

Effect of Fillers in the Binary Systems Containing TMTD–Amidinothiourea and MBTS–Amidinothiourea in NR Vulcanization

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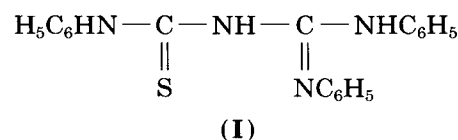
SYNOPSIS

In earlier studies,^{1,2} we have shown that in MBTS–amidinothiourea and TMTD–amidinothiourea binary systems of rubber vulcanization, amidinothiourea functions effectively as a secondary accelerator and improves the accelerator activity of these systems. These secondary accelerators enhance the physical properties of the vulcanizates and show better cure characteristics of the mixes compared to the reference systems studied. In this paper, we present the results of our study on the effect of various fillers in the sulfur vulcanization of natural rubber using amidinothiourea as the secondary accelerator. We have taken MBTS–amidinothiourea and TMTD–amidinothiourea binary accelerator systems and vulcanizates were prepared with carbon black, precipitated silica, and china clay as fillers. Different compositions of amidinothiourea were used in various mixes using standard recipes. Reference mixes were also studied. Curing characteristics of the mixes and various physical properties of the vulcanizates were evaluated. Optimum dosage of amidinothiourea required has also been derived. Among the different secondary accelerators tried including amidinothiourea, it may be stated generally that the more nucleophilic the secondary accelerator, the less the optimum cure times. This fact points to a nucleophilic reaction mechanism in the systems under review. In the evaluation of tensile and other physical properties of the vulcanizates, some of the systems containing amidinothiourea show better properties while others give comparable values with the reference mixes. Estimation of crosslink density also supports the above conclusion. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The exact mechanism of the chemical reactions involved when binary accelerator systems are used in rubber vulcanization is not fully understood even now. It differs with the varying systems used. Other earlier studies using different binary accelerated systems of vulcanization in natural and synthetic rubbers, both dry and in the latex stage,^{3,4} have proved that when a nucleophile is used as a secondary accelerator along with primary accelerators like

tetramethyl thiuram disulfide (TMTD), sulfenamides etc., where sulfur is combined as S—S, C—S—C, or S—N, the reaction mechanism is essentially nucleophilic, and is ionic in character. The more active the nucleophile, the higher is the rate of acceleration and hence the less the optimum cure time. In this context, we recently used 1-phenyl-3-(*N,N'*-diphenylamidino)thiourea (**I**) as a secondary accelerator along with TMTD and also with mercaptobenzothiazyl disulfide (MBTS) in the sulfur vulcanization of natural



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rubber (NR). These are found to be very effective accelerator combinations in gum vulcanizates. The evaluation of the different tensile properties, both before and after aging, also showed them to be very promising. The present study is an extension of our earlier work on the use of amidinothiourea (**I**) in natural rubber vulcanization. Here, amidinothiourea is used in the different filled vulcanizates containing carbon black, precipitated silica, and china clay. Amidinothiourea is more nucleophilic than simple thiourea. This is evident from the fact that amidinothiourea (**I**) can condense with arylisothiocyanates in the absence of alkali, unlike thiourea. Also the presence of a guanidinyll group will facilitate the polarization of the C=S bond. Hence it was presumed that mixes containing amidinothiourea will show a lower optimum cure time and a corresponding increase in cure rate compared to those containing thiourea.

Gum natural rubber vulcanizates, although high in physical strength, are suitable only for very few commercial applications. Fillers are generally incorporated for improved processability, reinforcement, or cost reduction. The effect of a filler on rubber vulcanizates depends on its physical properties, such as particle size, surface area per unit weight, surface reactivity, electrical charge on the particle, and chemical properties such as pH and reactivity with accelerators. In general, the best reinforcing fillers are those that have the smallest particle size. The basic aspects of polymer-filler interaction have been studied in a number of polymers.⁵⁻⁸ Studies on filled systems have also been reviewed by Kraus⁹ and Voet.¹⁰ The role of reinforcing blacks in the sulfuration processes in vulcanization has been discussed by Porter¹¹ as well as by Bhowmick and De.¹² Other reports¹³⁻¹⁶ also throw light on the reinforcing properties of carbon black. Bhowmick and De¹⁷⁻¹⁹ have also studied the polymer-filler interactions that control the properties of rubber vulcanizates.

Carbon blacks are the most effective reinforcing fillers. With the general purpose elastomers like NR, high abrasion furnace (HAF) blacks with average particle size in the range 24–28 nm are most widely used. Precipitated silica is the best nonblack reinforcing filler so far developed and comes closest to carbon black in its reinforcing properties. It has a particle size as fine as that of carbon black and also has an extremely reactive surface. Clays represent the largest volume of nonblack filler used in rubber. They owe this popularity to a combination of low cost, low to moderate reinforcement, and benefits in processing. They have a pronounced stiffening effect and impart hardness and a fairly good abrasion

resistance. Almost all these fillers are highly adsorptive^{20,21} in nature and hence they are known to consume an additional amount of accelerator due to adsorption. So in formulating filled NR compounds it is necessary to use more than the normal quantity of accelerator or the correct combination of accelerator system. In this context, we thought it would be worthwhile to investigate the filled vulcanizates of NR containing amidinothiourea (ATU) as a secondary accelerator along with MBTS or TMTD since our recent studies had shown^{1,2} that the above systems are very effective in NR gum vulcanizates.

The present study covers different aspects like mixing, curing, and determination of the various physical properties of the vulcanizates of all the filled systems of NR referred to above. Control mixes were also prepared and the above properties of the new mixes and those of the control mixes were compared. To understand the variation in physical properties of the different vulcanizates, chemical crosslinks were also estimated using the equilibrium swelling method.

EXPERIMENTAL

Materials

Natural rubber conforming to ISNR-5 grade of Mooney viscosity (ML 1 + 4, 100°C), 85 was obtained from Rubber Research Institute of India, Kottayam. The rubber additives used viz., zinc oxide, stearic acid, MBTS, TMTD, diphenyl guanidine (DPG), thiourea, sulfur, diethylene glycol (DEG), aromatic oil, naphthenic oil, carbon black (HAF N-330), precipitated silica (vulcasil-S), and china clay were all of commercial grade. 1-Phenyl-3-(*N,N'*-diphenylamidino)thiourea (**I**) was synthesized by the reaction of phenyl isothiocyanate and DPG in benzene, by refluxing over a steam bath, as reported by Kurzer and Sanderson.²² Chemical reagents used for the above synthesis and toluene used for swelling studies were of analar grade.

Formulations of the different mixes used in the present study are shown in Tables I and II. The various fillers used are carbon black, precipitated silica, and china clay. All mixes contain 50 parts per hundred rubber (phr) of the respective filler. Mixes A₁–A₃, C₁–C₃, and E₁–E₃ contain 0.5, 1.0, and 1.5 phr of ATU with 1 phr of MBTS, and mixes A'₁–A'₃, C'₁–C'₃, and E'₁–E'₃ contain 0.5, 1.0, and 1.5 phr of ATU with 1 phr of TMTD, respectively. The rest are control formulations.

All the above mixes were prepared as per ASTM designation D3182-89 in a two-roll mixing mill. Goettfert elastograph model 67.85 was used for determining the cure characteristics of the different mixes. The relevant cure data reported are the following.

1. Optimum cure time (t_{90}) is the time taken for attaining 90% of the maximum torque.
2. Scorch time (t_{10}) is the time taken for a two unit rise above the minimum torque (about 10% vulcanization).
3. Induction time (t_5) is the time taken for a one unit rise above the minimum torque (about 5% vulcanization).
4. Minimum torque is the torque attained by the mix at the test temperature before the onset of cure.
5. Maximum torque is the torque recorded after the curing of the mix is complete.
6. The cure-rate index is calculated and reported as $100/(t_{90} - t_{10})$.
7. The reinforcement factor α is calculated and reported as²³

$$\alpha = \frac{[\Delta L_{\max}(\text{filled}) - \Delta L_{\max}(\text{gum})]}{\Delta L_{\max}(\text{gum})}$$

where $\Delta L_{\max}(\text{filled})$ and $\Delta L_{\max}(\text{gum})$ are the maximum changes in torque during vulcanization for filled compounds and for gum compounds,^{1,2} respectively.

