Studies on a New Binary Accelerator System Containing TMTD and Amidinothiourea in Sulfur Vulcanization of Natural Rubber

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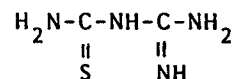
SYNOPSIS

It is well known that the use of binary accelerator systems in rubber vulcanization provide better physical and chemical properties to the vulcanizates. The present work reports the results obtained on the study of amidinothiourea as a secondary accelerator along with tetramethyl thiuram disulfide (TMTD) in the sulfur vulcanization of natural rubber. Vulcanizates containing amidinothiourea have an appreciable increase in mechanical properties and better retention of these properties after aging compared to the reference mixes used. These mixes containing amidinothiourea showed appreciable reduction in optimum cure time as well. This suggests a nucleophilic reaction mechanism in the vulcanization reactions under review. Mixes with varying concentrations of amidinothiourea were tried; and the optimum level of amidinothiourea required has been derived based on the cure characteristics of the mixes and physical properties of the vulcanizates. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Compared to the use of a single accelerator, mixed accelerator systems in rubber vulcanization are known to give superior chemical and physical properties to the vulcanizates.[1-4] Consequently binary accelerator systems are widely used in the rubber industry. Thiourea and its derivatives are known to have advantageous properties in this context, especially in the vulcanization of natural rubber (NR) and neoprene latices.[5-8] Some of the important members of this class are ethylene thiourea, N,N'-dimethylthiourea, diphenylthiourea, Sym di-o-tolylthiourea, N,N'-dibenzthiazolyl-N,N'-dimethyl-thiourea etc. In the vulcanization of NR latex using tetramethyl thiuram disulfide (TMTD)/thiourea binary systems, thiourea is found to enable TMTD to operate at lower vulcanization temperatures.[5] Dithiobiuret derivatives of thiourea were also tried in our laboratories as secondary accelerators in the sulfur vulcanization of NR[9] and styrene butadiene

rubber[10] with promising results. A nucleophilic reaction mechanism was established in these vulcanization reactions. Such a suggestion was also made by Philpot[5] in similar vulcanization systems even though no conclusive proof was given. It is known that accelerators in which sulfur is combined as S—S, C—S—C, or S—N are generally inactive at lower vulcanization temperatures because of the high thermal stability of their sulfur bonds. Philpot suggested an ionic mechanism in which the S—S bond in the primary accelerator is cleaved by the nucleophile produced from thiourea. Kuriakose et al.[9-11] extended this study to different dithiobiuret derivatives of thiourea and the results agree with the suggestions made by Philpot. As a continuation of this study we selected an amidinothiourea derivative of the general formula (I) as a

$$H_2N-C-NH-C-NH_2$$
$$\overset{\parallel}{S} \quad \overset{\parallel}{NH}$$

I

secondary accelerator. We used 1-phenyl-3(N,N'-diphenylamidino) thiourea (II) synthesized accord-

ing to Kurzer and Sanderson[12] along with TMTD as the primary accelerator.

$$H_5C_6-NH-\underset{\underset{S}{\parallel}}{C}-NH-\underset{\underset{NC_6H_5}{\parallel}}{C}-NH-C_6H_5$$

II

One of the aims of this study is to give further proof of the nucleophilic reaction mechanism proposed in similar sulfur vulcanization reactions referred to earlier. 1-Phenyl-3(N,N'-diphenylamidino)thiourea (ATU) is more nucleophilic in character and should give a lesser optimum cure time compared to the reference mixes used. Different mixes using varying amounts of ATU with TMTD were tried in standard recipes. Reference mixes containing thiourea, diphenyl guanidine (DPG), and mercaptobenzthiazyl disulfide (MBTS) were also prepared. The cure characteristics of the mixes were evaluated using an elastograph. Mechanical properties, total cross-link density, etc., of the vulcanizates were also determined. From the results obtained it is seen that the more nucleophilic the secondary accelerator is, the less the optimum cure time obtained. This points to a nucleophilic reaction mechanism in these vulcanization reactions. Moreover the vulcanizates containing ATU showed a definite increase in many of the tensile properties and good retention of these properties after heat aging. The optimum dosage of ATU required to get satisfactory cure time and favorable physical properties has also been derived.

