

A New Secondary Accelerator for the Sulfur Vulcanization of Natural Rubber Latex and Its Effect on the Rheological Properties

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Received 3 December 2003; accepted 22 March 2004

DOI 10.1002/app.20770

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The vulcanization of natural rubber (NR) latex can be effectively carried out at low temperatures by using binary accelerator systems containing thiourea (TU) as a secondary accelerator. It was reported that sulfur-containing nucleophiles such as thiourea enable the primary accelerator to become effective even at low temperatures, indicating a nucleophilic reaction mechanism in such vulcanization reactions. In the present study, a derivative of thiourea [viz. aminoiminomethyl thiourea (AMT)], which is more nucleophilic than thiourea, is used as a secondary accelerator in the sulfur vulcanization of NR latex. One of the aims of this study was to give conclusive evidence for a nucleophilic reaction mechanism. The synergistic effect of the above thiourea derivative with primary accelerators such as tetramethylthiuram disulfide (TMTD), zinc diethyldithiocarbamate (ZDC), and cyclohexylbenzthiazyl sulfenamide (CBS) was studied at two different temperatures (viz. 100

and 120°C). These binary systems were found to be very effective in reducing the optimum cure time of the different mixes compared to control formulations containing TU. The optimum amount of the secondary accelerator required was also determined. Mechanical properties such as tensile strength and tear strength of the vulcanizates were also evaluated. Chemical characterization of the vulcanizates was carried out by determining the total crosslink density. Values of the cure characteristics evaluated support a nucleophilic reaction mechanism in these vulcanization reactions under review. The effect of this secondary accelerator on the rheological behavior of compounded latex is also studied and was found not to affect adversely. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2781–2789, 2004

Key words: rubber; latices; compounding; vulcanization

INTRODUCTION

The vulcanization of latex is the result of chemical reactions taking place in the heterogeneous system. The use of organic accelerators in latex compounding accelerates the vulcanization process and also improves many of the physical properties of the product. A wide range of organic accelerators for the sulfur vulcanization of diene rubbers is available. In general, only those of the highest activity are important for the vulcanization of rubber latices, because latex vulcanization temperatures are relatively low¹ and there is no danger of scorching here.² Hence, the use of accelerators in latex is basically different from their use in dry rubber.^{3–5} The accelerators should become evenly distributed without causing the mixture to coagulate or to thicken.⁶ It was found that tetramethylthiuram disulfide (TMTD) can be used to cure natural rubber

(NR) latex with or without sulfur to prepare heat-resistant articles.⁷ It may also be used to prepare vulcanizates that can prevent copper-catalyzed oxidative degradation. The vulcanization of latex by using TMTD proceeds only at relatively high temperature.

It was proved⁸ that accelerators in which sulfur is combined as S—S, C—S—C, or S—N are inactive at temperatures < 100°C because of the high thermal stability of the sulfur bonds. Philpott⁸ showed that sulfur-containing nucleophiles such as thiourea (TU) enable such accelerators to become active even at lower temperatures. Moore et al.⁹ showed that the acceleration effect of thiourea is due to its interaction with TMTD under basic conditions to form thiuram polysulfides. Compound (I) will lose a proton to a suitable base in the medium and decompose rapidly to perthioanion. The perthioanion (II) interacts with TMTD to give polysulfides that react with rubber hydrocarbon to form crosslinks. The same mechanism occurs in the presence of elemental sulfur.¹⁰ Earlier studies^{11–13} in our laboratory showed that different derivatives of thiourea such as dithiobiurets and phenyl-substituted amidi-

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TABLE II
Formulation of the Mixes Containing TMTD

Ingredients, parts by weight (wet)	Mixes					
	C ₀	C ₁	C ₂	C ₃	C ₄	C ₅
60% Centrifuged latex	167	167	167	167	167	167
10% KOH solution	1	1	1	1	1	1
10% Potassium oleate solution	0.5	0.5	0.5	0.5	0.5	0.5
50% ZnO dispersion	1	1	1	1	1	1
33% TMTD dispersion	7.2	3.6	3.6	3.6	3.6	3.6
10% TU solution	—	3.8	—	—	—	—
10% AMT solution	—	—	8.85	5.9	2.95	1.47
50% Sulfur dispersion	3	3	3	3	3	3

group favors the polarization of the C=S bond. It is also to be emphasized that this amidinothiourea is a nontoxic chemical used in the pharmaceutical industry,¹⁴ whereas some of the conventional accelerators used in rubber compounding are reported to be toxic.¹⁵

