Studies on Novel Binary Accelerator System in Sulfur Vulcanization of Natural Rubber

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ABSTRACT: The synergistic activity of binary accelerator systems in rubber vulcanization is well known. Thiourea and its derivatives are important secondary accelerators in this context. It is suggested that thiourea containing binary systems of rubber vulcanization proceed by a nucleophilic reaction mechanism. Amidinothioureas (ATUs), which are derivatives of thiourea, have been investigated extensively as secondary accelerators. One of the aims of this study was to get further proof with regard to the theory of the nucleophilic reaction mechanism in such binary systems. In the present study phenyl substituted ATU was used as a secondary accelerator along with mercaptobenzothizyl disulfide, tetramethyl thiuram disulfide, or cyclohexyl benzthiazyl sulfenamide in the sulfur vulcanization of natural rubber. The results showed an appreciable reduction in the cure time for the mixes containing the ATU compared to the reference mixes. These results are indicative of a nucleophilic reaction mechanism in the vulcanization reaction under review. These vulcanizates also showed comparatively better tensile properties and good retention of these properties after aging. The optimum dosages of the secondary accelerator required for these vulcanization reactions were also derived. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 1–8, 2001

Key words: binary accelerator system; sulfur vulcanization; natural rubber; nucleophilic reaction; amidinothiourea; cure characteristics; tensile properties

INTRODUCTION

In rubber vulcanization reactions mixed accelerators are known to give superior properties. Thiourea (TU) and its derivatives are reported to be effective secondary accelerators with tetramethyl thiuram disulfide (TMTD) or cyclohexyl benzthiazylsulfenamide (CBS), especially in latex vulcanization systems. Some of the compounds in this group are ethylene thiourea, *N,N'*-dimethyl thiourea, and diphenyl thiourea. In the vulcanization of a natural rubber (NR) latex using the TMTD-TU binary system, thiourea enables the TMTD to operate at lower vulcanization temperatures. The exact mechanism of the chemical reactions involved in the binary accelerator system in rubber vulcanization is not fully understood even now. Philpot[1] studied the accelerator activity of certain sulfur bearing accelerators in the presence of S-reactive nucleophiles. It was proposed that the accelerator activity of sulfur bearing accelerators of the general formula XSSX, XSX, and so forth, depends partly on the nature of the X group and partly on the mode of attachment of the functional sulfur atom to other atomic groupings in the accelerator molecule. It has been proved that because of the high thermal stability of the S bond, the accelerator in which S is combined as S—S, C—S—C, or S—N is generally inactive at lower vulcanization temperatures. Philpot[1] sug-
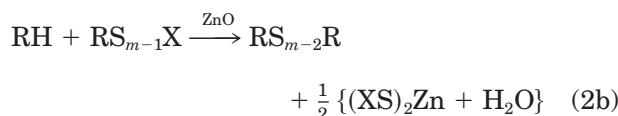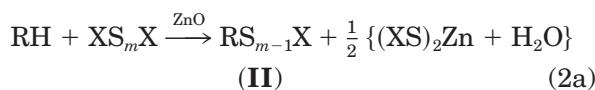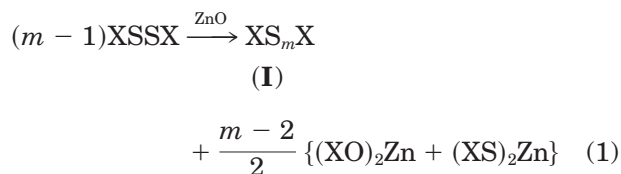
gested an ionic mechanism in which the S—S bond in the primary accelerator is cleaved by the nucleophile produced from TU. The more active the nucleophile the higher the rate of acceleration and hence the less optimum the cure time.

In a report by Moore et al.,[2] which presented the investigations on the TMTD-TU binary accelerator system, a novel probable mechanism for the synergistic activity of TU was suggested. This theory recognizes the importance of the polysulfidic intermediates (**I**) formed during the vulcanization process, which subsequently react with the rubber chain to yield further intermediates (**II**). These intermediates finally react to yield sulfurated crosslinks.