EXPERIMENTAL

Preparation of ATU

ATU was synthesized according to Kurzer and Sanderson.[12] A solution of DPG (0.01 mol) and

phenyl isothiocyanate (0.01 mol) in benzene (50 mL) was refluxed for 2 h. The reaction mixture was then concentrated under reduced pressure to 10–15 mL. Petroleum ether (60–80°C) was added until the solution became cloudy. After 12–14 h the product that crystallized out was collected and recrystallized from an acetone–ethanol mixture (MP 163°C).

NR conforming to ISNR-5 used in the study was obtained from the Rubber Research Institute of India, Kottayam. The rubber additives used, zinc oxide, stearic acid, MBTS, TMTD, DPG, thiourea (TU), and sulfur were all of rubber grade.

The formulations of the different mixes used in the present investigation are shown in Table I. Mixes B_1–B_4 are reference mixes. Mix B_1 contains only TMTD as accelerator. Mixes B_2–B_4 contain 1 phr of TMTD with 1 phr each of MBTS, DPG, and TU, respectively. Mixes A_1–A_3 contain different amounts of ATU ranging from 0.5 to 1.5 phr, with 1 phr of TMTD. Mix B_5 contained only ATU as accelerator and it cured so slowly that this mix was not used.

The mixes were prepared on a laboratory size two roll mixing mill (6 × 12 in.) per ASTM designation D3182-89. The cure characteristics of the mixes were obtained on a Goettfert elastograph (model 67.85) at 150°C. The stocks were then vulcanized up to the optimum cure time in an electrically heated hydraulic press at 150°C at a pressure of 120 kg/cm^2. Dumbbell tensile test specimens were punched out of the test sheets along the mill grain direction. The tensile properties of the vulcanizates were determined on a Zwick Universal Testing Machine model 1445 using a crosshead speed of 500 mm/min (ASTM D412-87 method A). Heat-aging resistance of the vulcanizates was studied by aging the samples for 48 h at 70°C in a laboratory air oven (ASTM D865-88). Angular test specimens were used to measure the tear resistance according to ASTM D 624-86. A Shore A type durometer was used to find the hardness of the vulcanizates (ASTM D2240-86).

Table I Formulation of Mixes

Ingredients	A_1	A_2	A_3	B_1	B_2	B_3	B_4	B_5
Natural rubber	100	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2
TMTD	1	1	1	2	1	1	1	—
MBTS	—	—	—	—	1	—	—	—
DPG	—	—	—	—	—	1	—	—
TU	—	—	—	—	—	—	1	—
ATU	0.5	1	1.5	—	—	—	—	2
Sulfur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5

Figure 1 Cure curves of the mixes A_1, B_1, B_2, B_3, and B_4.

Figure 2 Cure curves of the mixes A_2, A_3, and B_5.

Table II Cure Characteristics of Mixes (Cured at 150°C)

	Mixes						
	A_1	A_2	A_3	B_1	B_2	B_3	B_4
Min. Torque (dNm)	0.5	0.8	0.7	0.7	0.6	0.4	0.7
Max. torque (dNm)	20.4	22.2	23.2	22.6	24.0	17.8	25.0
Optimum cure time t_{90} (min)	2.6	1.8	1.6	4.4	7.4	2.6	1.8
Scorch time[a] t_{10} (min)	2	1.2	1	2.4	3	1.8	1.2
Induction time t_5 (min)	1.3	0.7	0.5	1.8	2.1	1.5	0.9
Cure rate index	166.66	166.66	166.66	50	22.72	55.55	166.66

[a] Elastograph scorch time.

To determine a compression set, samples of 1.25-cm thickness and 2.8-cm diameter were prepared in duplicate and compressed to constant deflection (25%) and kept for 22 h in an air oven at 70°C.