The feasibility of using latices in most of their applications depends upon the compounded latex being fluid and having appropriate rheological properties. The flow properties of latices are therefore of great practical relevance for the industrial applications of polymers in latex form. NR latex is a pseudoplastic fluid and is non-Newtonian. When sheared, the rubber particles are progressively aligned and offer less resistance to flow.¹⁶ Temperature also has a significant effect on the viscosity of latex.¹⁷ Among the various physicochemical properties, viscosity is the most important property that influences the processing characteristics. Rheological properties of the compounded latex were also investigated in this context.

EXPERIMENTAL

Preparation of (AMT)

AMT is synthesized from dicyandiamide and thioacetamide. An intimate mixture of dicyandiamide (0.1 mol; Merck, India) and thioacetamide (0.1 mol; Merck, India) was treated with concentrated hydrochloric

acid (10 mL, 0.1 mol) at 35°C and stirred. A vigorous reaction occurred and the mixture turned yellow. It was then heated in a water bath for 10 min. The reaction mixture was then diluted with water (100 mL), boiled for 2 min, cooled, and filtered. The filtrate was treated with concentrated HCl (5 mL), concentrated on a water bath to about 50 mL, and then cooled to 0°C. Amidinothiourea hydrochloride separated as colorless cubes was filtered and washed with ice-cold 20% HCl. An aqueous solution of the hydrochloride on treatment with 25% ammonia solution and cooling to 0°C gave AMT. It was recrystallized from ethanol [melting point (m.p.) 171°C]. It was also characterized by using the IR spectrum (Fig. 1).

Centrifuged NR latex (Harrison Malayalam, Ltd., Cochin, India) of 60% dry rubber content and conforming to BS 5430-1981 was used in this study. Other compounding ingredients were of commercial grade. One part by weight of 10% KOH and 0.5 parts by weight of potassium oleate were added to stabilize the latex throughout the compounding and processing stages. The insoluble compounding ingredients were prepared into dispersions. The materials were made to disperse in water by grinding action and the dispersing agent prevents the dispersed particles from re-aggregating. A ball mill was used for making the dispersions of the ingredients. For compounding, dispersions of zinc oxide (Meta Zine, Ltd., Mumbai, In-

TABLE III
Formulation of the Mixes Containing CBS

Ingredients, parts by weight (wet)	Mixes					
	E ₀	E ₁	E ₂	E ₃	E ₄	E ₅
60% Centrifuged latex	167	167	167	167	167	167
10% KOH solution	1	1	1	1	1	1
10% Potassium oleate solution	0.5	0.5	0.5	0.5	0.5	0.5
50% ZnO dispersion	1	1	1	1	1	1
33% CBS dispersion	8	4	4	4	4	4
10% TU solution	—	3.8	—	—	—	—
10% AMT solution	—	—	8.85	5.9	2.95	1.47
50% Sulfur dispersion	3	3	3	3	3	3

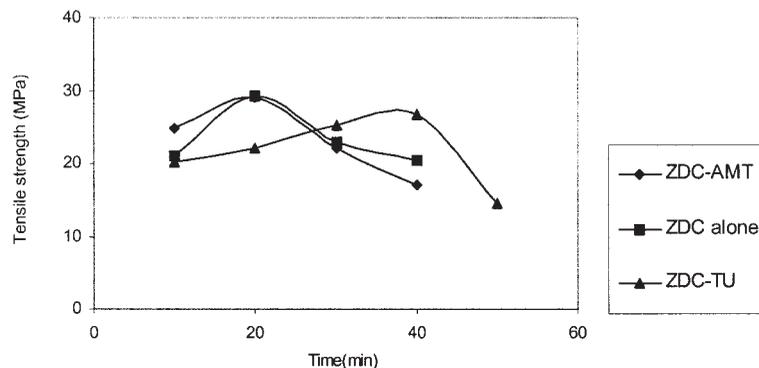


Figure 2 Variation of tensile strength with time for ZDC mixes cured at 120°C.

