Effect of vulcanization temperature and synergism of accelerators on the network and technical properties of efficiently vulcanized natural rubber mixes

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The effect of an increase in vulcanization temperature from 150° to 180°C on the network structure and technical properties of gum natural rubber vulcanizates has been studied using six different binary combinations of tetramethyl thiuram disulphide (TMTD) and 2-(morpholinodithio)benzothiazole (MDB) at fixed sulphur level (0.6 parts per hundred rubber). On the basis of processing safety, reversion resistance, technical properties, retention of properties after aging and percentage losses in properties on increasing the vulcanization temperature by 30°C, if was found that the combination with MDB (1.2 phr) TMTD (0.6 phr) showed the best synergism of the two accelerators. Results of chemical characterization of vulcanizate networks have been correlated with their technical properties. At higher vulcanization temperature, lower degree of crosslink density and with increasing extent of sulphidic main chain modification, a reduction in strength, modulus, hardness and resilience resulted and brought about a higher compression set and a greater heat build-up during Goodrich flexometer tests. The better cut growth and flex properties of vulcanizates cured at 180°C have been explained on the basis of the distribution of different types of crosslinks and stress relaxation caused by lower crosslink density.

INTRODUCTION

In a previous publication we have reported that vulcanization temperature and vulcanization systems affect the network structure and properties of rubber vulcanizates[1]. It was concluded that a satisfactory balance between reversion resistance of the compounds, technological properties and aging resistance of the vulcanizates can be obtained by using a formulation with 0.6 phr sulphur, 2.4 phr 2-(morpholinodithio)-benzothiazole (MDB).

High temperature vulcanization is useful particularly for curing injection moulded stocks. Mahoney[2] has suggested a low sulphur–high sulphenamide (MDB) combination in the presence of a secondary accelerator such as tetramethyl thiuram disulphide (TMTD) for injection moulding of *cis*-1,4-polyisoprene. Such a combination of curatives is believed to give satisfactory cure conditions (i.e. scorch safety, cure rate, reversion resistance) and modulus of the vulcanizates. In a similar investigation made by Chavich *et al.*[3] on the effect of varying contents of dithiodimorpholine and sulphur on a 70:30 blend of NR and *cis*-1,4-polybutadiene, using *N*-oxydiethyelene-2-benzothiazole sulphenamide as accelerator, it was found that the best mechanical properties were obtained with 1.5 phr of sulphur donor, 0.6 phr of sulphur and 1.6 phr of accelerator. In the present paper we have studied the effect of a binary combination of accelerators obtained by varying the proportions of TMTD and MDB in efficient vulcanization systems on the technological properties and network structure of natural rubber gum vulcanizates cured at 150° and 180°C.

EXPERIMENTAL

Table 1 gives the formulation of the mixes studied. *Table 2* gives their curing characteristics at 150° and 180°C, obtained from a Monsanto Rheometer R-100.

Details of experimental techniques including vulcanizate

Table 1 Composition of the mixes

Mix No.	C	C_1	C_2	C_3	C_4	C_5	C_2'	C_2''
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	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
MDB	2.4	2.1	1.8	1.2	0.6	–	1.8	1.8
TMTD	–	0.3	0.6	1.2	1.8	2.4	0.6	0.6
CTP*	–	–	–	–	–	–	0.5	1.0

* *N*-(cyclohexylthio)phthalimide

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Table 2 Curing characteristics of different mixes

Mix No.	C	C_1	C_2	C_3	C_4	C_5	C_2'	C_2''
Mooney scorch at 120°C, t_5 (min)	63	35	30	19	15	11	37	39
Optimum cure time (min) at 150°C	23.0	11.5	10.5	9.0	8.0	7.0	11.5	13.0
Optimum cure time (min) at 180°C	4.10	2.75	2.50	2.25	2.10	2.00	3.20	3.50
Reversion time at 180°C (min) (time required to reach 98% of maximum cure after the maximum has been attained)	6.5	7.5	12.5	12.5	10	8.5	13.5	13.0