All the above cure characteristics obtained for the various mixes are reported in Tables III and IV and the corresponding typical cure curves are shown in Figures 1-6.

The compounds were vulcanized up to the optimum cure time in an electrically heated laboratory type hydraulic press at 150°C at a pressure of 12 MPa. The tensile properties of the vulcanizates were determined on a Zwick universal testing machine model 1445 using a crosshead speed of 500 mm/min as per ASTM designation D412-87 (method A). Dumbbell specimens for the test were punched out of the moulded sheets along the mill grain direction. Heat aging was studied as per ASTM designation D865-88 at 70°C for 48 h.

The tensile properties are reported in Tables V

Table III Cure Characteristics of the MBTS Mixes (Cured at 150°C)

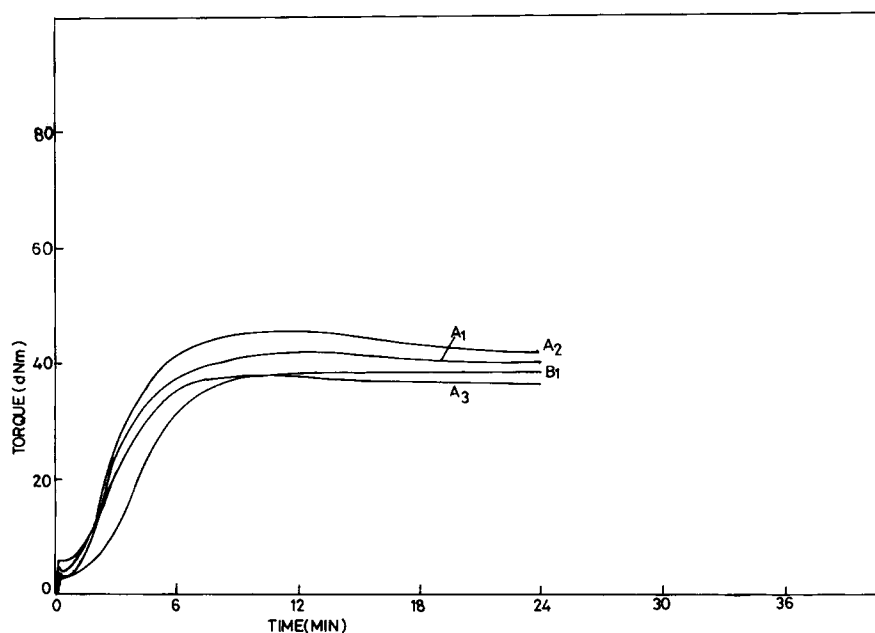
	Optimum Cure Time, (t_{90}), min	Scorch Time ^a , (t_{10}), min	Induction Time, (t_5), min	Cure-rate Index	Minimum Torque, dNm	Maximum Torque, dNm	Reinforcement Factor, α
A ₁	6.8	1.7	1.0	19.61	6.1	41.2	2.12
A ₂	5.8	1.5	0.9	23.26	4.7	44.9	1.74
A ₃	5.6	1.3	0.9	23.26	4.3	37.5	1.12
B	3.8	1.6	1.1	45.46	4.0	67.9	1.83
B ₁	7.1	2.3	1.4	20.83	3.0	38.4	1.98
B ₂	4.2	1.3	1.0	34.48	3.2	52.8	2.09
B ₃	8.1	1.6	1.3	15.39	3.8	29.8	0.58
C ₁	5.8	1.9	1.7	25.64	1.7	16.9	0.28
C ₂	4.4	1.2	1.1	31.25	3.7	40.3	1.46
C ₃	3.9	1.0	0.8	34.48	3.2	43.9	1.48
D	4.7	2.2	1.9	40.00	1.8	35.2	0.47
D ₁	8.4	3.7	3.2	21.28	2.1	27.0	1.09
D ₂	4.2	1.6	1.4	38.46	2.2	42.7	1.5
D ₃	5.4	1.6	1.2	26.32	3.0	26.8	0.42
E ₁	4.3	1.4	1.3	34.48	0.5	16.7	0.27
E ₂	3.7	1.2	1.1	40.00	0.5	17.6	0.07
E ₃	3.3	1.0	0.9	43.48	0.6	20.0	0.13
F	3.5	1.3	1.3	45.45	0.5	30.7	0.28
F ₁	3.8	1.8	1.7	50.00	0.8	18.6	0.44
F ₂	3.4	1.3	1.3	47.62	0.4	23.9	0.40
F ₃	4.5	1.3	1.2	31.25	0.8	18.5	-0.021

^a Elastographic scorch time (t_{10}).

Table IV Cure Characteristics of the TMTD Mixes (Cured at 150°C)

	Optimum Cure Time, (t_{90}), min	Scorch Time ^a , (t_{10}), min	Induction Time, (t_0), min	Cure-rate Index	Minimum Torque, dNm	Maximum Torque, dNm	Reinforcement Factor, α
A ₁	2.2	1.3	1.1	111.11	2.1	44.8	1.2
A ₂	2.1	1.2	0.8	111.11	3.4	41.5	0.87
A ₃	1.8	1.0	0.8	125.00	4.5	46.7	1.01
B	3.8	1.6	1.1	45.46	4.0	67.9	1.83
B ₁	2.8	1.5	1.1	76.92	3.7	64.8	1.87
B ₂	2.1	1.3	1.0	125.00	5.2	59.3	2.33
B ₃	2.6	1.4	1.2	83.33	6.4	60.4	1.42
C ₁	2.6	1.4	1.2	83.33	2.3	33.8	0.66
C ₂	1.9	0.9	0.8	100.0	3.0	41.1	0.85
C ₃	1.7	0.8	0.6	111.11	3.4	42.3	0.82
D	4.7	2.2	1.9	40.00	1.8	35.2	0.47
D ₁	2.9	1.8	1.6	90.91	1.8	34.4	0.52
D ₂	2.1	1.2	1.1	111.11	2.7	40.8	1.29
D ₃	2.3	1.3	1.2	100.00	2.7	33.9	0.36
E ₁	1.8	1.1	1.1	142.86	0.2	12.5	-0.39
E ₂	1.5	0.9	0.9	166.67	0.4	20.0	-0.099
E ₃	1.3	0.7	0.7	166.67	0.6	21.3	-0.082
F	3.5	1.3	1.3	45.45	0.5	30.7	0.28
F ₁	3.5	1.5	1.4	50.00	0.4	28.8	0.27
F ₂	2.2	1.2	1.2	100.00	0.5	21.9	0.23
F ₃	1.4	0.7	0.7	142.86	0.8	23.6	-0.056

^a Elastographic scorch time (t_{10}).