dia), accelerators, and sulfur (Standard Chemical Co. Pvt., Ltd., Ohennai, India) were added according to the formulation given in Tables I–III. NR latex compounds containing AMT/TU as secondary accelerator along with TMTD/CBS/ZDC were prepared by using standard formulations (TU, SISCO Research Laboratories, Mumbai, India; TMTD, Polyolefins, Ltd., Mumbai, India; CBS, Polyolefins, Ltd., Mumbai, India; ZDC, ICI India, Ltd., Kolkotha, India). Thiourea and AMT were added as 10% aqueous solutions. All the ingredients were added with slow and thorough stirring. After compounding, the mixes were kept for maturation at room temperature for 24 h.

The experimental mixes containing optimum dosage of AMT and the corresponding references were used for the rheological study. A Haake viscotester (VT 550) was used to study the effect of temperature and shear rate on viscosity. This viscometer was designed to meet the most sophisticated requirements of continuous shear rheometry with 60 different rotational speed steps covering a wide range from 0.5 to 800 rpm. The functional units consist of a viscotester and power supply unit, temperature control vessel with sensor system, temperature sensor (Pt 100), etc. The equipment operates over a temperature range

from -30 to 150°C . Sensor system NV was used for this study. Latex is located in the measuring gap of the sensor system. Rotational speed, measuring time, number of measuring points, and measuring temperature are preset. The rotor is rotated at the preset speed. The latex exerts a resistance to the rotational movement due to its viscosity, which becomes apparent as a torque value on the measuring shaft of the viscometer. The relevant values for the following factors from the measured variables of speed, torque, and sensor geometry can be calculated: viscosity η in mPa s, shear rate $\dot{\gamma}$ in s^{-1} , and shear stress τ in Pa. In the present study, measurements were taken at 25, 35, and 45°C at a shear rate from 1 to 150 s^{-1} .

The rheological behavior of the latex has been analyzed by using the power law equation:

$$\tau = k\dot{\gamma}^n$$

where τ is the shear stress (Pa), k is the viscosity index, $\dot{\gamma}$ is the shear rate (s^{-1}), and n is the flow index. By plotting $\log \tau$ versus $\log \dot{\gamma}$, the values k and n are obtained as slope and intercept by regression analysis. The apparent viscosity η is the ratio of shear stress to shear rate ($\eta = k\dot{\gamma}^{n-1}$).

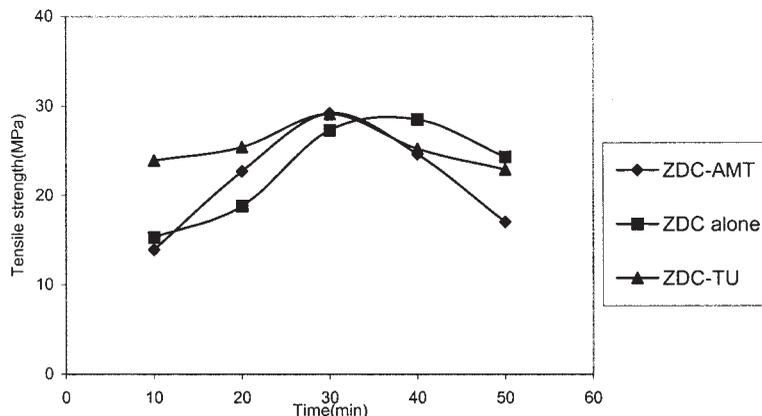


Figure 3 Variation of tensile strength with time for ZDC mixes cured at 100°C.

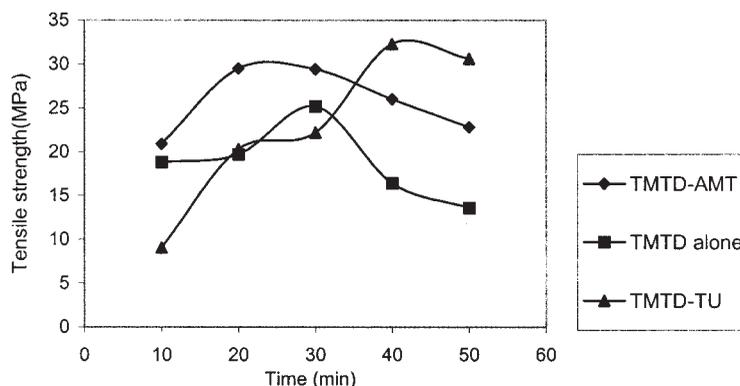


Figure 4 Variation of tensile strength with time for TMTD mixes cured at 120°C.