The process is schematized as follows:

$$(m - 1)XSSX \xrightarrow{\text{ZnO}} XS_mX$$
$$(\textbf{I})$$
$$+ \frac{m - 2}{2} \{(XO)_2Zn + (XS)_2Zn\} \quad (1)$$

$$RH + XS_mX \xrightarrow{\text{ZnO}} RS_{m-1}X + \tfrac{1}{2} \{(XS)_2Zn + H_2O\}$$
$$(\textbf{II}) \qquad\qquad (2a)$$

$$RH + RS_{m-1}X \xrightarrow{\text{ZnO}} RS_{m-2}R$$

$$+ \tfrac{1}{2} \{(XS)_2Zn + H_2O\} \quad (2b)$$

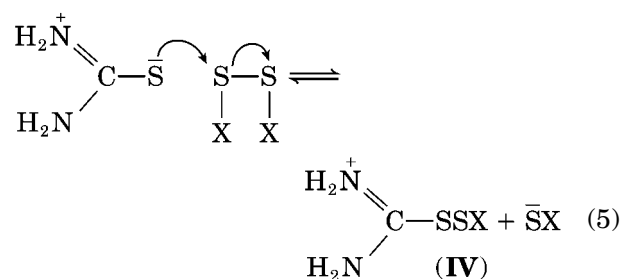where X represents $Me_2N \cdot C(:S)$ and RH is the rubber hydrocarbon.

Because the crosslinking reaction (2b) follows from the products of reaction (2a), which itself requires the thiuram polysulfides (**I**) produced in reaction (1), it follows that any acceleration of the latter must also lead to a corresponding increase in the overall vulcanization rate. Studies on the basic oxyanion type nucleophiles suggests that oxygen atoms of ZnO prefer to attack the thiocarbamyl carbon atoms of TMTD, causing the following polar substitution:
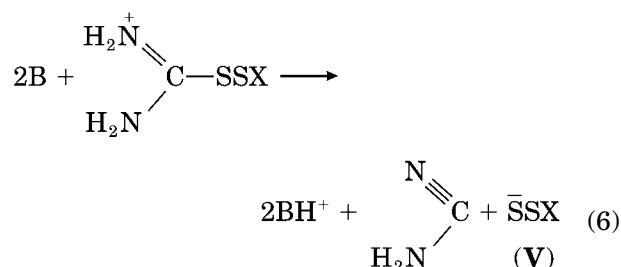
$$Zn^{++} \cdots O^{--} \frown XSSX \longrightarrow Zn^{++} \cdots \bar{O}X + \bar{S}SX \quad (3)$$
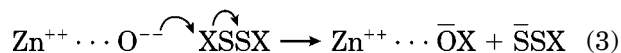
Reaction (3) yields a perthioanion (XS$\bar{\text{S}}$) that will rapidly effect the heterolysis of the S—S bond in another TMTD molecule to give the trisulfide (**III**).

$$XS\bar{S} + S \frown S \longrightarrow XSSSX + \bar{S}X \quad (4)$$
$$\begin{array}{cc} | & | \\ X & X \end{array} \qquad (\textbf{III})$$
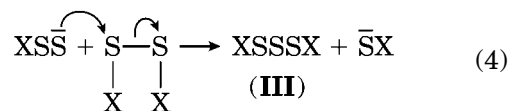
Participation of (**III**) in processes similar to (3) and (4) leads to the formation of the higher polysulfide **I** ($m \geq 4$). However, when TU is present, it is assumed that it will interact with TMTD under the prevailing basic conditions, providing an easier and faster route for the formation of polysulfide (**I**), and replace the slow processes (3) and (4) above. Thus, the addition of TU to TMTD causes acceleration in the production of polysulfide. The suggested mechanism is as follows. The TU will engage in a thioanion–disulfide interchange reaction of the following type:

$$\begin{array}{l} H_2\overset{+}{N} \\ \quad \diagdown \\ \qquad C - \bar{S} \frown S - S \rightleftharpoons \\ \quad \diagup \qquad\qquad | \quad | \\ H_2N \qquad\qquad X \quad X \end{array}$$

$$\begin{array}{l} H_2\overset{+}{N} \\ \quad \diagdown \\ \qquad C - SSX + \bar{S}X \quad (5) \\ \quad \diagup \\ H_2N \qquad (\textbf{IV}) \end{array}$$

IV easily loses a proton to a suitable base and rapidly decomposes to a perthioanion as in eq. (6).

$$2B + \begin{array}{l} H_2\overset{+}{N} \\ \quad \diagdown \\ \qquad C - SSX \longrightarrow \\ \quad \diagup \\ H_2N \end{array}$$

$$2BH^+ + \begin{array}{l} N \\ \diagdown\!\!\!\diagdown \\ \quad C + \bar{S}SX \quad (6) \\ \diagup \\ H_2N \qquad (\textbf{V}) \end{array}$$

These perthioanions (**V**) are the precursors of the thiurampolysulfide (**I**) required in the ultimate crosslinking reaction.