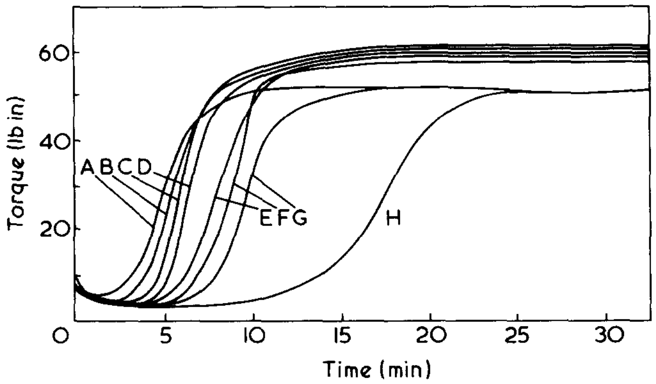

Figure 1 Rheographs of different mixes at 150°C. A, C_5; B, C_4; C, C_3; D, C_2; E, C_1; F, C_2'; G, C_2''; H, C

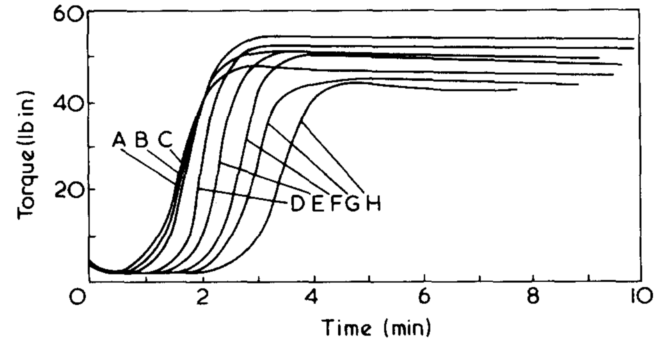

Figure 2 Rheographs of different mixes at 180°C. A, C_5; B, C_4; C, C_3; D, C_2; E, C_1; F, C_2'; G, C_2''; H, C

Table 3 Physical properties of different mixes

Curing temperature (°C)	Mix No.	Tensile strength (kg/cm^2)	Tear strength (kg/cm)	300% Modulus (kg/cm^2)	Elongation at break (%)	Hardness (shore A)
150	C	290	28	20	740	41
	C_1	315	32	23	720	44
	C_2	325	34	28	680	46
	C_3	310	31	30	650	48
	C_4	290	28	25	640	46
	C_5	270	27	21	630	45
180	C	235	22	15	780	37
	C_1	255	27	18	760	40
	C_2	275	30	24	730	43
	C_3	245	28	25	700	45
	C_4	230	25	20	680	44
	C_5	210	23	16	660	42

preparation, determination of vulcanizate properties, total chemical crosslink density, crosslink type, crosslinking efficiences and zinc sulphide have been described in the previous publication[1]. Heat build-up has been measured using a Goodrich Flexometer[4].

RESULTS AND DISCUSSION

Figures 1 and *2* show the rheographs of different mixes at 150° and 180°C, respectively. The Mooney scorch time and optimum cure time decrease with increase in the proportion of TMTD in the curatives, while the reversion time passes through a maximum (*Table 2*). As expected, optimum cure time decreases with increase in cure temperature from 150° to 180°C. The reversion time is reported only at 180°C. The reversion times at 150°C were too long to be calculated from the time span of the rheographs. Although mix C_2 and mix C_3 have good reversion resistance, mix C_2 has moderate scorch safety. In order to enhance further the scorch safety, a retarder, namely *N*-(cyclohexylthio)phthalimide, was added in mix C_2' and mix C_2'' (*Table 2*); this resulted in a considerable increase in Mooney scorch and a marginal increase in optimum cure time and reversion resistance.