Latex films were cast on glass cells by using the matured compound. About 30–35 mL of the latex compound was poured and distributed so that a film of thickness 1–1.25 mm was obtained upon drying. Optimum dosage of the secondary accelerator was determined by examining the cure characteristics of the different mixes with varying concentrations of AMT. To study the effect of temperature on vulcanization, these compounds were cured at two different temperatures (viz. 120 and 100°C) for definite time intervals in an air oven. The cure time was found out from the tensile strength/time graph (Fig. 2-7). From the graph, the time taken for attaining optimum tensile strength is taken as the optimum cure time. The tensile properties of the vulcanizates were determined by using a Zwick universal testing machine as per ASTM D412-83. The tear strength of the samples was determined as per ASTM D624-86. The total chemical crosslink density of the vulcanizates was determined at optimum conditions by using the equilibrium swelling method.¹⁸ Vulcanizate samples weighing 0.2–0.3 g were kept in toluene for 24 h. Swollen samples were weighed; the solvent was removed in vacuum, and the samples were weighed again. The volume fraction of rubber in

the swollen network was calculated according to Ellis and Welding.¹⁹

RESULTS AND DISCUSSION

Rheological behavior

In the present investigation, the viscosity and processibility of the different NR latex compounds were studied under different shear rates and temperatures. Figure 8 shows the effect of shear rate on the viscosity of TMTD mixes containing other secondary accelerators (viz. AMT and TU) at 25°C. On increasing the shear rate, viscosity of the latex compounds is found to decrease in accordance to the pseudoplastic behavior of these mixes. The effect is more pronounced at low shear rates, as it approaches near-Newtonian behavior at high shear rates. Figure 9 shows the effect of temperature on the viscosity (at constant shear rate) of these mixes. As the temperature is increased from 25 to 35°C, viscosity is found to be decreasing in all the three systems under review. However, as the temperature is increased to 45°C, mix containing TMTD alone shows a sharp increase in viscosity, causing the desta-

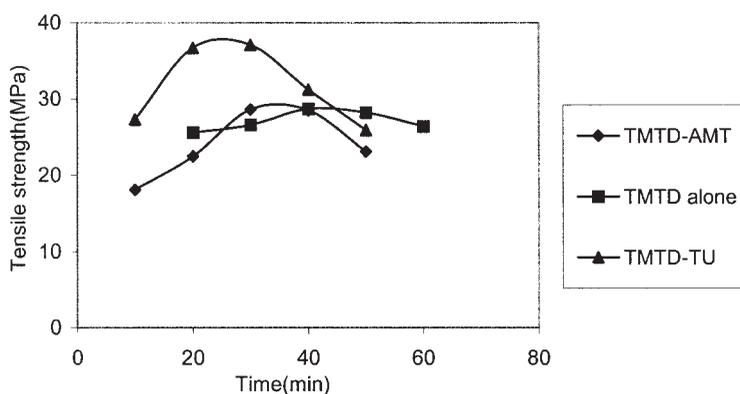


Figure 5 Variation of tensile strength with time for TMTD mixes cured at 100°C.

