

Bis(*N*-benzyl piperazino) Thiuram Disulfide and Dibenzothiazyl Disulfide as Synergistic Safe Accelerators in the Vulcanization of Natural Rubber

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ABSTRACT: Some investigation regarding the effect of binary system of accelerators comprising one safe thiuram disulfide, namely bis(*N*-benzyl piperazino) thiuram disulfide (BPTD) and dibenzothiazyl disulfide (MBTS), on the vulcanization of NR is carried out. The results are compared with those obtained with conventional tetra methyl thiuram disulfide (TMTD) presently considered as unsafe. The vulcanizates obtained from safe synergistic pair of accelerators (BPTD-MBTS) possess comparable mechanical properties [modulus, tensile strength, and elongation at break (%)] and exhibits some improvement in heat resistant behavior when compared with those obtained with TMTD-MBTS system. In the light of mechanical properties, safe BPTD-MBTS system introduces the safe noncarcino-

genic rubber accelerator in the vulcanization of rubber. Same type of synergistic activity may be due to comparable activation energy for both the TDs with the combination of MBTS. Although rate constant values are low for BPTD-MBTS (6 : 3) compared to TMTD-MBTS (6 : 3) in the high temperature vulcanization, the crosslinking efficiency of former is very large compared to later. This may be responsible for improvement in heat resistance behavior of the novel accelerator in the combination with MBTS. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: elastomer; safe amine; activation energy; mechanical properties; stiffness

INTRODUCTION

Thiuram disulfides, the parent compound of thiuram, either alone or in combination with thiazole group of accelerators,^{1,2} have been immensely important and popular during last few decades in the rubber industry for their efficient accelerated cross linking capacity leading to the preparation of vulcanized article of desired technological properties. Recent concern on potential health hazard of different rubber chemicals have thrown the subject quite open to the scientist. Rubber chemicals derived from secondary amine when exposed in heat forms nitrosamines in presence of atmospheric nitro sating agent. Although airborne and urinary *N*-nitrosamines levels have found to be very low, exposed workers should still be monitored constantly because some of these substances are known to be genotoxic and carcinogenic.³ Thiuram compound, e.g., tetra methyl thiuram disulfide as derived from secondary amine

has been reported⁴ to have generated carcinogenic nitrosamine. Thiuram disulfides are so important in the rubber industry that their absence could not be thought of. Naturally, unsafe thiuram disulfides are to be replaced by safe ones without changing their major activity.

Chemical compounds for rubber industry contain carcinogenic nitrosamines if they are obtained from the secondary amines like dimethyl amine, diethyl amine, morpholine, piperidine etc. In a recent survey by de Vocht et al.⁵ have shown that exposure to *N*-nitrosamines namely *N*-nitrosodimethylamine and to *N*-nitrosomorpholine (NMor) decreased on average two-to-fivefold in the German rubber industry with comparable concentration levels in other European countries. Although average levels are well below the current limits, exposure has not been eliminated, and incidental high exposures do still occur.⁵ A more general solution of the nitrosamine problem in rubber industry requires the introduction of new rubber chemicals, which cannot be nitrosated or which form noncarcinogenic nitrosamines. With this in mind, we have chosen in this study safe thiuram disulfide, e.g., bis(*N*-benzyl piperazino) thiuram disulfide (BPTD) derived from safe *N*-benzyl piperazine^{6,7} to introduce safe noncarcinogenic thiuram disulfide in the vulcanization of rubber and evaluated the synergistic activity in combination

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TABLE I
List of Compound Used

Sl. no.	Chemical structure	Chemical name	Abbreviation
1		2-Mercapto benzothiazyl disulfide	MBTS
2		Bis(<i>N</i> -benzyl piperazino)thiuram disulfide	BPTD
3		Tetra methyl thiuram disulfide	TMTD

with other safe accelerators like Dibenzothiazyl disulfide (MBTS). The effect of BPTD separately with MBTS on the resultant vulcanizates are compared with the corresponding unsafe TMTD compound in the light of mechanical properties of the vulcanizates to replace unsafe TMTD by newly synthesized BPTD. In addition, it would be our endeavor to investigate the heat resistance behavior and also cure kinetics of the vulcanizates obtained from these binary combinations at experimental temperatures.