On the basis of this theory it can be predicted that easy production of perthioanions (X$\bar{\text{S}}_x$) and hence polysulfides (**I**) and a consequent acceleration of the vulcanization in the NR-TMTD-ZnO system will result in the addition of any thioanion (R′$\bar{\text{S}}$) where the group R′ is more easily attacked by bases than the X of TMTD.

In general, this suggestion can be written as follows:

$$\acute{R}\bar{S}\ \overset{\frown}{}\ S\!\!-\!\!S\ \rightleftharpoons\ \acute{R}SSX + \bar{S}X \qquad (7)$$

$$\underset{X\quad X}{}$$

$$B\!:\ \overset{\frown}{\acute{R}SSX}\ \longrightarrow\ \overset{+}{B}R + \bar{S}SX \text{ etc.} \qquad (8)$$

$$\text{rapid} \downarrow \text{TMTD}$$

$$\text{polysulfides (\textbf{I})}$$

Equation (7), being a reversible one, is promoted by the removal of $\acute{R}SSX$ by a base and $\bar{S}X$ as $Zn(SX)_2$.

Because dithiobiurets and ATUs, are also similar nucleophiles, these compounds could also act in a manner similar to the above. In addition, the presence of a guanidyl group in the ATU will facilitate the polarization of the C=S bond. Based on these facts, investigations were made in our laboratory on binary systems containing the above TU derivatives as secondary accelerators in the vulcanization of different elastomers. Studies were made using 1-phenyl 2,4-dithiobiuret, 1,5-diphenyl 2,4-dithiobiuret, and TMTD/CBS as primary accelerators. An ATU derivative, 1-phenyl 3(N,N'-diphenyl) ATU, was also used in similar reactions. All these compounds showed an appreciable reduction in the optimum cure time compared to the reference formulations, suggesting a nucleophilic reaction mechanism in these vulcanization reactions.[3-8] Based on the above observations, another substituted derivative of ATU with different nucleophilic character, namely,

$$\underset{\displaystyle NH \qquad\qquad S}{H_2N\!-\!C\!-\!NH\!-\!C\!-\!NHC_6H_5}\qquad (\textbf{VI})$$

N-amidino,N'-phenyl TU (**VI**), was tried in the present study using mecaptobenzothizyldisulfide (MBTS)/TMTD/CBS as the primary accelerator. Because the different mixes containing this ATU showed an appreciable reduction in optimum cure time compared to reference formulations, these mixes were further investigated with regard to the cure characteristics, vulcanizate properties, and so forth.

The optimum dosage of ATU required to get a satisfactory cure time with favorable physical properties was also derived.

Table I Formulation of Mixes Containing ATU with MBTS, TMTD, or CBS

	A_1	A_2	A_3	A_4	B_1	B_2	B_3	B_4	C_1	C_2	C_3	C_4	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8
NR	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
ZnO	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
MBTS	1.66	1.66	1.66	1.66	—	—	—	—	—	—	—	—	3.32	—	—	1.66	—	1.66	—	—
TMTD	—	—	—	—	1.2	1.2	1.2	1.2	—	—	—	—	—	2.4	2.8	1.2	1.2	—	1.2	—
CBS	—	—	—	—	—	—	—	—	1.4	1.4	1.4	1.4	—	—	—	—	1.4	—	—	1.4
ATU	0.243	0.485	0.97	1.455	0.243	0.485	0.97	1.455	0.243	0.485	0.97	1.455	—	—	—	—	—	—	—	—
TU	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0.38	0.38	0.38
S	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5

Table II   Cure Characteristics of MBTS-ATU, TMTD-ATU, and CBS-ATU Mixes Cured at 150°C

	t_{90} (min)	t_{10} (min)	t_5 (min)	Cure-Rate Index	Torque (dNm) Minimum	Maximum
A_1	10.3	5.2	4.5	19.6	0.005	0.128
A_2	6.7	3.3	3	29.41	0.11	0.122
A_3	3.5	1.3	1.1	45.45	0.007	0.146
A_4	3.4	1.2	1	45.45	0.005	0.171
B_1	4.32	2.3	2.2	49.5	0.135	0.168
B_2	2.3	1.7	1.5	166.67	0.005	0.17
B_3	1.3	0.5	0.38	125	0.026	0.211
B_4	1.3	0.6	0.4	142.86	0.027	0.165
C_1	5.4	2.8	2.6	38.46	0.123	0.173
C_2	3.2	1.9	1.8	76.92	0.029	0.112
C_3	2.5	1	0.8	66.67	0.008	0.193
C_4	2	0.6	0.5	71.43	0.016	0.183
R_1	13.2	7.2	6	16.67	0.004	0.125
R_2	4.2	2.7	2.3	66.67	0.026	0.2
R_3	8.2	4	3.8	23.8	0.111	0.206
R_4	7.8	3.8	3.5	25	0.032	0.183
R_5	6	2.6	2.5	29.41	0.004	0.186
R_6	8.5	3.7	3.3	20.83	0.007	0.108
R_7	2.2	1.6	1.5	166.67	0.018	0.141
R_8	3.2	1.72	1.7	66.67	0.023	0.126

t_{90}, optimum cure time; t_{10}, scorch time; t_5, induction time.