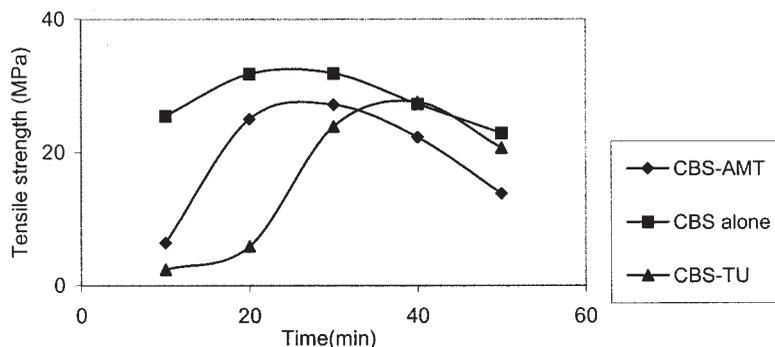


Figure 6 Variation of tensile strength with time for CBS mixes cured at 120°C.

bilization of latex. For TMTD alone, at a shear rate of 61.7 s^{-1} , viscosity is 59 mPa s , whereas that for TMTD-AMT is 19 mPa s at this temperature. A similar behavior is observed in TMTD-TU also. When there is TMTD alone, TMTD forms a complex with ZnO and this complex is unstable at 45°C and decomposes to ZnO. This ZnO causes a thickening effect. However, when there is TU or AMT, this reacts with ZnO further to form a complex and hence availability of ZnO is less in the medium containing TU or AMT.

The effect of shear rate on viscosity of compounded latex for CBS systems at 25°C is shown in Figure 10. In the CBS-AMT combination, the effect of shear rate on viscosity is found to be different from TMTD mixes. On increasing the shear rate, viscosity of CBS-AMT mixes increased. A similar trend is shown by thiourea systems also. In this case, AMT and TU seem to destabilize the system. This indicates that, when CBS systems are employed, AMT and TU are not useful, especially at temperatures $> 35^\circ\text{C}$. Figure 11 shows the changes in viscosity with an increase in temperature at constant shear rate for CBS systems. Figure 12 gives the effect of shear rate on the viscosity of the compounds containing ZDC as the primary accelerator. In these systems also, viscosity increases with shear rate at the three different temperature ranges

studied. Figure 13 shows the changes in viscosity with an increase in temperature at constant shear rate for ZDC systems. From these studies, it is clear that CBS-AMT and ZDC-AMT systems and the corresponding control formulations are comparatively unstable at higher shear rates and temperatures, whereas TMTD-AMT systems are reasonably stable. The different behavior of CBS and ZDC is due to the difference in the stability of complexes formed from CBS/ZDC with ZnO.

Cure characteristics and tensile properties

Table IV gives the cure time values and the physical properties of the ZDC-AMT mixes. It may be noted that the cure time values decrease as the concentration of secondary accelerator increases in the mix. At 120°C , ZDC-AMT mix (A_3) takes only 15.7 min to attain optimum tensile strength, whereas the system containing ZDC alone (A_0) takes 20 min and the ZDC-TU system (A_1) takes 36 min. At 100°C , the optimum cure time for ZDC-AMT system (B_3) is lower than that for ZDC alone (B_0) but is same as that for ZDC-TU (B_1). At 100°C also, there is a definite decrease in optimum cure time with an increase in the concentration of AMT. There is a

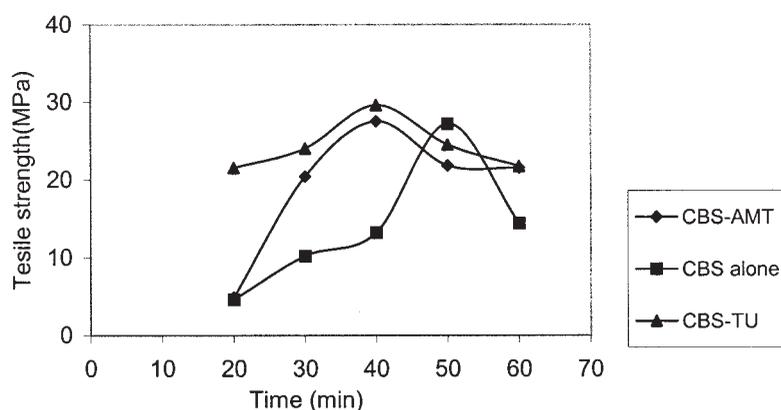


Figure 7 Variation of tensile strength with time for CBS mixes cured at 100°C .