After the heating period the samples were cooled to room temperature, the final thickness was measured, and the compression set was calculated (ASTM D395-89 method B). A Goodrich flexometer con-
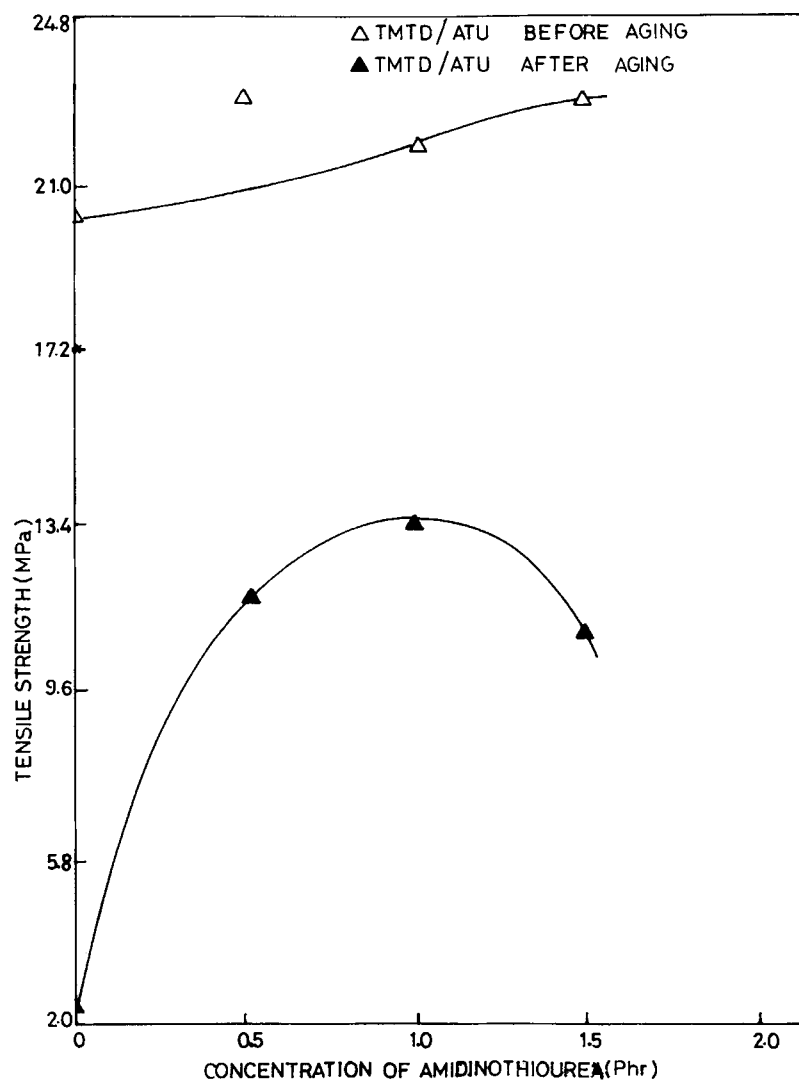
Figure 3 Variation of tensile strength of vulcanizates with concentration of ATU.

Table III   Tensile Properties of Various Vulcanizates

Mixes	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_1	22.88	12.00	52.4	1.92	2.00	104.2	702.10	560.45	79.8
A_2	21.91	13.36	61.0	1.85	1.94	104.9	704.70	602.75	85.5
A_3	22.82	10.91	47.8	1.92	2.00	104.2	704.52	530.68	75.3
B_1	20.23	2.47	12.2	0.78	1.24	159.0	607.01	168.31	27.7
B_2	2.39	1.88	78.7	1.32	1.38	104.5	192.36	143.05	74.4
B_3	23.29	21.16	90.9	1.02	1.16	113.7	749.20	695.70	92.9
B_4	23.39	20.37	87.1	1.00	1.20	120.0	779.36	673.73	86.4

forming to ASTM designation D623-88 (method A) was used for measuring heat build-up. Rebound resilience was measured using a Dunlop tripsometer (BS 903 Part A8) and the abrasion resistance was measured using a DIN abrader (DIN 53516).