Examination of the technological properties as shown in *Tables 3* and *4* reveals that mix C_2 and mix C_3 show the best set of properties excepting the cut growth and flexing properties. Mix C is the best among all the mixes, in so far as the flexing and cut growth properties are concerned. In general, for all mixes, the properties of vulcanizates cured at 180°C are inferior to those cured at 150°C. The percentage loss in properties in changing the vulcanization temperature from 150° to 180°C (*Table 5*) are minimum in mix C_2 and mix C_3. Retention of physical properties of vulcanizates after 4 days aging at 70°C is shown in *Tables 6* and *7*. In general, mix C_2 and mix C_3 show the maximum retention

Table 4 Physical properties of different mixes

Curing temperature (°C)	Mix no.	Cut growth (kilocycle)	Flex cracking (kilocycle) Grade A	Grade C	Failure	Heat build-up ΔT(°C)	Resilience (%)	Compression set (%)
150	C	30	70	115	80	8.5	80.5	28
	C_1	25	57	100	120	7.0	85.5	23
	C_2	21	45	55	75	6.0	87.5	21
	C_3	12	10	20	50	5.5	83.3	19
	C_4	17	22	30	55	6.0	82.5	20
	C_5	20	40	50	65	6.5	81.5	22
180	C	40	95	130	215	11.0	75.5	36
	C_1	35	80	120	130	8.5	81.5	27
	C_2	30	65	92	120	7.5	84.5	24
	C_3	15	35	60	95	6.5	81.5	22
	C_4	20	45	70	105	7.0	80.0	24
	C_5	25	55	75	115	8.0	78.5	26

of properties (excepting the flexing properties). The flexing properties of mix C_2 and their retention after aging are superior to that of mix C_3. The retention of vulcanizate properties of samples cured at 150°C is superior to those cured at at 180°C.

The total chemical crosslink density and distribution of different types of crosslinks (mono-, di- and polysulphidic) are shown in *Table 8* and *Figure 3.* The fall in chemical crosslink density as the cure temperature is increased from 150° to 180°C is due to a major decrease in polysulphidic crosslinks and a relatively small decrease in disulphidic and monosulphidic crosslinks, particularly in mixes with a smaller proportion of TMTD in curatives. Maximum crosslink density was shown by mix C_2. In all mixes, and at both curing temperatures, the monosulphidic crosslink concentration was a maximum. At 150°C, with increase in TMTD concentration in the curatives, polysulphidic crosslinks gradually decrease, monosulphidic crosslinks gradually increase and disulphidic crosslinks remain almost constant. However, at 180°C, with increase in TMTD concentration, polysulphidic crosslinks gradually decrease and monosulphidic crosslinks pass through a minimum in mix C_2 which registers a maximum in disulphidic crosslinks.

Results of chemical characterization of vulcanizate networks are shown in *Table 9*. The sulphur efficiences (E and E') values at 180°C are higher than that at 150°C. The E and E' values are minimum in mix C_2 at both cure temperatures. In general, F values are low for all mixes and at both cure temperatures. It is apparent from *Table 9* that in mix C_2, sulphur is most efficiently utilized at both cure temperatures. High values of E and E' at 180°C indicate less efficient use of sulphur in the formation of crosslinks and increased modifications of the main chain at high curing temperatures.

Lower degrees of crosslink density at higher vulcanization temperature and an increase in the extent of sulphidic main chain modification caused a reduction in strength, modulus, hardness and resilience and brought about a higher compression set and also a greater heat build-up during Goodrich flexometer test. Intramolecular groups such as cyclic sulphides can lower the strength properties because they inhibit strain-induced crystallization. Similar observations have been made earlier[1,5,6]. In the case of the EV system, increa-

Table 5 Percentage losses in physical properties in changing vulcanization temperature from 150° to 180°C

Mix no.	Tensile strength	Tear strength	300% Modulus	Hardness	Resilience
C	19	21	25	10	6
C_1	19	16	22	9	5
C_2	15	12	14	7	3
C_3	21	10	17	6	2
C_4	21	11	20	4	3
C_5	22	15	24	7	4