EXPERIMENTAL

Preparation of ATU

Guanidine carbonate (0.05 mol) and powdered sodium hydroxide (0.01 mol) were suspended in ace-

tonitrile (50 mL). Phenyl isothiocyanate (0.1 mol) was added dropwise to it with stirring until the smell of thiocyanate vanished. The reaction mixture was then diluted with cold water and the product precipitated out. It was filtered, washed
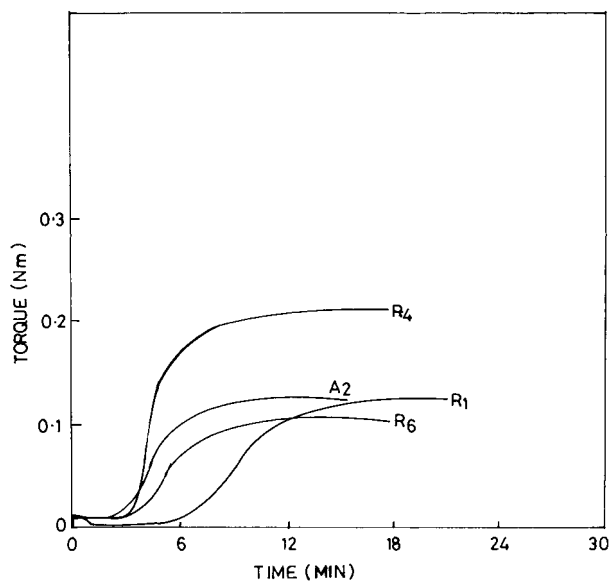
Figure 1   The cure curves of mixes A_2, R_1, R_4, and R_6.
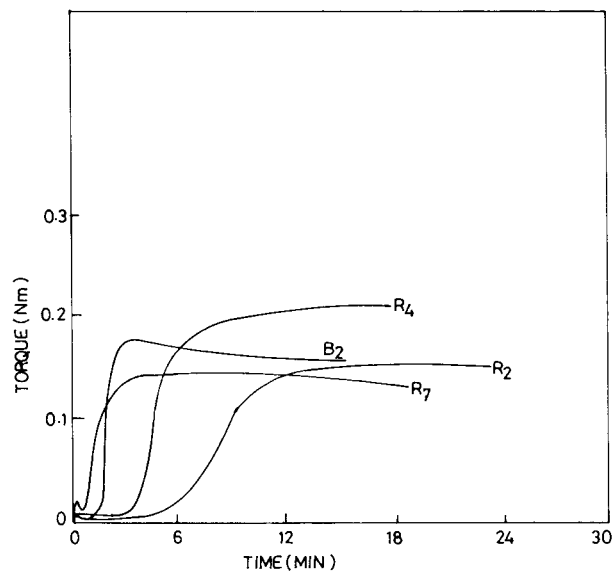

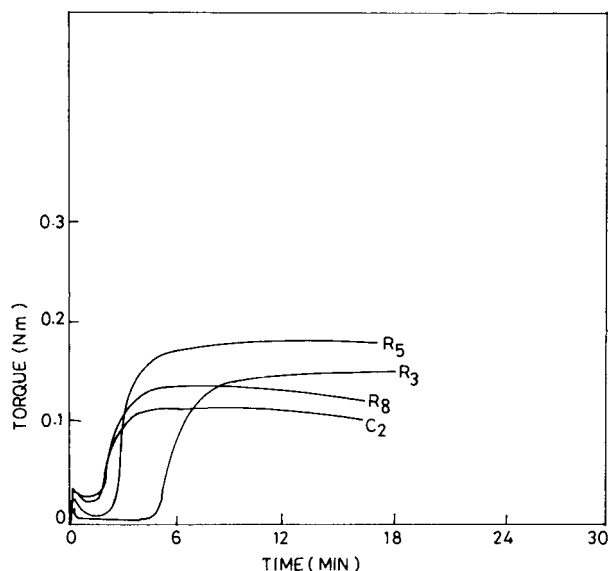**Figure 2**   The cure curves of mixes B_2, R_2, R_4, R_5, and R_7.