**Figure 1** Cure curves of the mixes A₁, A₂, A₃, and B₁.

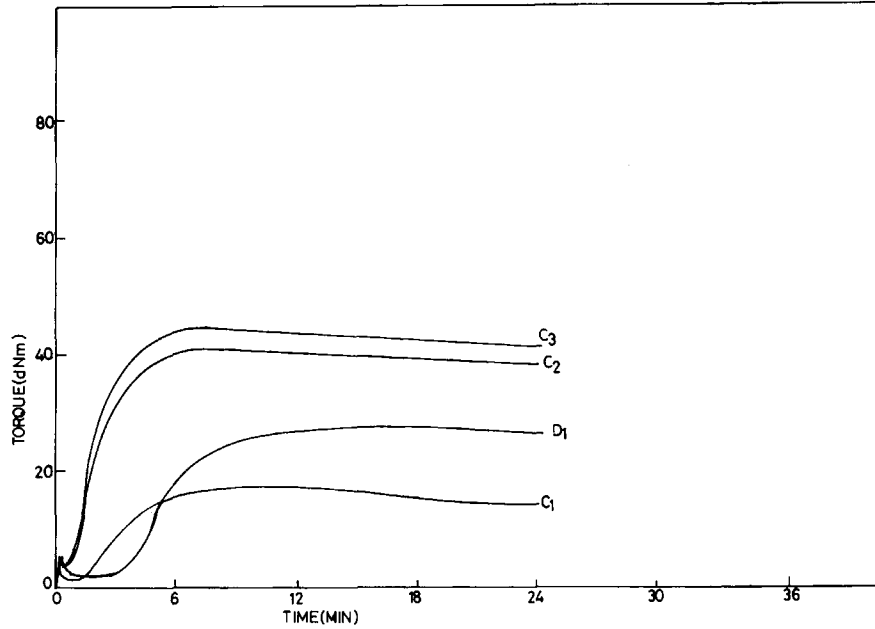


Figure 2 Cure curves of the mixes C₁, C₂, C₃, and D₁.

and VI. Tear resistance was tested as per ASTM designation D624-86 using angular test pieces. Compression set, hardness, and heat buildup were tested as per ASTM D395-89 (method B), D2240-86, and D623-88 (method A), respectively. Rebound resilience was evaluated using Dunlop tripsometer

(BS 903 Part 48) and abrasion resistance using DIN abrader (DIN 53516). These test data obtained are reported in Tables VII and VIII.

The concentration of the chemical crosslinks (crosslink density) of the vulcanizates was determined from the equilibrium swelling data. Swelling

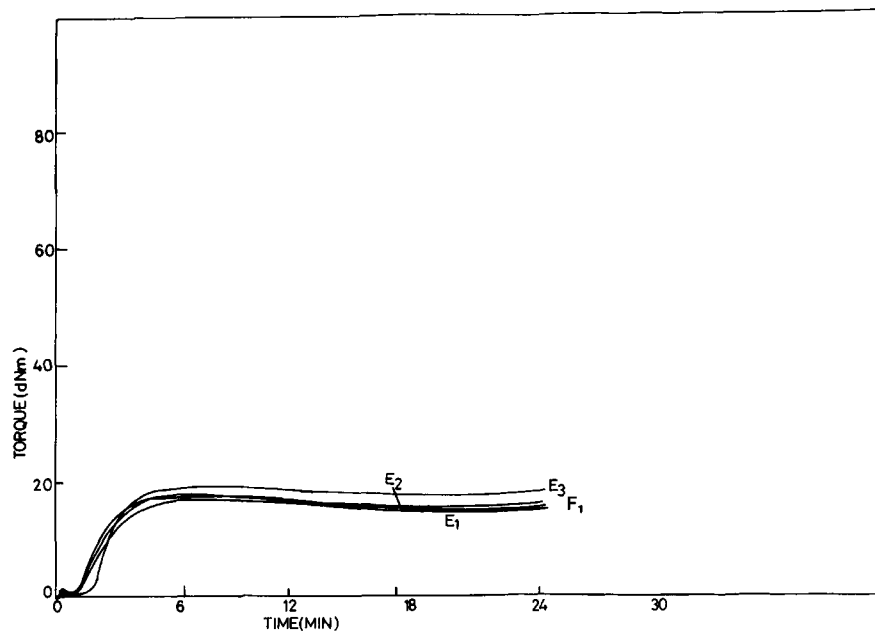


Figure 3 Cure curves of the mixes E₁, E₂, E₃, and F₁.

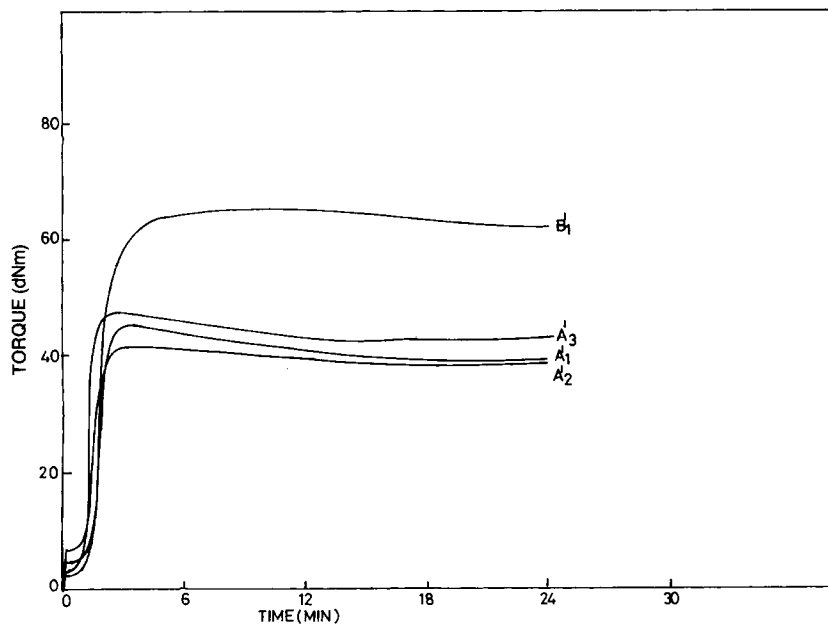


Figure 4 Cure curves of the mixes A'₁, A'₂, A'₃, and B'₁.

was done in toluene for 24 h using samples of 0.2 cm thickness, 1 cm diameter, and 0.2 g weight. The swollen samples were then taken out and weighed. The solvent was removed in vacuum and the samples weighed again. The volume fraction of rubber (V_r) in the swollen network is determined assuming that

the filler does not swell. V_r is calculated according to Ellis and Welding.²⁴

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

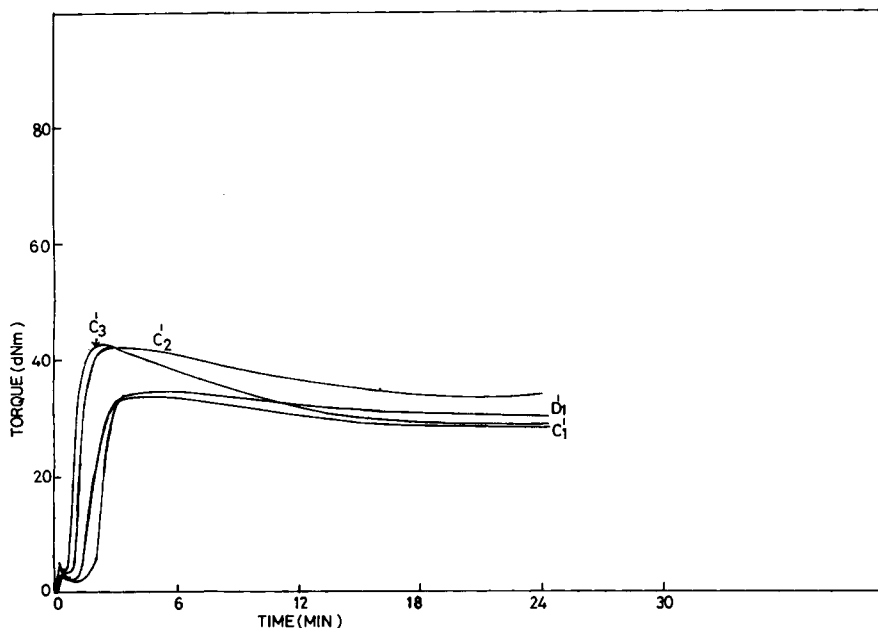


Figure 5 Cure curves of the mixes C'₁, C'₂, C'₃, and D'₁.