Table 6 Retention of physical properties after 4 days aging at 70°C

Curing temperature (°C)	Mix no	Tensile strength (% retained)	Tear strength (% retained)	300% Modulus (% retained)	Elongation at break (% retained)	Hardness change	Heat build-up (% retained)	Resiliance (% retained)	Compression set (% retained)
150	C	77	89	115	95	+1	117	97	79
	C_1	80	91	109	96	+1	114	98	83
	C_2	85	94	104	100	+1	108	99	86
	C_3	87	93	100	100	+1	136	98	84
	C_4	84	89	104	95	+1	150	97	85
	C_5	81	89	110	93	±0	161	96	82
180	C	60	73	93	79	+2	136	95	72
	C_1	65	78	88	85	+2	135	97	85
	C_2	71	80	87	90	+1	126	98	88
	C_3	71	79	88	89	+1	146	97	82
	C_4	67	76	90	85	+1	157	97	79
	C_5	67	74	94	80	±0	163	96	77

sed formation of pendant accelerator groups (monosulphidic) at higher cure temperatures has been suggested[7]. Quantitative analyses of sol–gel data for both conventional and *EV* accelerated natural rubber mixes have established that negligible chain scission occurred during vulcanization at 140°–200°C[1,7]. Therefore, loss of physical properties is not due to chain scission occurring during high temperature vulcanization.

The improved technical properties in mix C_2 and mix C_3 are due to high crosslink density and efficient utilization of sulphur in crosslinking (low E and E' values).

Both cut growth resistance and flex resistance properties, however, follow a different pattern compared with other properties. In this case: (a) both C_2 and C_3 mixes show inferior properties at both curing temperatures; (b) the properties of vulcanizates cured at 180°C are better than those at 150°C. The results can be explained on the basis of stress relaxation caused by the lower state of crosslinking at higher

Table 7 Retention of physical properties after 4 days aging at 70°C

Curing temperature (°C)	Mix no.	Cut growth	Flex cracking (% retained) Up to grade A	Up to grade C	Failure
150	C	80	86	83	86
	C_1	80	73	60	63
	C_2	86	78	78	80
	C_3	50	80	75	60
	C_4	59	82	83	73
	C_5	80	75	80	92
180	C	87	84	84	91
	C_1	86	56	55	69
	C_2	83	85	87	92
	C_3	80	57	75	68
	C_4	125	67	57	58
	C_5	120	91	93	83

Table 8 Relative proportions of different types of crosslinks

Cure temperature (°C)	Mix no.	Polysulphidic linkage (%)	Disulphidic linkage (%)	Monosulphidic linkage (%)
150	C	26.3	25.1	.48.6
	C_1	25.3	29.1	45.6
	C_2	25.3	28.8	45.9
	C_3	17.9	25.0	57.1
	C_4	14.7	24.8	60.5
	C_5	13.9	25.6	60.5
180	C	18.9	24.8	56.3
	C_1	18.7	28.5	52.8
	C_2	18.1	33.6	48.3
	C_3	14.0	28.8	57.2
	C_4	12.7	30.0	57.3
	C_5	11.8	29.5	58.7