Figure 3 The cure curves of mixes C_2, R_3, R_5, and R_8.

with cold water (50 mL), and recrystallized from an ethanol water mixture (mp 174°C).

Materials

The NR (ISNR-5) used in the study had a Mooney viscosity (ML 1 + 4, 100°C) of 85 and was obtained from the Rubber Research Institute of In-

dia (Kottayam). All the rubber additives used (zinc oxide, stearic acid, MBTS, TMTD, CBS, and sulfur) were rubber grade. The chemical reagents used for the preparation of the ATU (phenyl iso-thioyanate, guanidine carbonate, sodium hydroxide, ethanol), and toluene used for swelling studies were analytical grade.

The different rubber mixes were prepared on a laboratory size two-roll mixing mill according to ASTM D 3182-89. The formulations of the mixes are given in Table I. Mixes A_1–A_4 are MBTS-ATU binary systems containing varying amounts of ATU ranging from 0.25 to 1.5 mol equiv with 1 mol equiv of MBTS; B_1–B_4 used 0.25, 0.5, 1.0, and 1.5 mol equiv of ATU with 1 mol equiv of TMTD; and C_1–C_4 mixes used varying amounts of ATU as above with 1 mol equiv of CBS. Mixes R_1–R_8 are reference formulations where R_1, R_2, and R_3 are 2 mol equiv of MBTS, TMTD, and CBS, respectively; R_4 is MBTS-TMTD 1 : 1; R_5 is TMTD-CBS 1 : 1; R_6 is MBTS-TU 1 : 1; R_7 is TMTD-TU 1 : 1; and R_8 is CBS-TU 1 : 1.

The cure characteristics of the mixes were determined using a Goettfert elastograph (model 67.85) at 150°C. The optimum cure time (t_{90}), scorch time (t_{10}), induction time (t_5), minimum torque, maximum torque, and cure-rate index calculated are reported in Table II and the different cure curves are given in Figures 1–3.

Table III   Tensile Properties of Vulcanizates Containing MBTS-ATU, TMTD-ATU, and CBS-ATU

	Tensile Strength (MPa)			100% Modulus (MPa)			Elongation at Break (%)		
	Before Aging	After Aging	Retention (%)	Before Aging	After Aging	Retention (%)	Before Aging	After Aging	Retention (%)
A_2	20.17	24.13	119.63	0.83	0.95	114.46	866.01	731.87	84.51
A_3	25.09	27.17	108.29	1.16	1.12	96.55	739.87	760.02	102.72
A_4	15.67	15.26	97.38	1.09	0.97	88.99	766.31	640.08	83.53
B_2	25.51	19.67	77.12	1.49	1.24	83.22	661.37	604.55	91.41
B_3	22.83	23.14	101.33	1.01	1.15	113.86	719.55	745.76	103.56
B_4	23.3	16.72	71.76	0.97	0.92	94.85	749.52	627.42	83.71
C_2	23.26	24.35	104.69	0.77	0.83	107.79	875.35	862.57	98.54
C_3	23.18	23.73	102.37	0.93	0.97	104.3	804.58	832.78	103.5
C_4	21.97	25.08	114.15	0.97	1.01	104.12	770.41	728.28	94.53
R_1	22.86	25.04	109.54	1.21	0.98	80.99	752.65	733.22	97.42
R_2	18.29	11.59	63.37	1.74	1.37	78.74	527.85	430.81	81.62
R_3	19.5	22.4	86.9	1.84	1.22	150.8	594.66	588	100.9
R_4	2.03	1.72	84.73	1.63	1.52	93.25	129.85	114.3	88.02
R_5	2.1	2.28	108.5	1.19	1.53	128.57	172.17	119.58	69.45
R_6	19.67	19.89	101.12	0.93	0.72	77.42	743.1	836.75	112.3
R_7	16.89	19.7	116.64	0.87	1.05	120.69	646.35	677.01	104.74
R_8	15.34	20.91	136.36	0.66	1.2	181.82	834.68	646.57	77.46

Table IV   Other Physical Properties of MBTS-ATU, TMTD-ATU, and CBS-ATU Vulcanizates