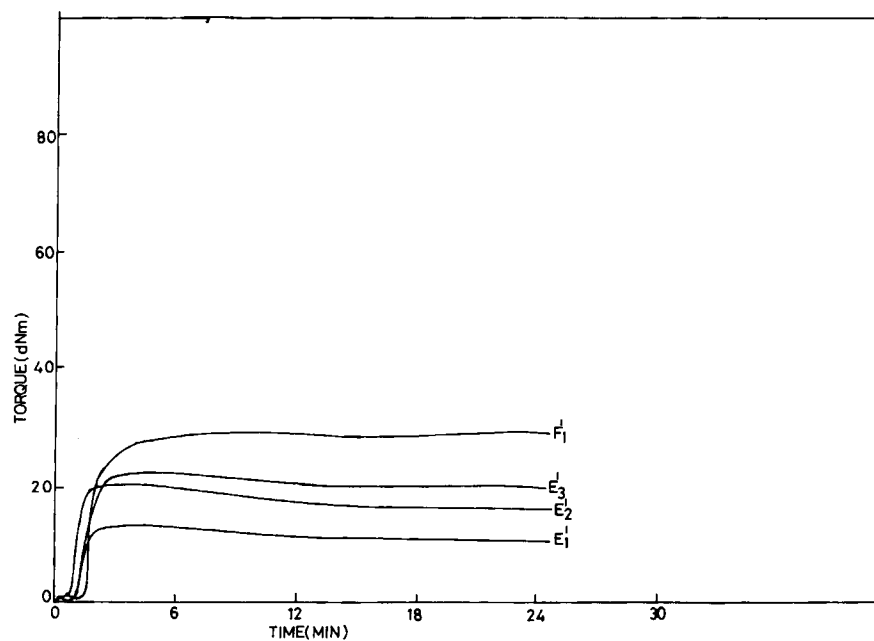


Figure 6 Cure curves of the mixes E_1' , E_2' , E_3' , and F_1' .

Table V Tensile Properties of the Various MBTS Vulcanizates

	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	23.29	24.8	106.48	3.11	1.24	39.87	516.83	559.88	108.33
A ₂	20.53	22.72	110.67	3.88	3.70	95.36	422.61	454.65	107.58
A ₃	22.10	23.58	106.70	2.53	1.20	47.43	503.55	543.73	107.98
B	22.56	19.20	85.11	5.15	5.80	112.67	317.08	257.71	81.28
B ₁	27.24	27.17	99.74	3.34	2.98	89.22	489.90	531.48	108.49
B ₂	29.78	29.5	99.06	3.08	3.60	116.88	533.02	491.15	92.14
B ₃	16.58	19.21	115.86	2.45	2.74	111.84	441.85	448.02	101.40
C ₁	17.43	17.39	99.77	1.76	2.08	118.18	626.95	577.96	92.19
C ₂	18.60	19.03	102.31	1.96	2.38	121.43	613.78	560.87	91.38
C ₃	19.10	19.25	100.79	2.10	2.47	117.62	595.90	558.47	93.72
D	20.05	17.44	86.98	2.72	2.91	106.99	527.26	469.87	89.12
D ₁	19.34	19.23	99.43	2.07	2.35	113.53	602.76	571.28	94.78
D ₂	20.44	20.76	101.57	2.48	2.83	114.11	560.7	537.45	95.85
D ₃	14.49	15.45	106.63	1.78	2.07	116.29	570.37	552.43	96.85
E ₁	19.95	20.75	104.01	1.02	1.33	130.39	820.10	757.87	92.41
E ₂	20.42	22.19	108.67	1.18	1.30	110.17	804.17	759.91	94.5
E ₃	20.99	22.24	105.96	1.12	1.47	131.25	813.51	717.35	88.18
F	17.72	3.28	18.51	1.59	1.80	113.21	619.76	178.76	28.84
F ₁	23.32	23.36	100.17	1.17	1.51	129.06	803.28	730.10	90.89
F ₂	23.80	24.84	104.37	1.55	1.55	100.00	733.16	713.88	97.37
F ₃	19.45	19.52	100.36	1.13	1.28	113.27	799.30	762.81	95.43

Table VI Tensile Properties of the Various TMTD Vulcanizates

	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 '	26.70	21.63	81.01	3.82	4.16	108.90	437.32	354.60	81.08
A ₂ '	25.63	23.16	90.36	3.09	3.67	118.77	474.22	410.42	86.55
A ₃ '	26.95	23.04	85.49	3.64	4.35	119.51	454.98	373.46	82.08
B	22.56	19.20	85.11	5.15	5.80	112.67	317.08	257.71	81.28
B ₁ '	21.62	18.89	87.37	5.35	5.79	108.22	296.96	256.40	86.34
B ₂ '	26.22	10.67	40.69	4.14	5.79	139.86	432.66	170.27	39.35
B ₃ '	26.57	22.71	85.47	4.02	4.80	119.40	429.06	347.78	81.06
C ₁ '	18.58	16.61	89.40	2.03	2.15	105.91	614.4	557.20	90.69
C ₂ '	18.11	16.82	92.88	2.23	2.40	107.62	559.82	528.76	94.45
C ₃ '	18.73	16.15	86.23	2.31	2.34	101.31	559.63	527.17	94.20
D	20.05	17.44	86.98	2.72	2.91	106.99	527.26	469.87	89.12
D ₁ '	18.86	17.96	95.23	2.94	3.00	102.04	486.98	476.52	97.85
D ₂ '	20.95	18.08	86.30	2.62	2.81	107.25	559.48	505.91	90.43
D ₃ '	17.1	15.61	91.29	2.12	2.20	103.77	559.05	525.97	94.08
E ₁ '	22.06	16.72	75.79	1.23	1.37	111.38	801.32	688.78	85.96
E ₂ '	22.51	17.7	78.63	1.21	1.35	111.57	812.83	702.91	86.48
E ₃ '	21.21	19.29	90.95	1.19	1.36	114.29	797.93	711.48	89.17
F	17.72	3.28	18.51	1.59	1.80	113.21	619.76	178.76	28.84
F ₁ '	12.72	3.04	23.90	1.51	1.83	121.19	574.07	182.7	31.83
F ₂ '	22.06	18.37	83.27	1.45	1.65	113.79	713.26	626.45	87.83
F ₃ '	17.85	17.43	97.65	1.31	1.47	112.21	679.7	666.70	98.09

where T is the weight of the test specimen; D , the deswollen weight; F , the weight fraction of the insoluble components of the vulcanizate; A_0 , the weight of the absorbed solvent corrected for the swelling increment; and ρ_r and ρ_s , the densities of rubber and solvent, respectively ($\rho_r = 0.921$ g/cm³ for NR and $\rho_s = 0.886$ g/cm³ for toluene).

The values of V_r obtained as above were then converted into V_{r0} (the value V_r would have had in the absence of the filler) according to the Cunneen-Russell equation.²⁵

$$V_{r0}/V_r = ae^{-z} + b$$

Here a and b are constants characteristic of the system, and z is the weight fraction of the filler in the vulcanizate. The values of a and b for HAF black filled system are $a = 0.56$ and $b = 0.44$. The corresponding values for silica and clay filled systems are²⁶ silica system, $a = 1.41$ and $b = -0.41$; clay system, $a = 0.21$ and $b = 0.79$. V_{r0} were then substituted in the Flory-Rehner equation²⁷ in place of V_r to obtain the crosslink density $1/2M_c$ as follows:

$$\frac{1}{2M_c} = \frac{-[\ln(1 - V_{r0}) + V_{r0} + \chi V_{r0}^2]}{\rho_r V_s (V_{r0})^{1/3}}$$

where V_s is the molar volume of solvent ($V_s = 106.2$ cm³/mol for toluene), χ is the parameter characteristic of interaction between rubber and solvent²⁸ (χ for NR-toluene = 0.42), and M_c is the number average molecular weight of the rubber chain between crosslinks.