The cure characteristics of the mixes were deter-
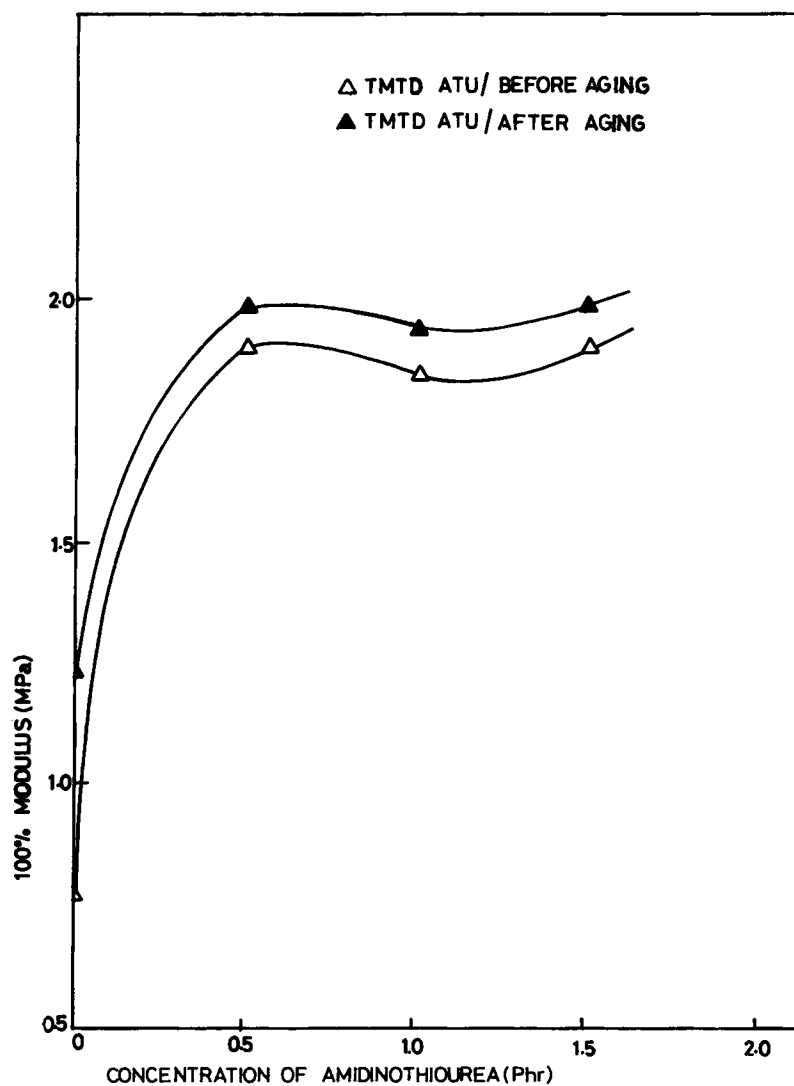
Figure 4   Variation of 100% modulus of vulcanizates with concentration of ATU.
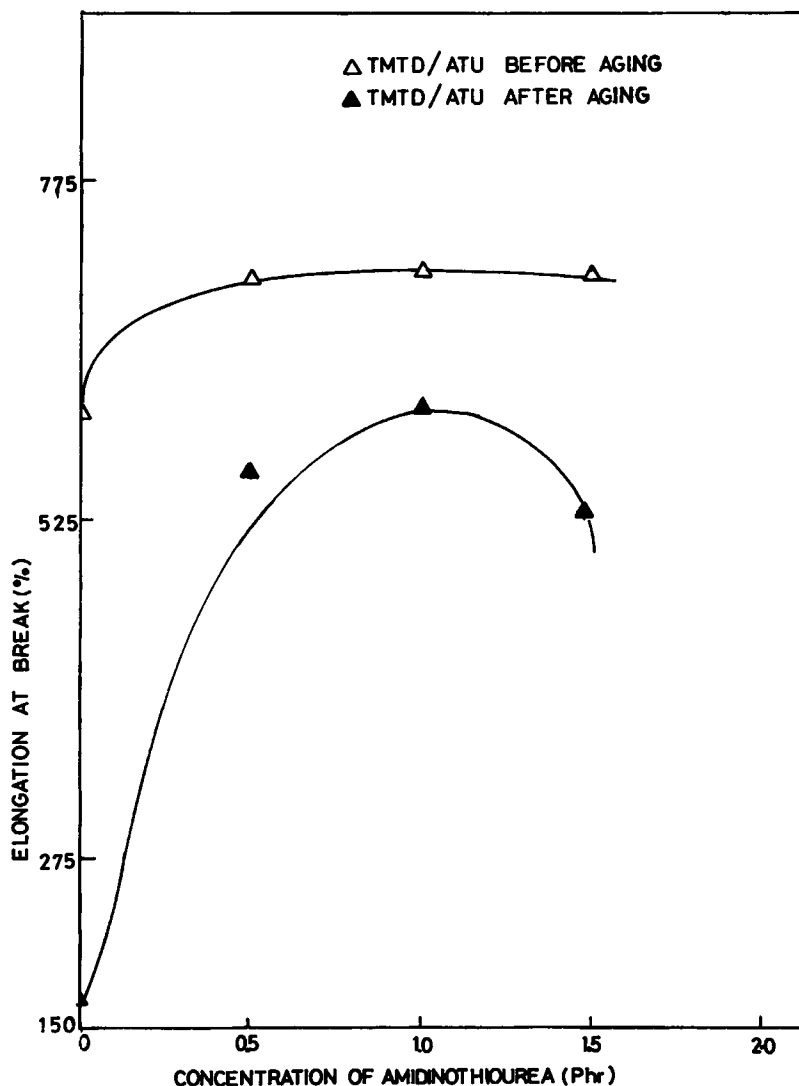
Figure 5   Variation of elongation at break of the vulcanizates with concentration of ATU.