EXPERIMENTAL

Preparation and characterization of BPTD

A total of 17.6 g (0.1 mol) *N*-benzyl piperazine is taken in a three-necked round-bottomed flask. A total of 4 g (0.1 mol) of NaOH in 50 mL of water is added drop wise when the temperature rose to 22°C. The flask is cooled in an ice bath to less than 0°C, and 7.6 g (0.1 mol) of CS₂ is added drop wise so that the temperature is less than 4°C. Sodium dithio carbamate is obtained as a liquid. A total of 50 mL of water is added to the flask to make a clear solution, the clear solution, which is then stirred at 30°C for 1.5 h. Iodine solution saturated with KI is added drop wise to this solution with efficient stirring till the iodine color persisted. A light yellow precipitate is appeared. The mixture is stirred for about 30 min more and then filtered. The precipitate

is thoroughly washed with water until the filtrate is neutral to litmus. The residue thus obtained is dried under vacuum and recrystallized from chloroform (CHCl₃). The yield is about 60%. The product (m.p. 136°C) is found to be pure BPTD as based on the following two analyses.

CHN analysis: Found 56.91% C, 5.87% H, 10.82% of N and 26.1% S; C₂₄H₃₀N₄S₄ by calculation 57.37% C, 5.97% H, 11.15% N, and 25.49 % S.

H-NMR analysis: ¹H NMR: δ (CDCl₃), 7.32–7.25(m, 10H, *J* = 4Hz ArH), 4.30(broad singlet 8H, –CH₂–N–C=S), 3.57 (singlet, 4H, –CH₂–C₆H₅), 2.63 (broad singlet, 8H, –CH₂–N–CH₂–CH₂–). The ¹H NMR spectrums at 400 MHz.

Bis(*N*-benzyl piperazino) thiuram disulfide is prepared in the laboratory. 2-Mercapto benzothiazyl disulfide (MBTS) and tetra methyl thiuram disulfide (TMTD) are commercial samples and are used as such or after necessary purification.

A list of chemical compounds with their abbreviation and structure are given in Table I. The compositions of the accelerators for the various stocks are provided in Tables II and III.

As the process of vulcanization is an extremely complicated process, gum vulcanization is deliberately chosen for its simplicity and thus understands the process clearly. Further, to avoid the complexity of the network a ratio of moderately high accelerator (9 mmol phr) to sulfur (0.5 phr) is chosen.

TABLE II
Physical and Cure Data of Stocks (Gum) Cured at 140°C

Mix ^a no. & composition (mmol)	Maximum torque, R _z (N m)	Scorch safety t ₂ (min)	Optimum cure time, t ₉₀ (min)	Modulus at 200% elongation (MPa) ± 0.01	Tensile strength (MPa) ± 0.082	Elongation at break (%) ± 10
1. TMTD-9	3.9	3.0	10.0	0.86	18.50	800
2. TMTD-6 MBTS-3	4.4	6.0	22.5	0.75	14.90	770
3. TMTD-4.5 MBTS-4.5	4.55	7.5	21.0	0.80	15.14	670
4. TMTD-3 MBTS-6	4.3	8.0	20.5	0.75	13.40	690
5. MBTS-9	2.95	24.0	46.5	0.75	13.33	825
6. BPTD-9	4.5	3.5	19.5	1.13	12.57	705
7. BPTD-6 MBTS-3	5.0	7.0	23.5	1.31	18.49	675
8. BPTD-4.5 MBTS-4.5	4.9	8.25	21.5	1.40	16.66	650
9. BPTD-3 MBTS-6	4.85	9.5	23.0	1.39	16.48	650

^a Each mix contain ZnO (5 phr), stearic acid (2 phr), and S (0.5 phr).