RESULTS AND DISCUSSION

The results obtained clearly indicate the acceleration activity of ATU in the carbon black, silica, and clay-filled NR vulcanization systems containing either TMTD or MBTS as the primary accelerator. It is seen that the nucleophilic reaction mechanism proposed by us^{1,2} in similar gum vulcanization reactions holds good for the filled systems also. This is clearly evident from the reduction in cure time for mixes containing amidinothiourea compared to those containing equivalent amounts of thiourea. Even though

Table VII Other Physical Properties Evaluated (MBTS Systems)

	Hardness (Shore A)	Compression Set (%)	Heat Buildup (ΔT °C)	Resilience (%)	Abrasion Loss (cm ³ /h)	Tear Strength (N/mm)	Total Crosslink Density, $\times 10^5$ g/mol/cm
A ₁	49	42.28	39	48.77	3.79	64.74	3.1101
A ₂	53	38.5	40	49.38	4.25	103.84	2.3929
A ₃	43.5	37.34	35	47.54	5.00	60.69	2.7149
B	60	18.74	21	63.12	2.60	83.88	7.4864
B ₁	45	42.17	30	51.89	3.92	106.27	3.9179
B ₂	51	32.93	27	56.39	3.66	118.12	4.0852
B ₃	45	55.58	57	44.56	5.07	32.93	3.2025
C ₁	31	43.22	31	63.12	7.44	53.63	1.6929
C ₂	42	43.83	25	65.20	6.37	58.33	1.6753
C ₃	47	39.12	23	64.51	6.24	70.40	1.9882
D	52	30.07	16	74.59	5.48	53.10	1.8790
D ₁	45	40.40	25	65.91	5.95	63.43	1.3996
D ₂	48	44.00	21	68.03	5.42	70.84	1.6865
D ₃	43	50.00	44	59.04	7.87	45.65	1.6331
E ₁	26	37.69	18	77.59	9.82	25.25	2.9236
E ₂	27	39.44	19	75.34	9.48	25.29	2.8083
E ₃	30	38.00	19	73.85	7.32	26.16	2.6956
F	40	24.32	07	82.97	8.94	32.02	6.4511
F ₁	31	43.51	14	80.64	7.54	28.59	3.0291
F ₂	31	35.97	11	81.41	7.14	26.2	3.3051
F ₃	28	34.78	17	77.59	9.36	24.00	2.9361

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.²⁹

The vulcanization systems containing MBTS and ATU (mixes A₁-A₃, C₁-C₃, and E₁-E₃) are found to be better than the corresponding reference systems containing MBTS alone (mixes B₁, D₁, and F₁) as far as the cure characteristics are concerned, irrespective of the filler used (Table III and Figs. 1-3). A substantial reduction in the optimum cure time with increase in the concentration of ATU is observed when carbon black or silica is the filler used. However, a corresponding reduction in scorch safety is observed in these mixes. In the case of clay-filled systems also, a more or less similar trend is observed. In all the filled systems under investigation, a practical cure system seems to be the one containing 1.0 phr of ATU and that may be taken as the optimum dosage of ATU to be used with MBTS. The lowest cure times are shown by the clay-filled systems and the highest by the carbon black-filled systems. Consequently clay-filled MBTS/ATU mixes show the highest values for cure-rate index and the carbon black-filled mixes show the lowest values. The other cure characteristics of the experimental mixes con-

taining MBTS and ATU are comparable to those of the corresponding reference mixes. Maximum torque, minimum torque, and reinforcement factor α of the experimental mixes containing MBTS and ATU is best when carbon black is the filler (mixes A₁-A₃) and least in clay-filled systems (mixes E₁-E₃).

Cure characteristics of the vulcanization systems containing TMTD and ATU (mixes A'₁-A'₃, C'₁-C'₃, and E'₁-E'₃) are found to be better than those of the corresponding reference mixes containing TMTD alone (B'₁, D'₁, and F'₁) (see Table IV and Figs. 4-6). Here too, the addition of ATU has reduced the optimum cure time considerably. However, scorch time of the mixes has also been reduced. From the data, the optimum dosage of ATU to be used with TMTD may be taken as 0.5 phr since this gives the most practical combination of optimum cure time and scorch safety. All the other cure characteristics of the TMTD/ATU systems are comparable to those of the reference mixes and the trend in the variation of these properties with respect to filler is the same as that for the MBTS/ATU mixes.

Tensile properties of the vulcanizates containing ATU are found to be good in both the binary systems under review. The effects of ATU concentration on tensile properties of the carbon black, silica, and

Table VIII Other Physical Properties Evaluated (TMTD Systems)

	Hardness (Shore A)	Compression Set (%)	Heat Buildup (ΔT °C)	Resilience (%)	Abrasion Loss (cm ³ /h)	Tear Strength (N/mm)	Total Crosslink Density, $\times 10^5$ g/mol/cm
A ₁ '	52	25.85	24	61.06	3.33	78.92	5.2443
A ₂ '	50	24.73	34	55.08	3.58	68.19	4.8168
A ₃ '	52.5	22.96	30	58.37	3.87	96.87	5.0721
B	60	18.74	21	63.12	2.6	83.88	7.4864
B ₁ '	62	24.16	22	61.74	3.67	73.04	7.6011
B ₂ '	57.5	27.2	30	43.97	3.53	107.42	6.8367
B ₃ '	55	25.52	31	59.04	2.96	98.09	6.5830
C ₁ '	42	35.09	31	59.04	6.61	65.20	1.7999
C ₂ '	46	37.31	26	63.81	6.48	57.63	1.7937
C ₃ '	47	33.7	24	68.03	6.21	55.86	1.9963
D	52	30.07	16	74.59	5.48	53.10	1.8790
D ₁ '	50	31.51	19	71.64	6.18	50.09	1.7643
D ₂ '	52	19.87	24	63.12	6.59	62.55	1.3805
D ₃ '	44	44.44	29	59.71	7.18	51.89	1.6721
E ₁ '	32	30.87	14	76.09	7.74	28.35	4.0240
E ₂ '	33	25	14	76.08	6.89	29.65	4.0240
E ₃ '	34	24.68	13	74.59	6.66	30.32	3.4275
F	40	24.32	07	82.97	8.94	32.02	6.4511
F ₁ '	39	30.83	11	79.88	7.85	26.65	3.8827
F ₂ '	33	28.29	12	76.84	9.23	26.64	3.6586
F ₃ '	32	35.81	16	76.08	7.43	28.78	3.7601

clay filled vulcanizates (MBTS/ATU), both before and after aging, are shown in Figures 7–9. These properties of the vulcanizates from TMTD/ATU systems are similarly shown in Figures 10–12. For both silica and clay-filled vulcanizates of the MBTS/ATU systems, the tensile strength increases with increase in the concentration of ATU whereas the tensile strength of the carbon black-filled vulcanizates first decreases to a minimum and then increases. The values of tensile strength for vulcanizates with MBTS alone (mixes B₁, D₁, and F₁), in all three filler types are higher than that of any of the MBTS/ATU binary combinations (Fig. 7). The 100% modulus of the silica-filled vulcanizates shows a variation similar to that of the tensile strength. However, modulus (100%) of carbon black- and clay-filled vulcanizates increases to a maximum and then decreases with increase in the concentration of ATU. Variation of this property in the case of clay-filled vulcanizates is only minimal. Vulcanizates with MBTS alone is seen to have 100% modulus, slightly higher than or almost the same as that of the MBTS/ATU combinations (Fig. 8). Elongation at break of both clay- and silica-filled vulcanizates de-

creases marginally with increase in the concentration of ATU while that of the carbon black filled vulcanizate first decreases and then increases. Elongation at break values for the vulcanizates containing MBTS alone are seen to be in between that of the values of the three MBTS/ATU combinations (Fig. 9). As expected, the highest values of tensile strength and modulus in the MBTS/ATU systems are given by the carbon black filled vulcanizates. Aging resistance of the vulcanizates with amidinothiourea is seen to be comparable to other mixes used in the study.