mined from the cure curves (Figs. 1, 2) and the values are reported in Table II. Induction time is the time for one unit rise above minimum torque (i.e., about 5% vulcanization). Elastographic scorch time t_{10}, is the time for two units rise above the minimum torque; the cure rate index is reported as $100/t_{90}-t_{10}$ where t_{90} and t_{10} are the times corresponding to the optimum cure and the elastograph scorch, respectively.

Determination of Chemical Cross-Links

The chemical cross-link density $(1/2M_c)$ was calculated using the Flory–Rehner equation,[13]

$$-[\ln(1-V_r) + V_r + \chi V_r^2] = \frac{\rho_r V_s (V_r)^{1/3}}{M_c}$$

where ρ_r = density of test specimen (0.921 g/cm^3); V_s = molar volume of solvent [V_s (toluene) $= 106.2$ cc/mol]; χ = the parameter characteristic of the interaction between rubber and solvent[14] [$\chi_{(NR\text{-}toluene)} = 0.42$]; M_c = number average molecular weight of the rubber chains between cross-links; and V_r = volume fraction of rubber in the swollen network. Samples of approximately 1-cm diameter, 0.2-cm thickness, and 0.2-g weight were punched out from the central portion of the vulcanizate. These were then allowed to swell in toluene for 24 h. The swollen samples were taken out and weighed. The solvent was removed in vacuum and the samples weighed again. The V_r in the swollen network was then calculated by the method reported by Ellis and Welding[15] from the equation:
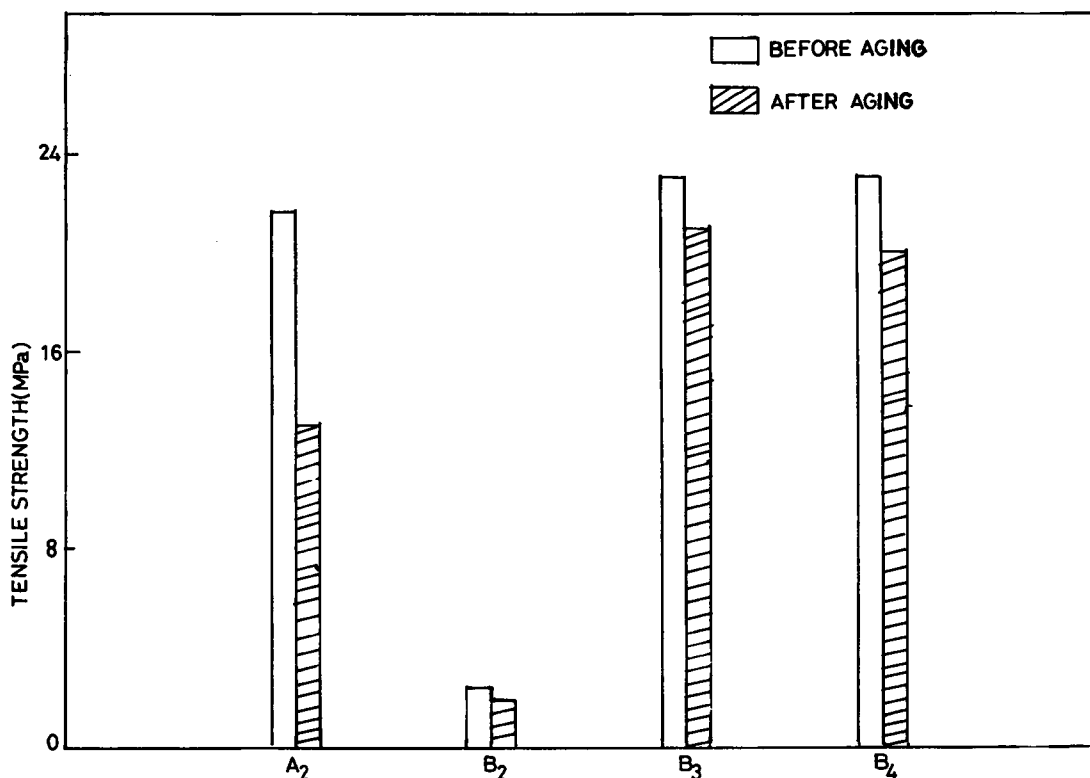
Figure 6 Tensile strength of vulcanizates containing equivalent concentrations of TMTD with ATU, MBTS, DPG, and TU.