	Tear Strength (N/mm)	Hardness (Shore A)	Compression Set (%)	Abrasion Loss (mL/h)	Total Crosslink Density, $\times 10^5$ (g/mol/mL)
A_2	32.11	25.5	28.19	5.84	4.1975
A_3	32.16	26	37.93	5.77	4.4225
A_4	36.32	27	29.38	5.57	4.4114
B_2	48.88	39	20.39	3.88	5.8633
B_3	43.95	38	24.28	4.08	5.3478
B_4	46.74	37	25.71	5.7	5.5325
C_2	35.67	27.5	27.12	3.56	5.1967
C_3	33.65	30	31.45	1.73	5.001
C_4	37.12	29	26.61	2.54	5.5325
R_1	29.73	29	21.97	6.7	4.5205
R_2	43.29	38.5	13.18	3.39	6.8655
R_3	37	31	13.8	5.4	6.1005
R_4	17.72	32	12.45	6.49	7.4102
R_5	42.49	34	16.12	6.29	7.2533
R_6	22.4	24	31.4	5.73	3.521
R_7	37.71	33	33.1	6.27	5.2504
R_8	40.96	31	31.32	5.84	4.0645
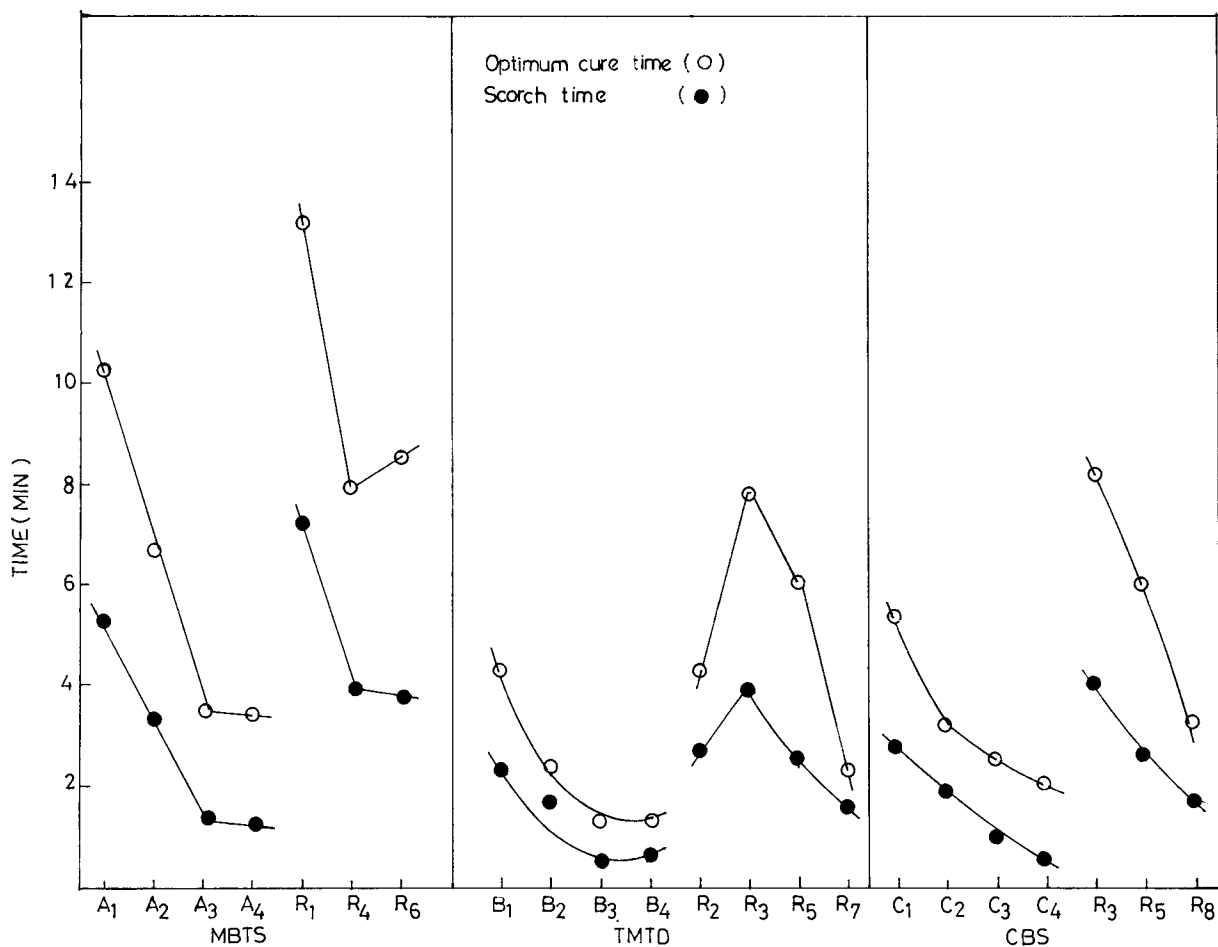
Figure 4   The variation in the optimum cure time and scorch time of various mixes containing MBTS/TMTD/CBS.