The variation in tensile properties of the vulcanizates (TMTD/ATU systems) with concentration of ATU, both before and after aging, is shown graphically in Figures 10–12. Here the variations are not as marked as in the case of MBTS/ATU combinations. Tensile strength, 100% modulus, and elongation at break of the clay-filled TMTD/ATU systems show very little variation with increase in the concentration of ATU. For silica-filled systems also there is no significant variation in the tensile strength and 100% modulus. But elongation at break decreases initially with increase in the concentration

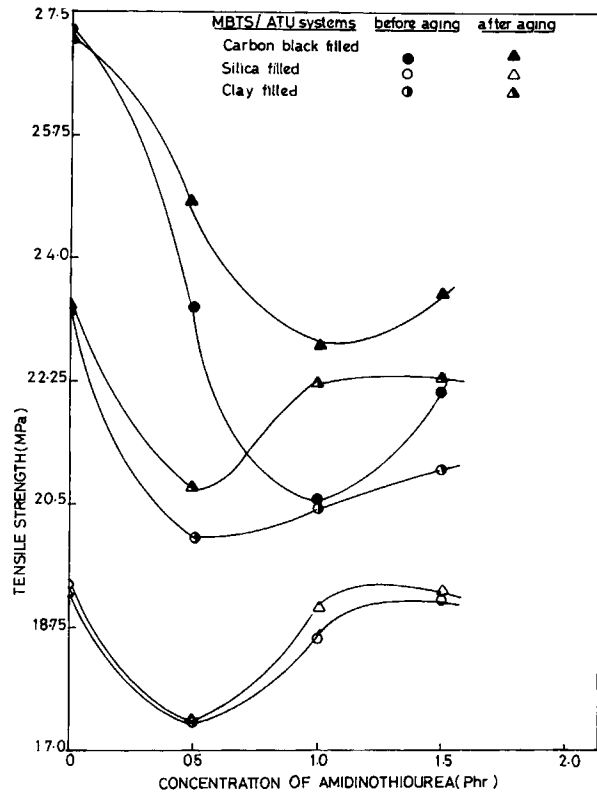


Figure 7 Effect of concentration of amidinothiourea on tensile strength of MBTS/ATU vulcanizates.

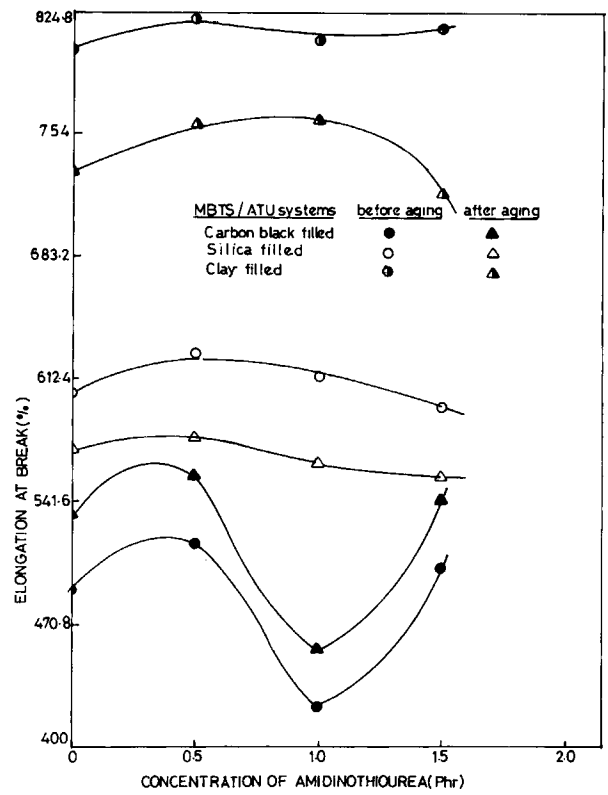


Figure 9 Effect of concentration of amidinothiourea on elongation at break of MBTS/ATU vulcanizates.

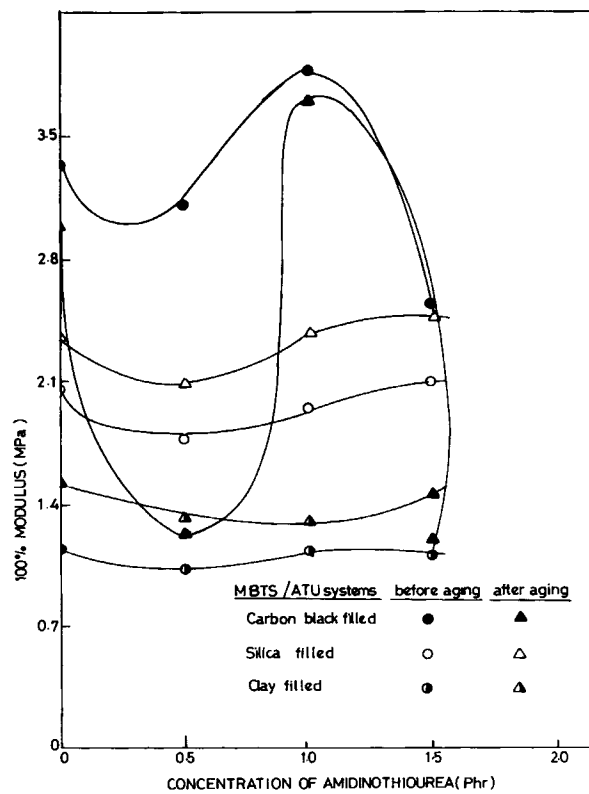


Figure 8 Effect of concentration of amidinothiourea on 100% modulus of MBTS/ATU vulcanizates.

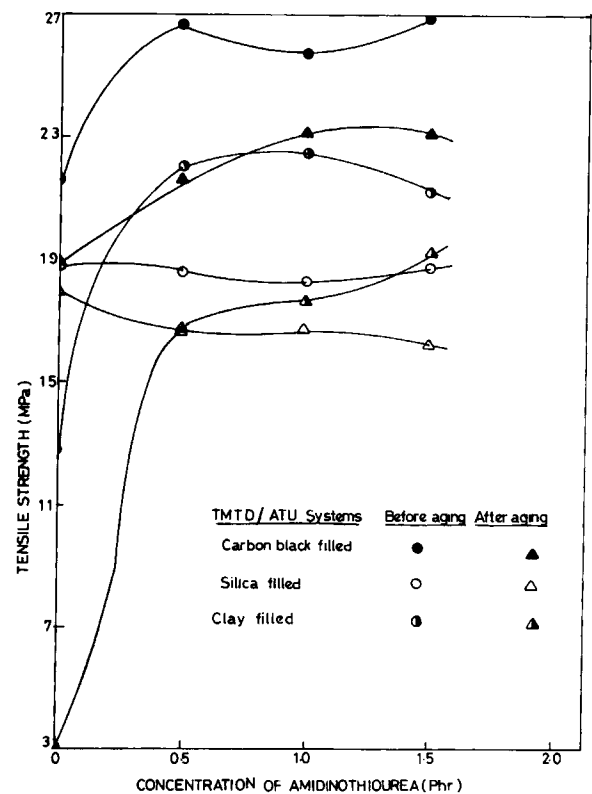


Figure 10 Effect of concentration of amidinothiourea on tensile strength of TMTD/ATU vulcanizates.

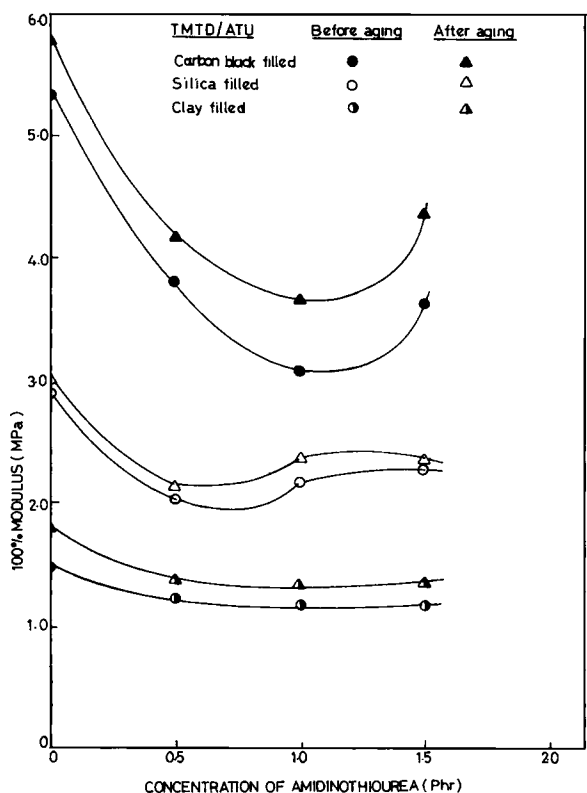


Figure 11 Effect of concentration of amidinothiourea on 100% modulus of TMTD/ATU vulcanizates.

of ATU and then stabilizes. Carbon black-filled TMTD/ATU systems are the only ones that show any marked variation in its tensile properties with change in concentration of ATU. But in this case also tensile strength shows no significant variation. The 100% modulus first decreases and then increases and elongation at break shows the reverse trend; 100% modulus is higher and elongation at break is lower for the systems containing TMTD alone compared to TMTD/ATU combinations in all the three filler types. The values of tensile strength of the carbon black-filled and clay-filled vulcanizates containing only TMTD are lower than those of TMTD/ATU combinations. However, the silica-filled TMTD vulcanizate has a tensile strength approximately the same as that of the TMTD/ATU systems. All the three filler types of the TMTD/ATU systems show very good retention of tensile strength, elongation at break, and modulus after heat aging.