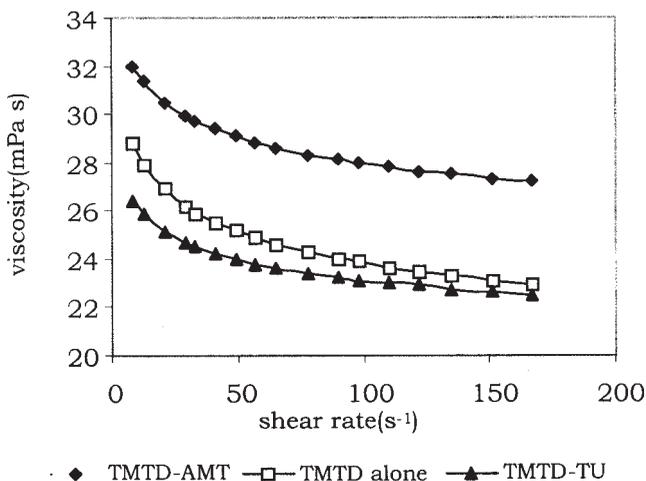


Figure 8 Variation of viscosity with shear rate for TMTD mixes at 25°C.

definite increase in tensile strength also with the concentration of AMT. The aging resistance of the vulcanizates was determined by heating the samples in an air oven at 70°C for 7 days. The percentage retention of tensile strength is also found to be higher for the experimental mixes compared to the reference formulations. Based on the above evaluations, it may be reasonably inferred that the optimum dosage of the secondary accelerator required is one molar equivalent of AMT. The optimum cure time and other properties evaluated for the TMTD-AMT systems are given in Table V. In TMTD-AMT systems also, the optimum cure time decreases as the dosage of AMT increases. The cure time for the mix containing optimum concentration of AMT (C₃) is less than those of the reference mixes (C₀ and C₁) at both 120 and 100°C. The tensile strength values of the experimental mixes containing AMT are found to be better than those of the control mixes (Table

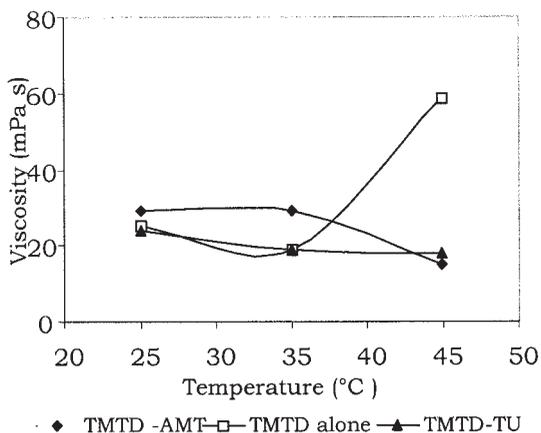


Figure 9 Variation of viscosity with temperature at shear rate 61.7 s⁻¹.

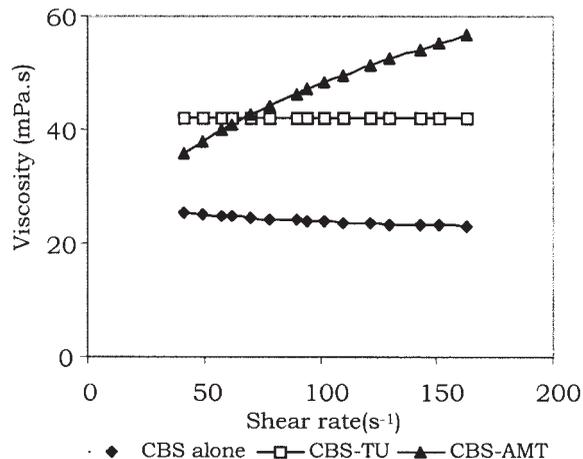


Figure 10 Variation of viscosity with shear rate for CBS mixes at 25°C.

V). The tear strength values of the vulcanizates from these mixes are comparable to those of control formulations. In the case of TMTD-AMT system also, one molar equivalent of AMT can be considered to be the optimum level.