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MBTS/ATU Before aging (▲) After aging (○)
TMTD/ATU Before aging (△) After aging (□)
CBS/ATU Before aging (■) After aging (●)
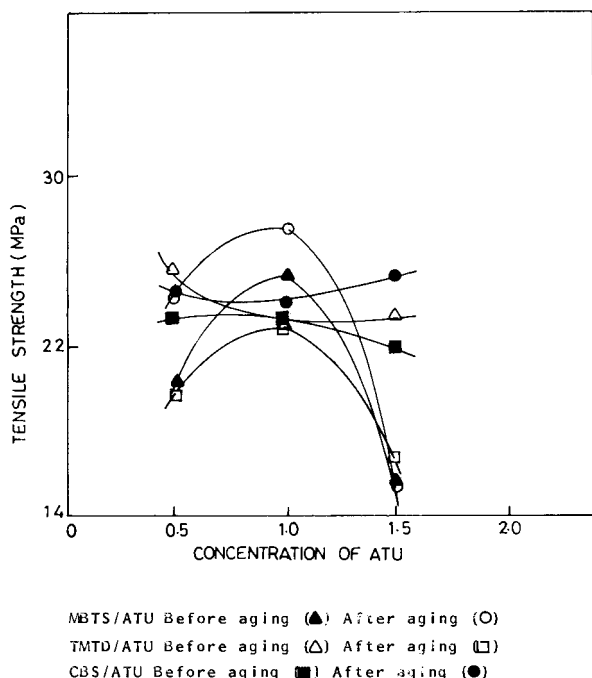
Figure 5 The variation of the tensile strength of the vulcanizates with the concentration of ATU.

The tensile strength, tear strength, compression set, abrasion resistance, hardness, and heat aging resistance were determined according to relevant ASTM standards. The values for the tensile properties (both before and after aging) are reported in Table III. Other physical properties studied (tear strength, hardness, compression set, abrasion loss, and total crosslink density) are reported in Table IV. The concentration of the chemical crosslinks (crosslink density) of the various vulcanizates was determined from the equilibrium swelling data.[9–11]

RESULTS AND DISCUSSION

The results of the study indicate that ATU shows good acceleration activity with MBTS, TMTD, or CBS as the primary accelerator. The cure characteristics given in Table II are a clear indication of this conclusion. Figure 4 shows the variation in optimum cure time and scorch time with varying concentrations of ATU and the optimum cure time and scorch time of the corresponding reference mixes. The addition of 0.5 mmol of ATU/100 parts rubber reduces the optimum cure time to almost half of that using MBTS, TMTD, or CBS alone. ATU is a better nucleophile, so this reduction in optimum cure time can be anticipated. The

scorch time of this mix is also practical enough to not cause processing problems. Increasing the concentration of ATU further produces a reduction in the optimum cure time. However, a corresponding reduction in scorch time also occurs and evokes processing problems. A concentration of ATU of less than 0.5 mmol does not give scorch problems but then the optimum cure time is not appreciably reduced. A comparison of the optimum cure time of the experimental mixes containing ATU with MBTS, TMTD, or CBS with those of the reference mixes containing MBTS, CBS, or TMTD alone, MBTS-TMTD, or TMTD-CBS shows the effectiveness of ATU as a secondary accelerator. Considering the overall cure properties, even though a nucleophilic reaction mechanism is proposed in these vulcanization systems, the possibility of a mixed mechanism involving ionic and radical types cannot be ruled out.[12] Mixes containing ATU show almost comparable results with those containing TU (Fig. 4). Also, based on the above facts, it is reasonable to conclude that 0.5 mmol of ATU/100 parts rubber can be considered as the optimum dosage of ATU required as secondary accelerator along with MBTS, TMTD, or CBS.

