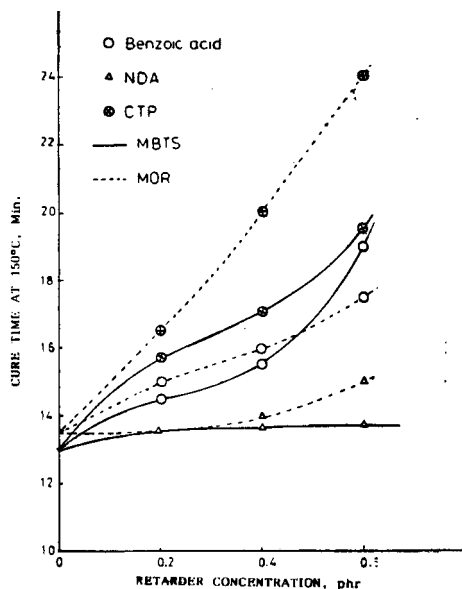
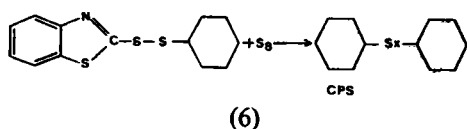


Fig. 2. Effect of type of retarder and dosage on cure time at 150°C.

was remarkable when CTP was used as the retarder, even at a lower dosage. This effect was more pronounced in the MOR based compound at a higher dosage of CTP. There are two probable reasons for this behaviour of CTP. As described in the previous section, the reaction between CDB and sulphur to form BPS is slow (scheme 4). In addition to this, CDB and sulphur react to form cyclohexyl polysulphide (CPS) which does not take part in the vulcanization reaction (Son, 1973).



Thus the effective quantity of sulphur available for crosslinking reaction is reduced when CTP is used. This observation is further supported by the change in kinetic parameters and is also reflected in some of the physical properties.

Kinetic parameters

Typical plots of $\ln(M_h - M_t)$ against 't' given in Fig. 3 indicated that the vulcanization reaction of compounds C_3 and F_3 is first order in nature. Typical Arrhenius plot of $\log t_{90}$ against $1/T$ of compound K_1 is shown in Fig. 4, from the slope of which, the activation energy is calculated. The first order rate constant k and the activation energy values at 150°C of the compounds containing different dosages of retarders are given in Figs. 5 and 6, respectively.

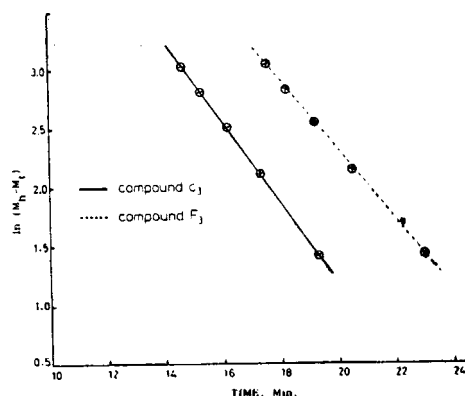


Fig. 3. $\ln(M_h - M_t)$ vs time for different extents of cure at 150°C of compounds C_3 and F_3 .

In the MOR accelerated compound the effect of retarders on rate constant k was less pronounced to their effect on the MBTS accelerated compound (Fig. 5). At dosages beyond 0.4 phr. the effect of BA was higher compared to that of the other two retarders. However, wide difference in the effect of retarders on the rate constant was noted for the MBTS accelerated compound. In this case also, BA reduced the rate constant drastically when its concentration exceeded 0.4 phr. This is due to the acidic nature of BA which exerted a permanent retardation effect on vulcanization. It has been reported that organic acids can interact with