$$V_r = \frac{(D - FT)\rho_r^{-1}}{(D - FT)\rho_r^{-1} + A_0\rho_s^{-1}}$$

where T = weight of the test specimen; D = weight of the deswollen test specimen; F = weight fraction of insoluble components; A_0 = weight of the absorbed solvent corrected for the swelling increment; ρ_r = density of test specimen (0.921 g/cm^3); and ρ_s = density of solvent (0.886 g/cm^3).

RESULTS AND DISCUSSION

The various experimental observations of the present investigation indicate a definite accelerator activity of the ATU in TMTD/ATU binary systems. It also points to a nucleophilic reaction mechanism in these systems of NR vulcanization. The cure characteristics of the various mixes are given in Table II and the cure curves in Figures 1 and 2. The reference system B_1 contains TMTD alone as accelerator and when compared to mix A_3 containing 1.5 phr of ATU, the latter shows an optimum cure time of almost one-third of that of the former. This shows that the ATU derivative has very effective accelerator activity in these systems. But the latter mix shows very low scorch time, which may cause

processing problems. When the amount of ATU is reduced to 1 phr (mix A_2) cure time is found to increase slightly but the mix is still scorchy. However, when the amount of ATU is reduced to 0.5 phr (mix A_1) there is substantial reduction in optimum cure time (almost half compared to mix B_1). But