A bar graph comparison of the tensile properties of the reference mixes with those of the MBTS/ATU systems of equivalent concentration (1 : 1) both

before and after aging is given in Figures 13–15 for the carbon black, silica-, and clay-filled systems, respectively. A similar type of comparison, of the TMTD/ATU systems, is given in Figures 16–18.

Other physical properties such as hardness, compression set, heat buildup, resilience, abrasion loss, and tear strength were also evaluated and are reported in Tables VII and VIII. All the above properties of the MBTS/ATU and TMTD/ATU vulcanizates give values that are comparable to the corresponding reference mixes irrespective of the type of filler used. The values for these properties do not show much variation with variation in concentration of ATU in both MBTS/ATU and TMTD/ATU systems. For both the above systems, better values for hardness, abrasion resistance, and tear strength are shown by carbon black-filled vulcanizates and least by clay-filled systems. As far as heat build-up and resilience are concerned, clay-filled vulcanizates are better than silica-filled ones, which in turn are better than carbon black-filled systems. Compression set values are almost the same for all the three fillers.

The total crosslink density values are also given

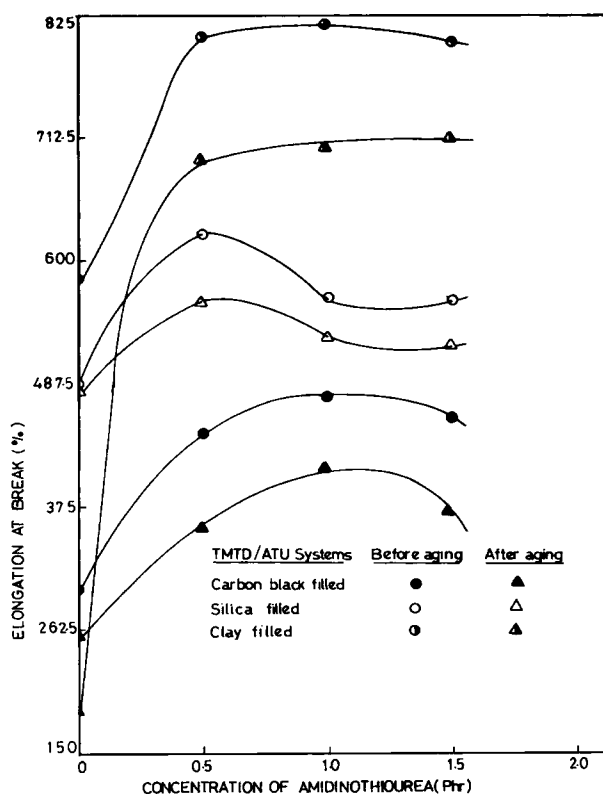


Figure 12 Effect of concentration of amidinothiourea on elongation at break of TMTD/ATU vulcanizates.

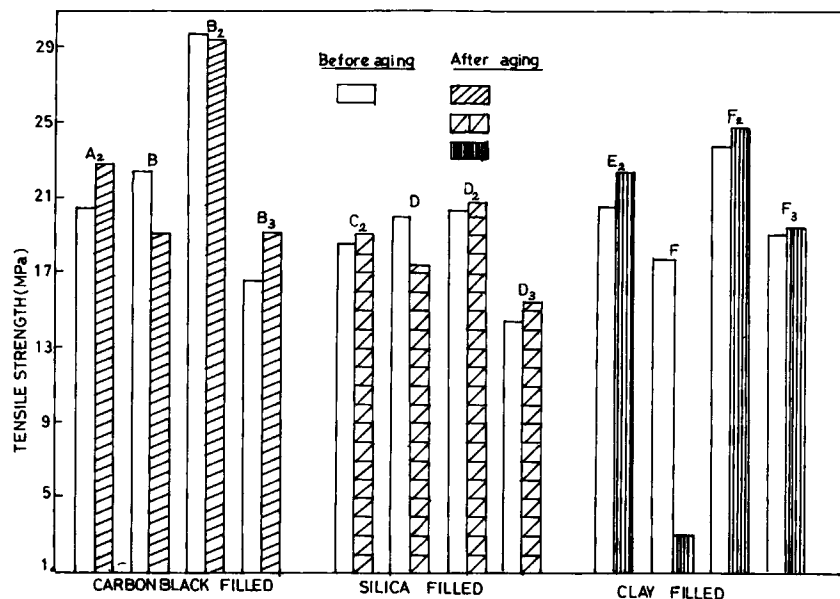


Figure 13 Tensile strength of vulcanizates containing equivalent concentrations of MBTS with ATU, TMTD, DPG, and thiourea.

in Tables VII and VIII. As expected, higher values for tensile strength and also crosslink density are obtained in the case of carbon black-filled vulcanizates for both the binary systems. The above values

are found to be least for silica-filled vulcanizates. It is seen that the variation in crosslink density can be correlated to the variation in the different tensile properties of both the binary systems.

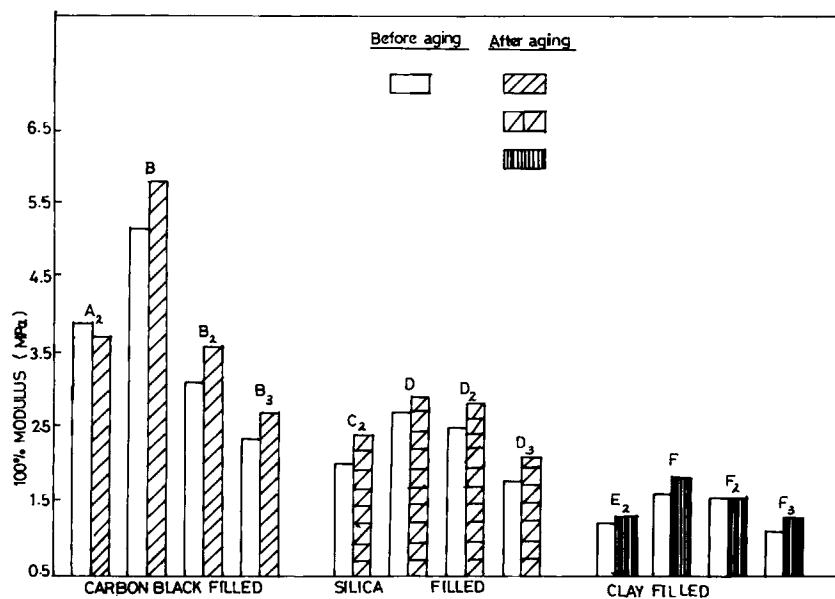


Figure 14 One hundred percent modulus of vulcanizates containing equivalent concentrations of MBTS with ATU, TMTD, DPG, and thiourea.

