

Effect of curing systems and temperatures on the activity of retarder in natural rubber mixes

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The effect of vulcanization temperature (150° and 180°C) on the structure and technical properties of gum natural rubber vulcanizates with four different 2-(morpholinodithio)-benzothiazole (MDB) – sulphur ratios in presence of *N*-(cyclohexyl thio)-phthalimide (CTP, 0.5 phr) has been determined at the respective optimum cure times. The influence of curing system, temperature and retarder on (a) the chemical crosslink density, (b) the distribution of crosslink types, (c) the extent of sulphidic main chain modification and (d) the zinc sulphidic formation have been investigated. The network results have been correlated with the technical properties. Increasing the cure temperature by 30°C (from 150° to 180°C) does not alter the activity of CTP. It is effective in all curing systems, but effectiveness was maximum in the conventional system. At 0.5 phr level, CTP caused reduction in most technical properties.

INTRODUCTION

Reduced scorch time is a problem associated with high temperature curing. One way to increase the scorch time is to add retarder in compounding. It has been claimed recently^{1,2} that *N*-(cyclohexyl thio)-phthalimide (CTP) acts as an efficient retarder without having detrimental effect on the physical properties. Anand, Blackby and Lee³ have studied the effects of various levels of CTP upon the vulcanization behaviour of natural rubber gum stock containing conventional levels of sulphur and CBS. They have observed that the induction period increases with increasing level of CTP, but the effect decreases with increasing temperature. They have also shown that crosslink insertion is slightly retarded in the presence of CTP, whereas crosslink degradation is accelerated and the maximum crosslink is also reduced. Son *et al.*⁴ have also studied the mechanism of the CTP–MBT reaction and substantiated these findings. More recently workers at the Lomonsov Institute of Fine Chemical Technology in Moscow⁵ have shown indications of changes in the structure of NR vulcanizates when the well-known retarder *N*-nitrosodiphenylamine (NDPA) was added to the mix of conventional curing system (S 2.5, CBS 0.5 phr) at the vulcanization temperature of 143°C. Addition of retarder reduces the tensile strength and modulus significantly.

MDB is a sulphur donor-cum-primary-accelerator and by varying the ratio of sulphur to MDB, vulcanization systems grading from conventional to EV can be obtained⁶. In the present paper, we have studied the effect of curing temperature (150° and 180°C) on the activity of *N*-(cyclohexylthio)-phthalimide as retarder at 0.5 phr level in such graded systems. We have explained the results in terms of structure and technological properties of gum natural rubber vulcanizates.

EXPERIMENTAL

The composition of the different mixes is shown in *Table 1*. Their curing characteristics as obtained using a Monsanto Rheometer (R-100) are summarized in *Table 2*. Details of mixing, vulcanization, testing procedures, methods of determination of chemical crosslink density, types of crosslinks and crosslinking inefficiencies are as described earlier^{6–9}.

RESULTS AND DISCUSSION

It is evident from *Table 2* that Mooney scorch increases in presence of retarder and the percentage increase is maximum in the case of the conventional system. As expected, the optimum cure times increase in the presence of retarder. Reversion time (measured at 180°C) in general increases in all mixes except in mix A. The behaviour, however, could not be explained from the distribution of different types of crosslinks (*Table 8*).

The physical properties of the vulcanizates in the presence and in the absence of retarder are tabulated in *Tables 3* and *4*. At both curing temperatures retarder caused a decrease

Table 1 Composition of the mixes

Mix No.	A	A'	B	B'	C	C'	D	D'
NR	100	100	100	100	100	100	100	100
ZnO	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2
S	2.4	2.4	1.5	1.5	0.6	0.6	—	—
MDB	0.6	0.6	1.5	1.5	2.4	2.4	3.0	3.0
CTP	—	0.5	—	0.5	—	0.5	—	0.5

Table 2 Curing characteristics of different mixes using Monsanto rheometer (R-100)

Mix No.	A	A'	B	B'	C	C'	D	D'
Mooney scorch at 120°C (min)	36.0	88.0	50.0	80.0	63.0	85.0	84.0	108.0
Optimum cure time at 150°C (min)	19.0	26.0	17.0	22.0	23.0	29.0	49.0	55.0
Optimum cure time at 180°C (min)	3.9	4.5	3.7	4.2	4.1	4.8	9.1	9.5
Reversion time at 180°C (time required to reach 98% of maximum cure after the maximum has been attained)	6.5	6.0	4.8	5.2	7.0	11.0	14.0	16.0

Table 3 Physical properties of different mixes. (The values in parentheses are the results without retarder)