Different properties such as optimum cure time, tensile strength, tear strength, etc., for CBS-AMT systems are given in Table VI. As in the case of other two systems, the optimum cure time decreases with an increase in the concentration of AMT and cure times are substantially lower (higher cure rates) than the control formulations. The lower optimum cure time exhibited with AMT in the above systems can be attributed to the nucleophilic attack by AMT, which enhances the S-S bond cleavage in the primary accelerator, leading to a faster cure. The cure time values obtained in these different systems of latex vulcanizates point to a nucleophilic reaction mechanism as suggested by Philpot. The tensile strength values for

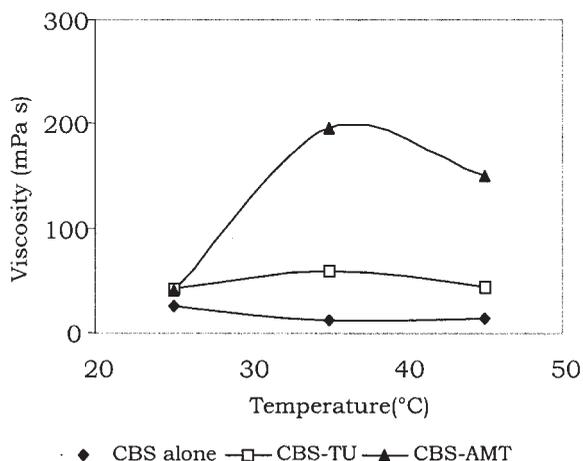


Figure 11 Variation of viscosity with temperature at shear rate 61.7 s⁻¹.

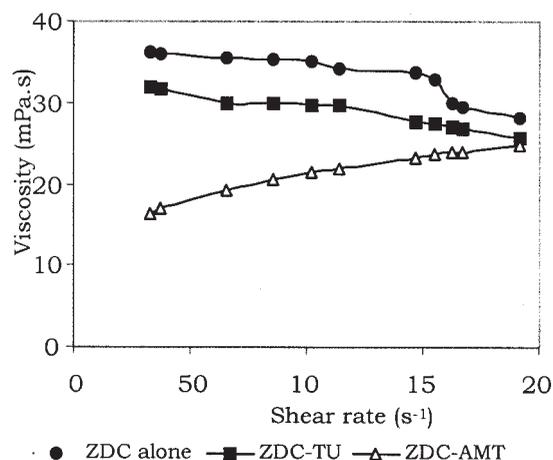


Figure 12 Variation of viscosity with shear rate for ZDC mixes at 25°C.

these experimental mixes are found to be comparable to those of the reference mixes. The percentage retention of tensile properties after heat aging is also better for the mixes containing AMT. When cured at 100°C also, a similar trend is followed. Mix E₃ containing optimum concentration of AMT gives more or less optimum tensile properties and this can be taken as the optimum dosage.

To understand the variation in physical properties, chemical characterization of the samples was also carried out by using the equilibrium swelling method. These results are also reported in Tables IV–VI. It may be noted that at 100°C also these systems studied cures during a reasonable time period, supporting the suggestions made by Philpot.

CONCLUSION

The results obtained in this study support a nucleophilic reaction mechanism in the binary accelerator

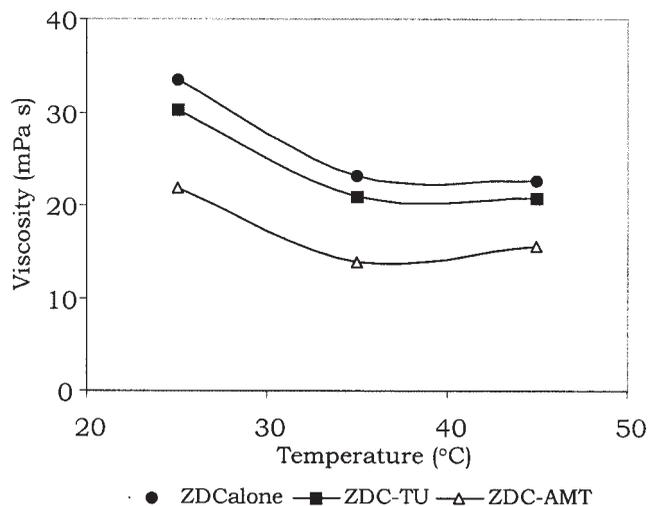


Figure 13 Variation of viscosity with temperature at shear rate 61.7 s⁻¹.