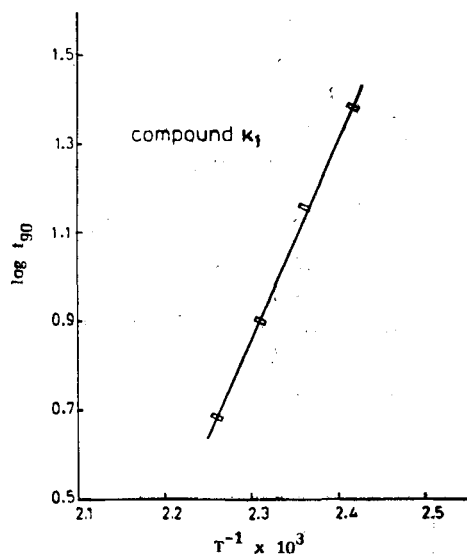
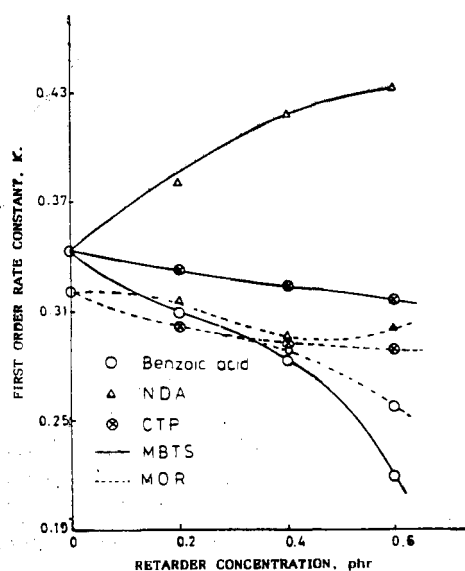
Fig. 4. Typical Arrhenius plot for compound K₁

Fig. 5. Effect of type of retarder and dosage on first order rate constant at 150°C

accelerator degradation/dissociation products to form compounds which exert comparatively less effect on the rate of vulcanization than the degradation products themselves (Dogadkin *et al.*, 1962). However,

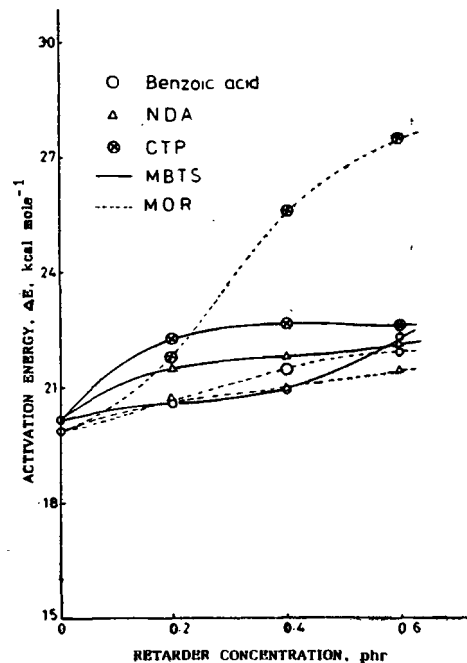


Fig. 6. Effect of type of retarder and dosage on activation energy at 150°C

scorch and cure times of compounds A₁, A₂ and A₃ were lower than those of compounds C₁, C₂ and C₃ due to the lower activation energy required for the reaction (Fig. 6). For both MBTS and MOR based compounds which contained NDA as retarder, the rate constant 'k' was much higher than that of the respective compounds which contained CTP and BA. At the same time, activation energy of the MBTS based compound containing NDA, was in between that of the compounds containing CTP and BA. However, in the case of the MOR based compounds, the one containing NDA had the lowest ΔE value, beyond 0.2 phr level. The combined effect of higher rate constant and comparable/lower ΔE values was reflected in reduced scorch and cure times of B₁, B₂, B₃ and those of E₁, E₂ and E₃.

In the case of NDA, when the temperature,

was raised to 140–160°C, there was hardly any retardation effect. This is because of the apparent difference in the ratio between the concentration of the radicals from NDA and that from the sulphur containing compounds. As the temperature is raised, dissociation of the polysulphide compounds into active molecules containing smaller number of sulphur atoms takes place and the crosslinking reaction proceeds at a faster rate (Dogadkin *et al.*, 1962). In MOR accelerated compounds also, the rate constants were in the order $\text{NDA} > \text{CTP} > \text{BA}$ and the activation energy requirement was in the order $\text{CTP} > \text{BA} > \text{NDA}$. Thus, the extended scorch and cure times of the compounds which contained CTP as retarder is due to higher activation energy required for the reaction and due to lower k values.