TABLE III
Physical and Cure Data of Stocks (Gum) Cured at 140, 160, and 170°C

Mix ^a no. & composition (mmol)	Maximum torque, R_x (N m)	Scorch safety, t_2 (min)	Optimum cure time, t_{90} (min)	Modulus at 200% elongation (MPa) \pm 0.01	Tensile strength (MPa) \pm 0.082	Elongation at break (%) \pm 10	Temperature (°C)
2.TMTD-6 MBTS-3	4.4	6.0	22.5	0.75	14.90	770	140
7.BPTD-6 MBTS-3	5.0	7.0	23.5	1.31	18.49	675	
2. TMTD-6 MBTS-3	3.7	3.5	5.75	1.24	14.5	750	160
7.BPTD-6 MBTS-3	4.7	2.5	7.5	1.17	15.77	705	
2. TMTD-6 MBTS-3	3.4	2.0	3.25	1.19	13.14	730	170
7. BPTD-6 MBTS-3	4.4	1.75	4.0	1.10	18.41	760	

^a Each mix contain ZnO (5 phr), stearic acid (2 phr), and S (0.5 phr).

The vulcanizing ingredients (5 phr ZnO, 2 phr stearic acid, 0.5 phr sulfur, and accelerators) are incorporated in the untreated natural rubber (NR) (RMA-1X) on a laboratory-mixing mill. The total concentration of accelerator (s) is kept at 9 mmol phr. The cure characteristics of the different stocks are obtained using the Monsanto Rheometer R-100 at 140, 160, and 170°C. The data for torque R_∞ , scorch time (t_2), and optimum cure time (t_{90}) are presented in Tables II and III.

The stocks are cured under pressure at 140, 160, and 170°C for optimum cure time, and the vulcanizates are kept for 24 h at ambient temperature before measuring the modulus at 200% elongation and tensile strength according to ASTM D 412-51 T using dumbbell-shaped test pieces in an Amsler (Sweden) tensile tester. The mechanical data concerning modulus, tensile strength, and elongation at break of the vulcanizates are also provided in Table II and III.

We are also studied the kinetics of various gum stocks in Table IV. The kinetic studies have been based on the following equation as deduced by Coran.⁸

$$V_t = V_\infty \{1 - \exp[k(t_i - t)]\}$$

where V_t = crosslink density at time t , V_∞ = crosslink density at infinite time, t = vulcanization time, t_i = the delay time, and k is the first order specific rate. According to Coran,⁸ crosslink formation to be

proportional to the relevant torque R , in the absence of reversion, a plot of $\ln(R_\infty - R_t)$ versus time yields a straight line with negative slope from which k is evaluated. R_∞ and R_t correspond to torque at points V_∞ and V_t and have usual significance.

The cure rate index (CRI), which is a measure of the rate of the cure reaction, is estimated by the method reported by Yehia and Stoll.⁹

$$\text{CRI} = 100/(t_{90} - t_2)$$

The activation energy of cure, E , is determined by assuming the dependence of the optimum cure time t_{90} on cure temperature T to follow an Arrhenius relationship:

$$t_{90} = A \exp(-E/RT)$$

where A is the pre-exponential factor, R is the universal gas constant, and T is the temperature in Kelvin. E is obtained from the slope of Arrhenius plots of $\log t_{90}$ versus $1/T$ over the temperature range 140, 160, and 170°C.

RESULTS AND DISCUSSIONS

In this study, our attentions are focused mainly on the study of the synergistic activity, cure behavior of the binary mixtures as already mentioned, and the results are discussed step wise as presented below.