Considering the fact that practical rubber mixes can be obtained using ATU as the secondary accelerator in the sulfur vulcanization of NR, the vulca-
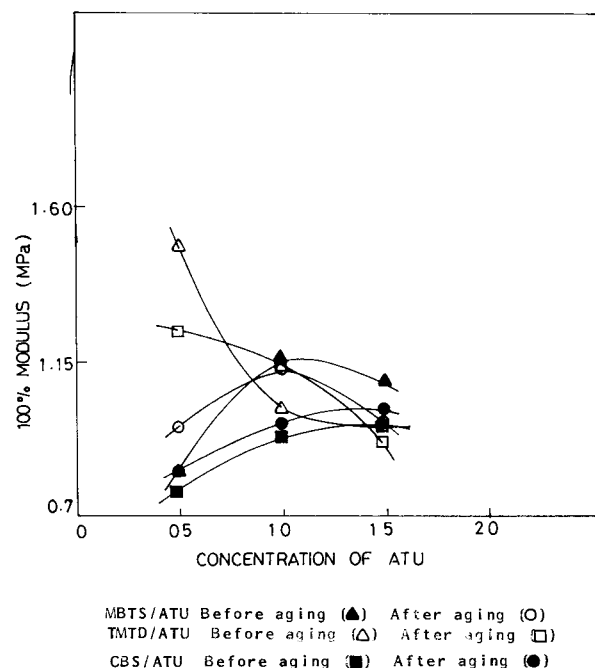

MBTS/ATU Before aging (▲) After aging (○)
TMTD/ATU Before aging (△) After aging (□)
CBS/ATU Before aging (■) After aging (●)

Figure 6 The variation of the 100% modulus of the vulcanizates with the concentration of ATU.

MBTS/ATU Before aging (▲)   After aging (O)
TMTD/ATU Before aging (△)   After aging (□)
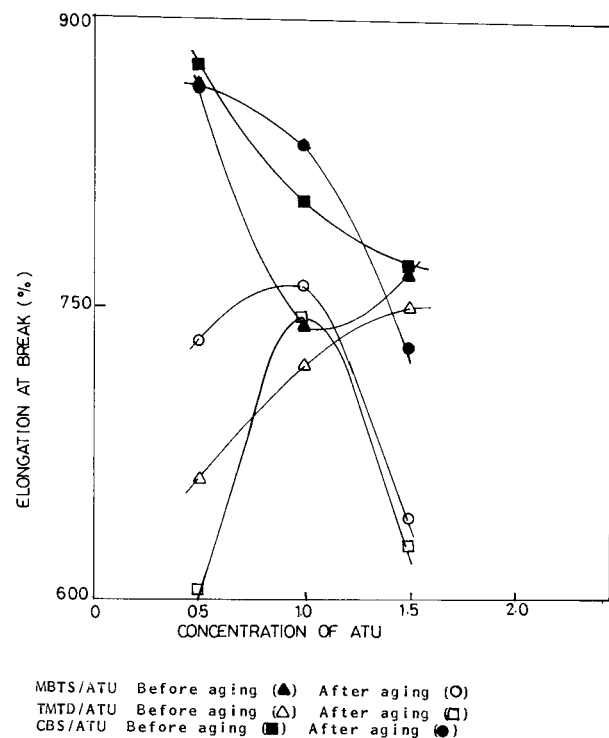CBS/ATU   Before aging (■)   After aging (●)

Figure 7 The variation of the elongation at break of the vulcanizates with the concentration of ATU.

nizate properties of these mixes were investigated further. To correlate the variation in physical properties, the total number of crosslinks of the different vulcanizates was also estimated. The tensile properties for the three binary systems containing ATU were found to be satisfactory. These results are listed in Table III. The effect of the concentration of ATU on the tensile properties of the vulcanizates from all three systems before and after aging are shown in Figures 5–7. We saw that the variation of these properties with the concentration of ATU cannot be generalized. It is clear that these properties of the experimental mixes of all three binary systems are comparable to or better than those of the reference mixes with regard to postaging properties.

Other physical properties of the vulcanizates such as hardness, compression set, abrasion resistance, and tear strength were also evaluated and are reported in Table IV. These values were found to be more or less comparable to the corresponding values of the reference mixes. However, binary systems containing TMTD were found to give better results.

SUMMARY AND CONCLUSIONS

The effect of phenyl substituted ATU as a secondary accelerator in the binary systems of MBTS-ATU, TMTD-ATU, and CBS-ATU in NR vulcanization was investigated. All three binary systems were found to be effective in practical vulcanization systems. The cure behavior of the NR gum formulations provided supporting evidence to the nucleophilic reaction mechanism of the accelerator activity in these systems where the S—S bond of the primary accelerator was cleaved by the nucleophile from the secondary accelerator. ATU considerably reduced the optimum cure time of the mixes and practical cure systems with an optimum concentration of ATU were proposed. The tensile and other physical properties (hardness, compression set, abrasion loss, tear strength, etc.) of these vulcanizates were better than or comparable to those of the reference mixes. The ATU also showed promising results in the after aging properties.

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