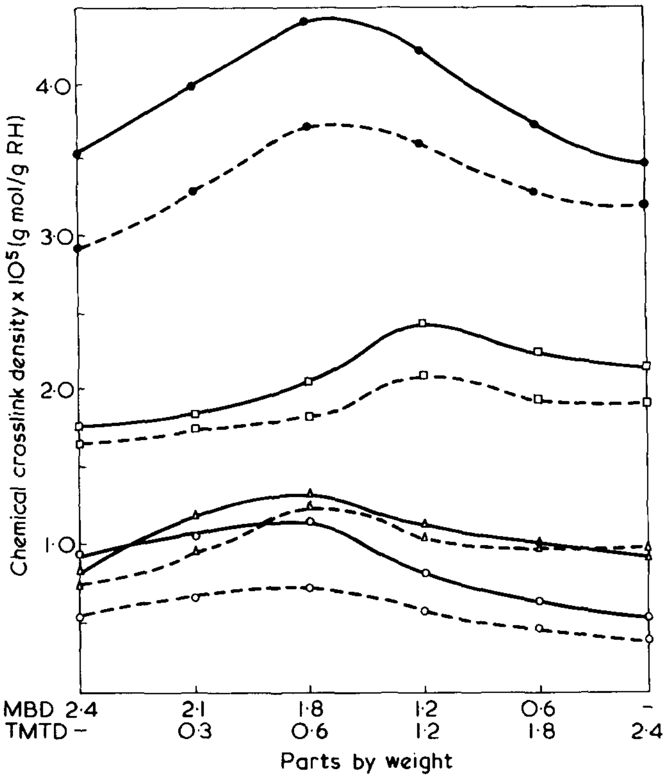

Figure 3 Total chemical crosslink density and distribution of crosslinks of different mixes. (———), Cured at 150°C; and (– – – –), 180°C. ●, Total crosslink; ○, polysulphidic crosslink; △, disulphidic crosslink; □, monosulphidic crosslink

Table 9 Chemical characterization of vulcanizate networks

Curing temperature (°C)	Mix No.	$[2M_{c,\text{chem}}]^{-1} \times 10^5$ (g mol/g RH)	Network combined sulphur $\times 10^4$ (g atom/g RH) $[S_c]$ before Ph_3P treatment	$[S_c']$ after Ph_3P treatment	Sulphur efficiencies (atoms/chemical crosslink) E, before Ph_3P treatment	E', after Ph_3P treatment	$[S_c]$ removed by Ph_3P treatment (%)	$[S^{2-}]$ Sulphide sulphur $\times 10^4$ (g ion/g RH)	F (Sulphide ion/chemical crosslink)
150	C	3.54	3.32	2.06	9.4	5.8	38	0.28	0.79
	C_1	3.99	2.59	1.84	6.5	4.6	29	0.26	0.65
	C_2	4.38	2.26	1.67	5.2	3.8	26	0.19	0.44
	C_3	4.20	3.14	2.16	7.3	5.1	31	0.16	0.38
	C_4	3.67	3.56	2.38	9.8	6.5	33	0.13	0.35
	C_5	3.39	4.06	2.64	12.0	7.8	35	0.10	0.30
180	C	2.90	3.31	2.56	12.1	8.8	27	0.41	1.41
	C_1	3.26	2.97	2.38	9.1	7.3	20	0.33	1.01
	C_2	3.69	2.73	2.26	7.4	6.1	17	0.25	0.68
	C_3	3.57	3.46	2.74	9.7	7.7	21	0.18	0.50
	C_4	3.23	3.95	3.02	12.2	9.4	23	0.16	0.48
	C_5	3.13	4.48	3.36	14.3	10.7	25	0.13	0.42

cure temperature and in mixes other than C_2 and C_3. Moreover, at higher cure temperature, the proportion of polysulphidic crosslinks decreases at the expense of monosulphidic and disulphidic crosslinks, which also contributes to better cut growth resistance at higher cure temperatures[1]. Blow and Loo[8] as well as Shvartz *et al.*[9] have reported that high temperature curing gives a longer fatigue life and greater resistance to crack growth.

It is evident that a binary combination of accelerators as in C_2 and C_3 mixes displays the best synergism and shows a good level of physical properties and retention of the properties after aging. However, if we take the processing safety into consideration, C_2 is the preferred formulation for high temperature vulcanization of natural rubber. The processing safety can be further enhanced by including *N*-(cyclohexylthio)phthalimide as retarder in the formulation. The retarder is not believed to affect the properties of the vulcanizates[10].

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