Curing temperature (°C)	Mix no.	Tensile strength (kg/cm ²)	Tear strength (kg/cm)	Modulus 300% (kg/cm ²)	Elongation at break (%)	Hardness (Shore A)
150	A'	220 (280)	33 (30)	20 (22)	780 (775)	42 (41)
	B'	235 (290)	38 (32)	21 (23)	770 (765)	41 (42)
	C'	260 (295)	31 (29)	19 (20)	780 (770)	40 (39)
	D'	180 (240)	21 (22)	13 (16)	810 (775)	34 (33)
180	A'	150 (210)	25 (24)	11 (14)	820 (805)	36 (35)
	B'	175 (240)	28 (28)	13 (17)	810 (755)	38 (36)
	C'	185 (230)	25 (26)	13 (16)	820 (765)	36 (35)
	D'	130 (185)	19 (21)	7 (10)	840 (830)	30 (30)

Table 4 Physical properties of different mixes. (The values in the parentheses are the results without retarder)

Curing temperature (°C)	Mix no.	Flex cracking (kilocycle)			Heat build-up ΔT (°C)
		Crack growth up to 0.5 in.	Complete failure	Resilience (%)	
150	A'	30 (22)	100 (155)	79.9 (81.8)	6.6 (5.5)
	B'	30 (25)	110 (130)	83.7 (85.7)	7.0 (6.0)
	C'	65 (20)	230 (125)	82.2 (78.7)	9.3 (8.0)
	D'	90 (55)	300 (115)	66.9 (56.7)	21.8 (15.5)
180	A'	250 (35)	350 (90)	73.3 (75.5)	9.5 (6.0)
	B'	215 (40)	350 (95)	76.1 (78.0)	14.8 (7.0)
	C'	200 (30)	400 (100)	72.4 (67.0)	19.3 (9.0)
	D'	300 (75)	500 (125)	58.4 (53.5)	36.3 (26.3)

in physical properties. For example, tensile strength, modulus, tear strength, and resilience are smaller, elongation at break and heat build-up are greater in the presence of retarder. However, the flexing properties are improved upon addition of retarder. The percentage of different physical properties retained after addition of retarder is shown in Tables 5 and 6.

Table 5 Percentage retained of physical properties after addition of retarder

Curing temperature	Mix no.	Tensile strength	Tear strength	Modulus	Elongation	Hardness
150	A'	78.6	110.0	90.9	100.6	102.4
	B'	81.0	118.7	91.3	101.6	97.6
	C'	88.1	106.9	95.0	101.3	102.6
	D'	75.0	95.5	81.2	104.5	103.0
180	A'	71.4	104.2	78.6	101.9	102.8
	B'	72.9	100.0	76.5	107.3	105.6
	C'	80.4	96.1	81.2	107.2	102.8
	D'	70.3	90.5	70.0	101.2	100.0

Table 6 Percentage retained of physical properties after addition of retarder

Curing temperature (°C)	Mix no.	Flex cracking (kilocycle)		Resilience	Heat build-up
		Crack growth up to 0.5 in.	Complete failure		
150	A'	136	65	97	120
	B'	120	85	98	117
	C'	325	184	104	116
	D'	164	261	118	141
180	A'	714	389	97	158
	B'	537	368	98	214
	C'	667	400	108	214
	D'	400	400	109	138

We have attempted to explain the effect of retarder in terms of changes of vulcanizate structure. Results of chemical characterization of vulcanizate network are given in Table 7 which also includes results of vulcanizates without retarder for comparison. It is evident that for all types of mixes (conventional to EV systems) and at both curing temperatures (150° and 180°C) chemical crosslink densities decrease by addition of retarder. However, the network combined sulphur did not change remarkably due to retarder. As a result of this, sulphur inefficiencies (E and E') increase in CTP-containing vulcanizates. This result indicates that the vulcanizate network contains a higher proportion of sulphur-containing main chain modifications in the presence of CTP. The lower crosslink density and increased main chain modifications are responsible for the changes in physical properties (lower strength, modulus, resilience and higher heat build-up). Intramolecular groups like cyclic sulphides can lower the strength properties because they inhibit strain-induced crystallization and hinder the flexibility of the rubber chain. The lower modulus and higher modifications of the main chain are responsible for the increased flexing

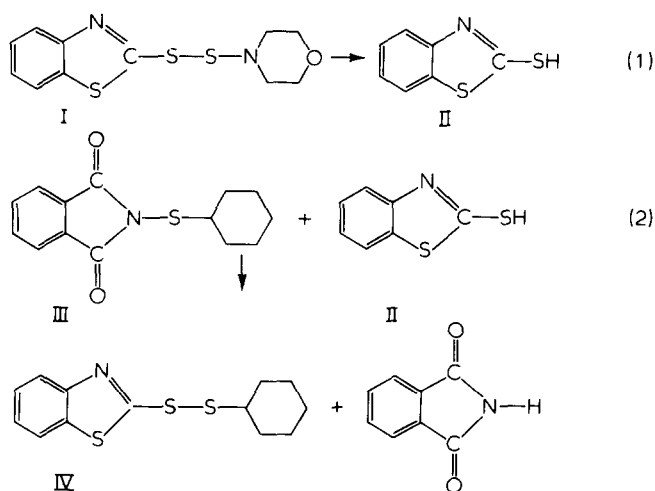
Table 7 Chemical characterization of vulcanizate networks. (Values in the parentheses are the results without retarders)