TABLE IV
Properties of ZDC Systems

Mixes	Cure time (min)	Tensile strength (MPa)			Tear strength (N/mm)	Total crosslink density, ×10 ⁵ (g mol/cm ³)
		Before aging	After aging	Retention (%)		
Mixes cured at 120°C						
A ₀	20.0	29.2	20.9	71.5	45.7	4.98
A ₁	20.5	26.8	18.5	69.0	42.0	4.99
A ₂	12.0	29.3	27.2	92.8	69.1	4.34
A ₃	15.7	29.0	25.4	87.0	51.6	4.8
A ₄	16.0	25.7	13.2	51.3	47.1	5.54
A ₅	28.0	28.6	21.1	72.2	30.7	4.34
Mixes cured at 100°C						
A ₀	38	29.0	22.3	76.8	52.7	4.71
A ₁	29	29.1	20.2	69.0	55.8	5.26
A ₂	29	28.7	34.3	119.0	60.6	4.08
A ₃	30	29.2	27.7	94.8	58.8	4.24
A ₄	35	26.0	20.6	79.0	54.8	4.07
A ₅	37	26.1	20.0	76.6	50.1	3.9

systems under review. AMT, being more nucleophilic than TU, is found to be a more effective secondary accelerator in the sulfur vulcanization of NR latex with primary accelerators such as ZDC/TMTD/CBS. The systems containing optimum dosages of AMT give satisfactory values for mechanical properties such as tensile strength and tear strength. The rheological studies of these mixes show that the addition of AMT does not adversely affect the processing characteristics, especially when TMTD is used as the primary accelerator. At higher temperatures also, AMT is found to stabilize the TMTD

TABLE V
Properties of TMTD Mixes

Mixes	Cure time (min)	Tensile strength (MPa)			Tear strength (N/mm)	Total crosslink density, ×10 ⁵ (g mol/cm ³)
		Before aging	After aging	Retention (%)		
Mixes cured at 120°C						
C ₀	30.0	25.2	17.3	68.6	46.3	4.82
C ₁	41.2	32.3	18.4	56.9	50.3	4.71
C ₂	19.6	31.7	20.5	64.6	61.3	4.65
C ₃	22.8	29.5	15.1	51.1	56.3	4.98
C ₄	30.4	24.5	16.8	68.5	54.8	4.6
C ₅	39.0	24.9	23.8	95.5	39.4	4.36
Mixes cured at 100°C						
C ₀	40.0	28.7	29.6	103.0	48.7	2.28
C ₁	42.4	37.1	15.9	42.8	46.8	4.1
C ₂	31.2	32.3	17.0	52.6	52.3	4.47
C ₃	32.8	28.6	20.7	72.3	53.2	3.26
C ₄	40.0	26.6	13.1	49.0	66.0	3.82
C ₅	43.2	20.7	19.8	95.0	54.6	4.2

TABLE VI
Properties of CBS Mixes

Mixes	Cure time (min)	Tensile strength (MPa)			Tear strength (N/mm)	Total crosslink density, $\times 10^5$ (g.mol/cm ³)
		Before aging	After aging	Retention (%)		
Mixes cured at 120°C						
E ₀	35.1	31.9	14.3	45.0	42.6	6.1
E ₁	46.7	27.6	3.06	11.0	41.2	4.88
E ₂	22.4	29.7	26.0	87.5	46.6	3.78
E ₃	26.4	27.2	18.0	66.0	48.1	3.74
E ₄	29.3	22.6	20.5	91.0	41.2	4.5
E ₅	50.7	28.4	25.1	88.0	39.5	5.5
Mixes cured at 100°C						
E ₀	44.5	27.2	14.6	53.6	44.1	4.37
E ₁	40.0	29.6	22.2	75.0	44.3	4.82
E ₂	31.0	30.3	27.2	89.0	48.7	5.4
E ₃	39.2	27.5	25.6	93.0	51.5	5.42
E ₄	48.1	19.9	14.0	70.0	41.9	5.35
E ₅	48.4	23.5	12.9	55.0	46.0	5.06

mixes. However, in ZDC and CBS mixes, both AMT and control mixes containing TU are seen to destabilize the latex compounds. The main advantage here is that AMT is a nontoxic chemical used in the pharmaceutical industry, whereas many of the conventional accelerators are reported to be toxic/carcinogenic.

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