Physical properties

Physical properties of the vulcanizates from MBTS and MOR accelerated compounds are given in Tables 3 and 4, respectively. It is observed that physical properties of the MBTS accelerated compounds were not

significantly affected by the presence of any of the three retarders. There was marginal improvement in tensile strength, 300% modulus and rebound resilience in compounds containing NDA and CTP. Compression set of the compounds A_1 , A_2 , A_3 and that of C_2 and C_3 showed marginal improvement. However, the extent of crosslinking, as indicated by V_r values, was unaffected by the presence of retarders. In the MOR accelerated compounds also, physical properties were not seriously affected by the presence of any of the three retarders. However, the effect of NDA and CTP was contrary to their effect on the MBTS accelerated compounds, especially at a higher dosage. In this case, 300% modulus, elongation at break and tensile strength were reduced by the presence of NDA and CTP. Compression set showed marginal improvement in the case of compounds D_1 , D_2 , D_3 , F_2 and F_3 . It can also be noted that the extent of crosslinking was slightly lower for the compounds containing NDA and CTP compared to that of the control compound as indicated by V_r values. These observa-

Table 3. Physical properties of MBTS based compounds

Properties	Control	BA			NDA			CTP		
	K_1	A_1	A_2	A_3	B_1	B_2	B_3	C_1	C_2	C_3
Modulus 300% (MPa)	1.61	1.66	1.68	1.71	1.74	1.78	1.84	1.76	1.78	1.75
Elongation at break (%)	1184	1226	1221	1222	1207	1216	1228	1248	1255	1211
Tensile strength (MPa)	20.4	20.5	20.9	21.1	21.4	21.9	22.4	21.9	22.1	22.7
Hardness (Shore A)	34	34	34	34	34	34	34	35	35	35
Rebound resilience (%)	79.2	77.1	78.8	76.8	82.9	83.6	82.2	82.1	81.2	85.3
Compression set (%) 22 h, 70°C	22.0	19.8	20.3	18.1	23.0	25.0	24.0	22.0	18.4	19.2
Volume fraction of rubber in swollen sample (V_r)	0.203	0.201	0.200	0.199	0.203	0.209	0.210	0.201	0.200	0.197

Table 4. Physical properties of MOR based compounds

Properties	Control	BA			NDA			CTP		
	K ₂	D ₁	D ₂	D ₃	E ₁	E ₂	E ₃	F ₁	F ₂	F ₃
Modulus 300% (MPa)	1.87	1.97	1.99	1.99	1.84	1.84	1.78	1.84	1.82	1.76
Elongation at break (%)	1223	1201	1193	1200	1190	1153	1141	1186	1118	1095
Tensile strength (MPa)	23.7	23.9	24.3	24.6	22.6	22.1	22.4	22.7	22.6	22.4
Hardness (Shore A)	36	37	38	37	36	37	37	36	36	36
Rebound resilience (%)	85.0	87.0	86.5	85.0	88.3	89.2	88.1	87.7	84.5	85.3
Compression set (%) 22 h, 70°C	25.5	23.9	22.1	19.5	26.1	25.7	26.1	26.0	23.1	19.4
Volume fraction of rubber in swollen sample (V _r)	0.205	0.205	0.205	0.205	0.199	0.203	0.199	0.199	0.199	0.196

tions further support the various mechanisms described in the previous sections.

CONCLUSIONS

The following conclusions emanate from this study:

1. Among the three retarders evaluated, N-nitrosodiphenyl amine is the least effective in enhancing scorch safety of both MBTS and MOR accelerated natural rubber compounds. Benzoic acid is a more effective retarder than N - (cyclohexylthio) phthalimide in MBTS based NR compounds whereas, the latter is more effective in MOR based compounds.
2. Use of benzoic acid or CTP as retarder prolongs the optimum cure time of NR compounds and this effect is more pronounced in the case of CTP.
3. NR compounds containing CTP as retarder require higher energy of activation for the vulcanization reaction and the first order reaction rate constant of the compounds containing benzoic

acid is lower than that of compounds containing CTP or NDA.

4. Some of the physical properties of MOR accelerated NR compounds are adversely affected by higher dosage of NDA and CTP.

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