at the same time scorch time is satisfactory and this can be considered as the optimum level of the secondary accelerator. The stocks A_2, B_2, B_3, and B_4 contain 1 phr of TMTD with 1 phr each of ATU, MBTS, DPG, and TU, respectively. The optimum cure time for mix A_2 is almost one-fourth of the TMTD/MBTS system (mix B_2). The results definitely show that ATU is a better secondary accelerator compared to the other reference mixes. ATU being more nucleophilic than the other secondary accelerators tried, the results also point to a nucleophilic reaction mechanism in the systems under review. However, based on a recent review of the fundamentals of accelerated and unaccelerated vulcanization,[16] the possibility of an ionic mechanism initially and a free radical mechanism subsequently cannot be ruled out. In view of the fact that practical cure systems can be obtained using ATU in the sulfur vulcanization of NR, these systems were further investigated with respect to physical properties of the different vulcanizates. To correlate the variation in physical
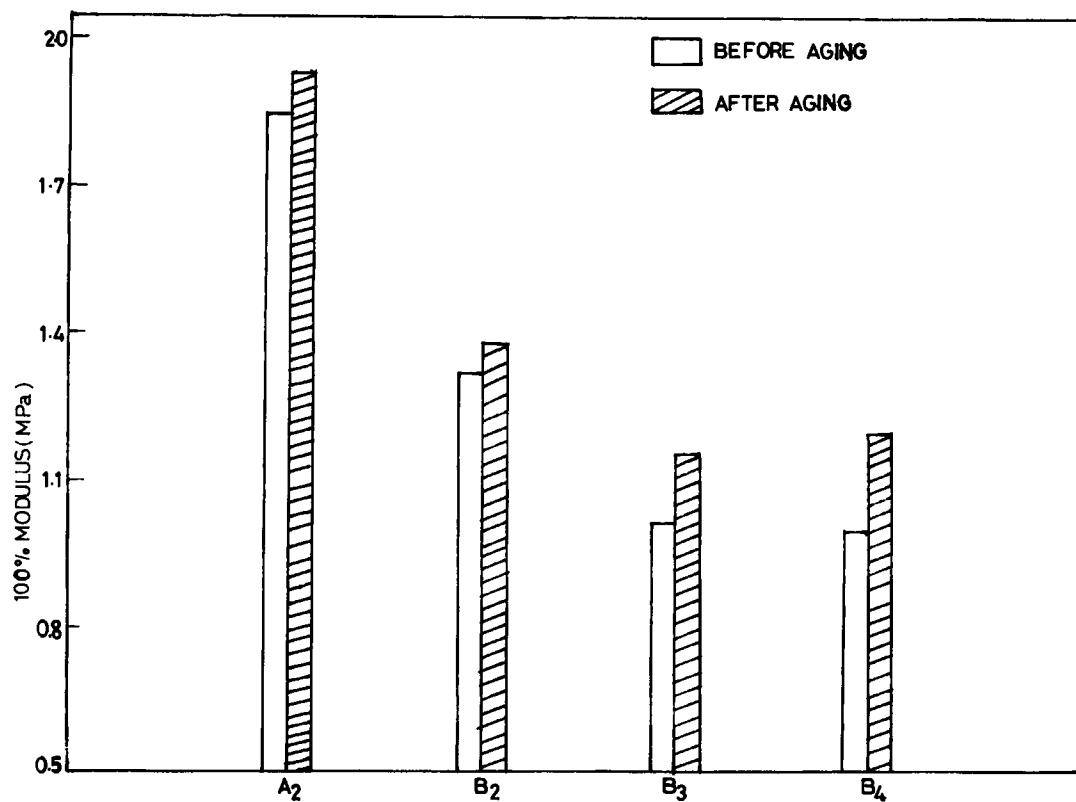
Figure 7   Modulus, 100%, of the vulcanizates containing equivalent concentrations of TMTD with ATU, MBTS, DPG, and TU.
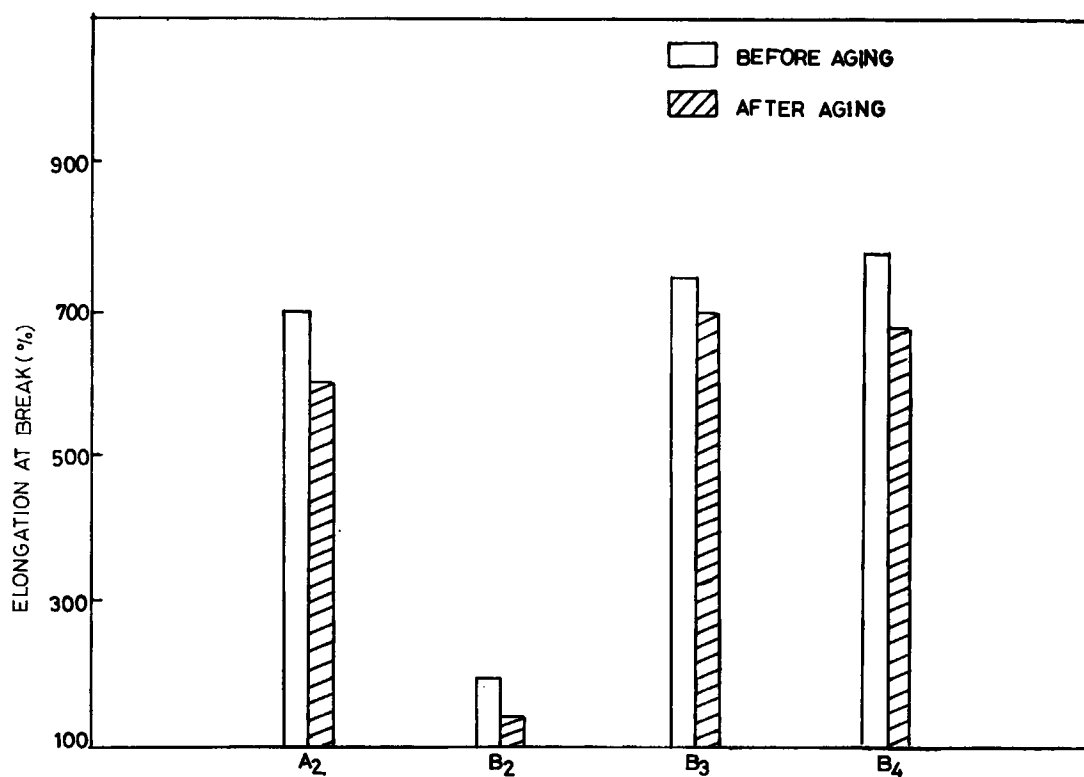
Figure 8   Elongation at break of vulcanizates containing equivalent concentrations of TMTD with ATU, MBTS, DPG, and TU.