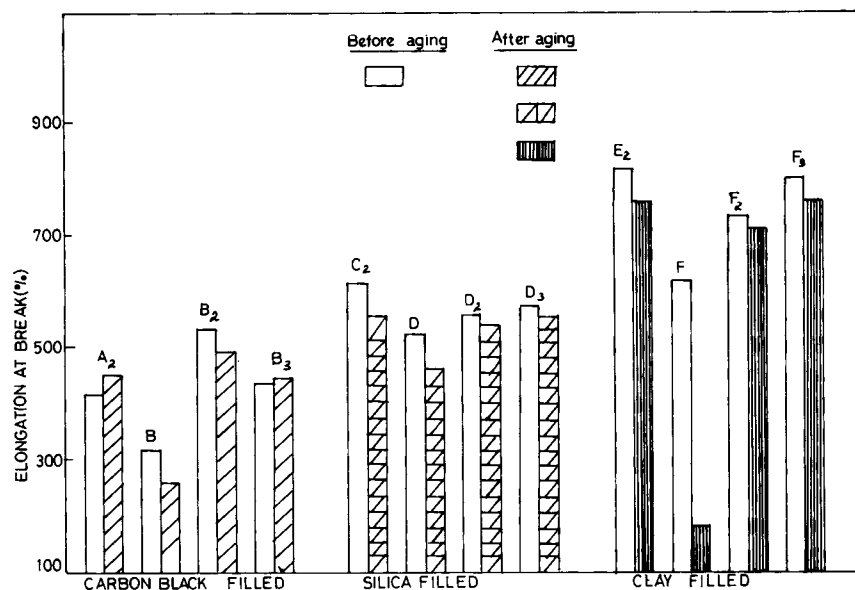


Figure 15 Elongation at break of the vulcanizates containing equivalent concentrations of MBTS with ATU, TMTD, DPG, and thiourea.

SUMMARY AND CONCLUSIONS

The effects of ATU as a secondary accelerator in the binary systems of MBTS/ATU and TMTD/ATU in NR vulcanizates containing carbon black, silica, and china clay as fillers have been investi-

gated. The study covered different aspects, like mixing, curing, and determination of the various physical properties of the vulcanizates, and the results obtained can be summarized as follows.

Both the binary systems are found to be very effective in filled NR vulcanizates. The results ob-

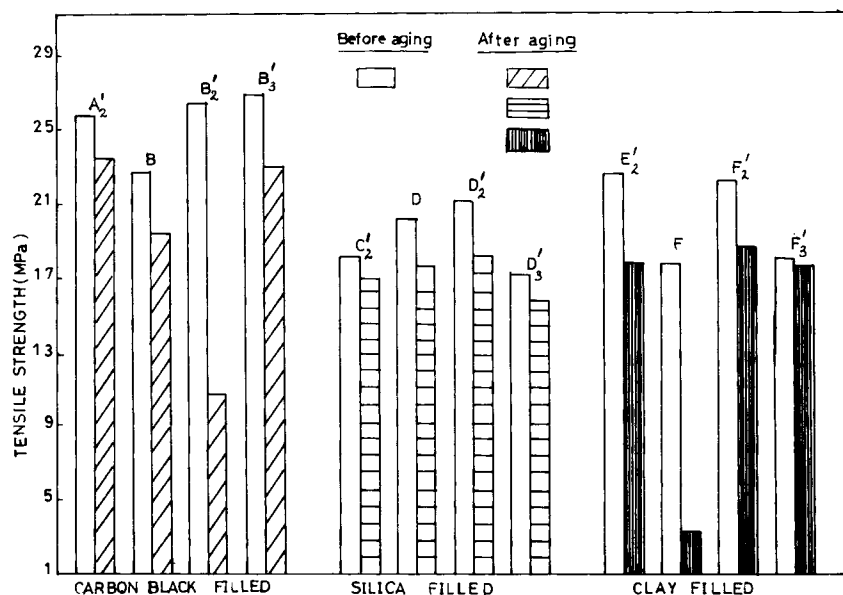


Figure 16 Tensile strength of the vulcanizates containing equivalent concentrations of TMTD with ATU, MBTS, DPG, and thiourea.

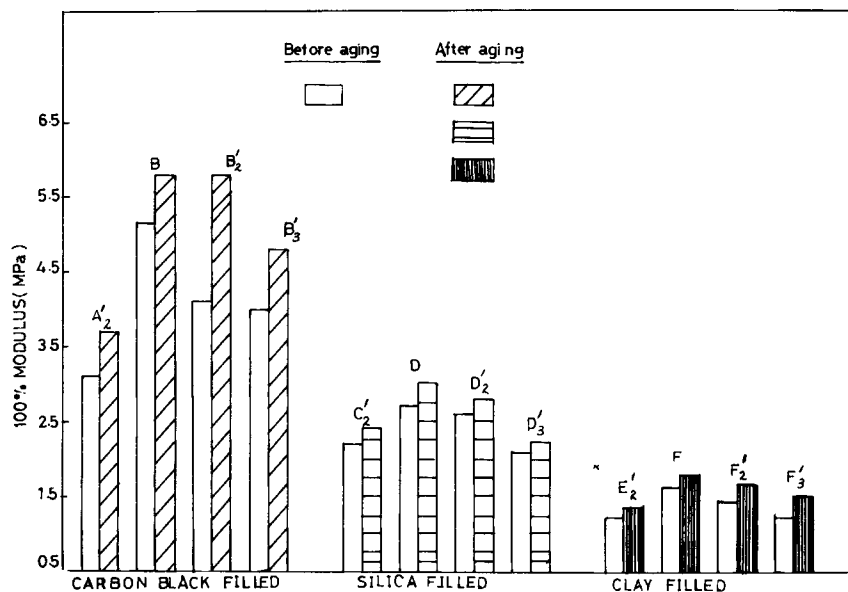


Figure 17 One hundred percent modulus of the vulcanizates containing equivalent concentrations of TMTD with ATU, MBTS, DPG, and thiourea.

tained point to a nucleophilic reaction mechanism in the systems under review. The cure characteristics of the mixes and tensile properties of the vulcanizates containing ATU are better than or comparable to those of the reference mixes. The optimum dosage of ATU required for the above binary systems has

been derived. The variation of cure characteristics and tensile properties with filler types does not indicate a set pattern and is dealt with in detail using figures and tables. The percentage retention of tensile properties of the vulcanizates containing ATU is found to be very good. Other physical properties

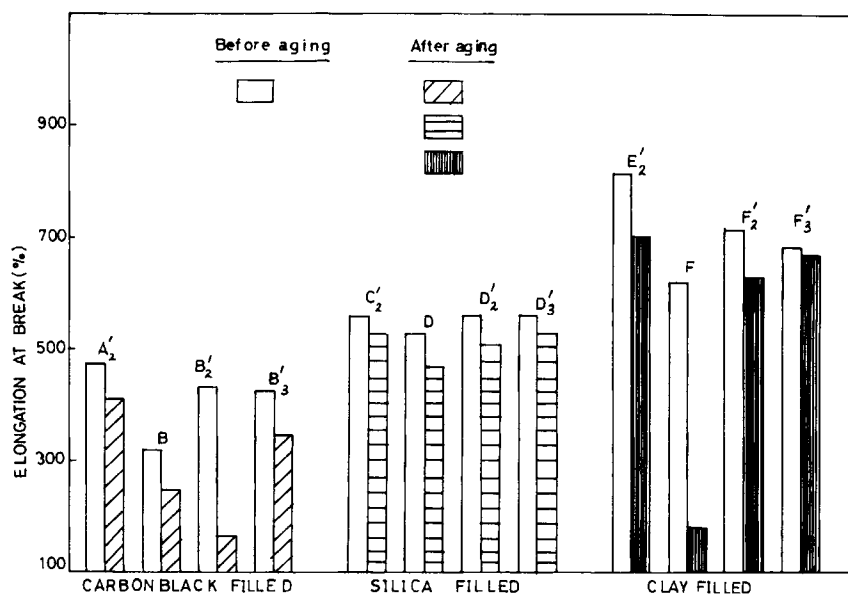


Figure 18 Elongation at break of the vulcanizates containing equivalent concentrations of TMTD with ATU, MBTS, DPG, and thiourea.

such as hardness, resilience, compression set, heat buildup, abrasion resistance, and tear strength of these vulcanizates from both the binary systems give values comparable to those of the reference mixes.

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