Cure temperature (°C)	Mix no.	$[2M_{C,chem}]^{-1} \times 10^5$ (g.mol/g.RH)	Network combined sulphur $\times 10^4$ (g.atom/g.RH)		Sulphur inefficiencies (atoms/chemical crosslinks)		$[S_C]$ (%) removed by PPh_3 treatment	$[S^{2-}]$ sulphide sulphur $\times 10^4$ (g ion/g RH)	F (sulphide ion/chemical crosslink)
			$[S_C]^a$	$[S_C]^b$	E^a	E^b			
150	A'	2.76 (3.45)	5.69 (5.15)	2.23 (2.68)	20.6 (14.9)	8.4 (7.8)	59 (48)	0.690 (0.460)	2.50 (1.33)
	B'	2.90 (3.62)	4.35 (4.21)	2.30 (2.28)	15.0 (11.6)	7.9 (6.3)	47 (46)	0.540 (0.500)	1.86 (1.36)
	C'	2.71 (3.53)	3.49 (3.50)	2.86 (2.33)	12.9 (9.9)	10.5 (6.6)	18 (33)	0.084 (0.05)	0.31 (0.14)
	D'	2.16 (2.65)	2.55 (2.06)	2.04 (1.32)	11.8 (7.8)	7.5 (5.0)	20 (36)	0.005 (negligible)	0.02 (negligible)
180	A'	2.05 (2.88)	5.20 (4.93)	2.86 (2.99)	25.4 (17.1)	13.9 (10.4)	45 (39)	0.810 (0.690)	3.95 (2.39)
	B'	2.51 (3.15)	3.88 (3.87)	2.75 (2.87)	16.5 (12.3)	10.9 (9.1)	29 (26)	0.690 (0.560)	2.75 (1.77)
	C'	2.35 (2.93)	3.70 (3.75)	2.99 (2.69)	15.7 (12.8)	12.7 (9.2)	19 (28)	0.122 (0.080)	0.52 (0.27)
	D'	1.61 (2.27)	2.23 (2.15)	1.76 (1.71)	13.8 (9.4)	10.9 (7.5)	21 (20)	0.008 (negligible)	0.05 (negligible)

^a Before PPh_3 treatment; ^b after PPh_3 treatment

properties. It has been shown earlier¹⁰ that the presence of appreciable main chain modification is conducive to good fatigue resistance and detrimental for good resilience. Dontsov *et al.*⁵ have shown that addition of the well-known retarder *N*-nitrodiphenylamine (NDPA) to a conventional natural rubber mix reduced the tensile strength and modulus significantly. Anand, Blackby and Lee³ have recently shown that CTP reduced the maximum crosslink density.

It appears that CTP probably changes the course of the MDB-accelerated sulphur vulcanization of natural rubber. On the basis of results obtained earlier with sulphenamide accelerators¹¹⁻¹³, it may be urged that in the first stage, MBT(II) is obtained from MDB(I) which undergoes metathesis reaction with CTP(III) producing 2-cyclohexyl dithiobenzothiazole (IV) and phthalimide.



It is very likely that IV is itself an accelerator of vulcanization. D'Amico *et al.*¹⁴ and Son¹⁵ have provided evidence that IV is a fairly good accelerator. Perhaps its activity is not as good as the conventional thiazoles and sulphenamides. This could explain some of the observations such as reduced strength properties and chemical crosslink densities, and increased sulphur inefficiencies. Further work particularly on the kinetics of sulphuration reactions, and detection of

Table 8 Distribution of different types of crosslinks. (Values in the parentheses are the results without retarder)

Cure temperature (°C)	Mix no.	Total crosslink density $[2M_{C,chem}]^{-1} \times 10^5$ (g mol/g RH)	Disulphidic and monosulphidic crosslinks $\times 10^5$ (g mol/g RH)	
			Polysulphidic crosslinks $\times 10^5$ (g mol/g RH)	Disulphidic and monosulphidic crosslinks $\times 10^5$ (g mol/g RH)
150	A'	2.76 (3.45)	1.02 (1.32)	1.74 (2.13)
	B'	2.90 (3.62)	0.95 (1.30)	1.95 (2.32)
	C'	2.71 (3.53)	0.64 (0.93)	2.07 (2.60)
	D'	2.16 (2.65)	0.27 (0.43)	1.39 (2.22)
180	A'	2.05 (2.88)	0.50 (0.33)	1.55 (2.55)
	B'	2.51 (3.15)	0.71 (0.99)	1.80 (2.16)
	C'	2.35 (2.93)	0.56 (0.60)	1.79 (2.33)
	D'	1.61 (2.27)	0.29 (0.22)	1.32 (2.05)

intermediate products at different stages of crosslinking is needed for any conclusive discussion.

In summary, at both curing temperatures CTP increases the network complexity and as a retarder it is effective in all curing systems (conventional, semi-EV and EV); but the effectiveness was found to be most pronounced in the conventional system (Table 2).

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