Table IV   Other Properties Evaluated

Mixes	Hardness (Shore A)	Compression Set (%)	Heat Build-Up ($\Delta T^{\circ}C$)	Resilience (%)	Abrasion Loss (cm^3/h)	Tear Strength (N/mm)	Total Cross-link Density ($\times 10^5$ gm mol/cm^3)
A_1	30	28.30	12.1	72.74	5.09	31.92	4.90
A_2	30	33.43	12.5	74.59	4.8	28.48	5.44
A_3	31	34.42	11.9	73.13	5.38	31.97	5.18
B_1	39	19.21	7.8	78.35	7.6	34.52	6.31
B_2	36	13.55	5.0	85.32	15.2	31.66	6.87
B_3	32	20.04	9.1	77.23	2.54	33.24	5.82
B_4	37	33.10	12.4	76.48	4.8	34.16	5.66

properties observed, total chemical cross-links in the vulcanizates were also estimated.

Table III shows the various tensile properties of the vulcanizates. Figures 3–5 represent the variation of tensile properties with the concentration of ATU. The tensile strength and 100% modulus of the vulcanizates do not change much with an increase in the amount of ATU up to a concentration of 1.5 phr. This is in agreement with the estimation of total chemical cross-links that do not show much variation with variation in the concentration of ATU. The aging resistance of the vulcanizates from mixes A_1–A_3 is comparable to that of the reference mixes B_1–B_4. A bar graphical representation of the tensile strength, 100% modulus, and elongation at break both before and after aging of the reference mixes and 1 : 1 mix of TMTD and ATU is given in Figures 6–8. Other physical properties studied are hardness (Shore A), compression set, heat build-up, resilience, abrasion loss, and tear strength. These data are given in Table IV. The values of hardness and compression set are seen to increase with the concentration of ATU. The other properties do not show much variation. The total cross-link density does not show appreciable change with an increase in the amount of ATU (mixes A_1–A_3, Table IV) and the values are comparable with those of the reference mixes.

CONCLUSIONS

ATU can be advantageously used as a secondary accelerator in combination with TMTD in the sulfur vulcanization of NR. There is appreciable reduction in optimum cure time by the use of ATU in these vulcanization systems. Because ATU is more nucleophilic than the reference compounds, the results clearly indicate a nucleophilic reaction mechanism in the systems under investigation. The physical properties studied also showed favorable trends compared to the reference mixes. Practical cure systems with optimum concentration of ATU have also

been suggested. The after-aging properties of vulcanizates containing ATU are also found to be favorable.

REFERENCES

1. M. M. Das, D. K. Basu, and A. K. Choudhari, *Kautsch Gummi Kunstst.*, **36**(7), 569 (1983).
2. S. Kucharik, *Sb Vys Sk Chem. Technol. Praze (Oddil) (Czech)*, **S8**, 203 (1982).
3. B. A. Dogadkin and V. A. Shershnev, *Rubber Chem. Technol.*, **35**(1), 1 (1962).
4. T. D. Skinner and A. A. Watson, *Rubber Chem. Technol.*, **42**, 404 (1969).
5. M. W. Philpot, IRI IVth Rubber Technology Conference, London.
6. L. A. Brooks and J. C. Bacon, U.S. Pat. 29,111,394 (to RT Vanderbilt).
7. T. R. Dawson, *J. Res. Assoc. Brt. Rubber Manufac.* **9**(3), 11 (1940).
8. A. Periminov, *Kauch. Razina*, **10**, 85 (1938).
9. A. P. Kuriakose and G. Mathew, *Indian J. Technol.*, **26**, 344 (1988).
10. G. Mathew, P. V. Pillai, and A. P. Kuriakose, *Rubber Chem. Technol.*, **65**, 277 (1992).
11. G. Mathew, B. Kuriakose, and A. P. Kuriakose, *Kautsch Gummi Kunstst.*, **45**(6), 490 (1992).
12. F. Kurzer and P. M. Sanderson, *J. Chem. Soc.*, 3240 (1960).
13. P. J. Flory and J. Rehner, *J. Chem. Phys.*, **11**, 512 (1943).
14. C. J. Sheelan and A. L. Basio, *Rubber Chem. Technol.*, **39**, 144 (1966).
15. B. Ellis and G. W. Welding, *Techniques of Polymer Science*, Soc. Chem. Ind., London, 1964, p. 46; *Rubber Chem. Technol.*, **37**, 571 (1969).
16. M. R. Krejsa and J. L. Koenig, *Rubber Chem. Technol.*, **66**, 376 (1993).