TABLE IV
Cure Characteristics of Various Accelerators in NR Gum Stocks at Various Temperatures

Mix ^a no. & composition (mmol)	Maximum torque, R_∞ (N m)	Scorch safety, t_2 (min)	Optimum cure time, t_{90} (min)	Cure rate index $\text{CRI} = 100/(t_{90} - t_2)$	Rate constant, k (min^{-1} 100 k)	Activation energy (kJ/mol)	Temperature (°C)
2.TMTD-6 MBTS-3	4.4	6.0	22.5	6.06	10.6	96.22	140
	3.7	3.5	5.75	44.44	52.4		160
	3.4	2.0	3.25	80	113.4		170
7.BPTD-6 MBTS-3	5.0	7.0	23.5	6.06	15.7	92.59	140
	4.7	2.5	7.5	20.0	34.7		160
	4.4	1.75	4.0	44.44	85.1		170

^a Each mix contain ZnO (5 phr), stearic acid (2 phr), and S (0.5 phr).

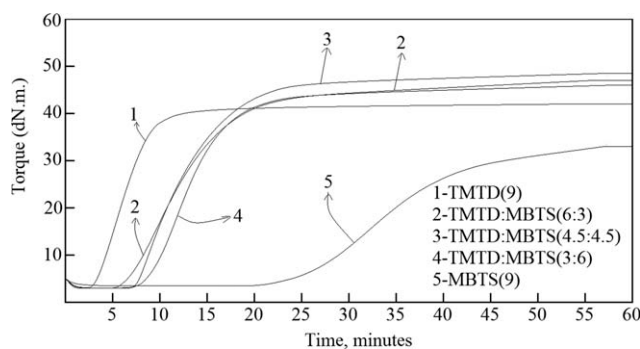


Figure 1 Rheograph of NR gum stocks cured at 140°C.

Evaluation of synergistic interaction between thiuram disulfide and MBTS

In this part, our attempt is gone to explore the efficiency of TD-MBTS systems in the vulcanization of rubber. The cure data of several mixes and the kinetics as well as mechanical properties of the corresponding vulcanizates are recorded in Table II, and the progress of cure is depicted in the rheographs as well as from Figure 3 that maximum rheometric torque for all the two thiuram disulfide-MBTS compounds is attained at the milli molar ratio of 4.5 : 4.5 for TMTD (Mix 3) and at the milli molar ratio of 6 : 3 for BPTD (Mix 7).

It is evident from the results that the scorch time (t_2) and the optimum cure time (t_{90}) for the BPTD-MBTS system are somewhat higher than the corresponding values obtained in TMTD-MBTS system (Table II). Unlike the torque values, 200% modulus values of TD-MBTS systems vary with gradual change of proportion of TD and MBTS and attain a maximum value at the milli molar ratio of 4.5 : 4.5 for both the cases (Table II, Fig. 4). The results indicate that BPTD-MBTS combination definitely improve the modulus values (1.40 M Pa) of vulcanizates compared to TMTD-MBTS binary (0.80 M Pa) system. As for the tensile strength, the maximum values for BPTD-MBTS accelerated system are obtained at the milli molar ratio of 6 : 3, and for

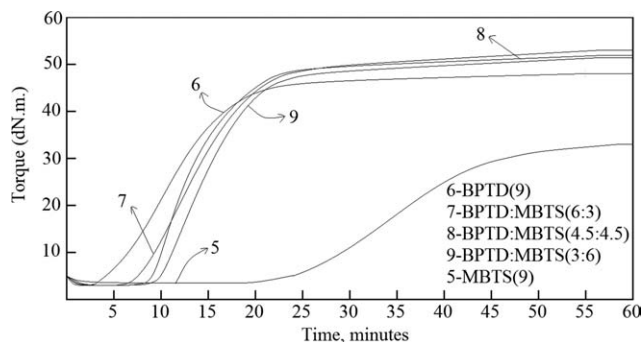


Figure 2 Rheograph of NR gum stocks cured at 140°C.

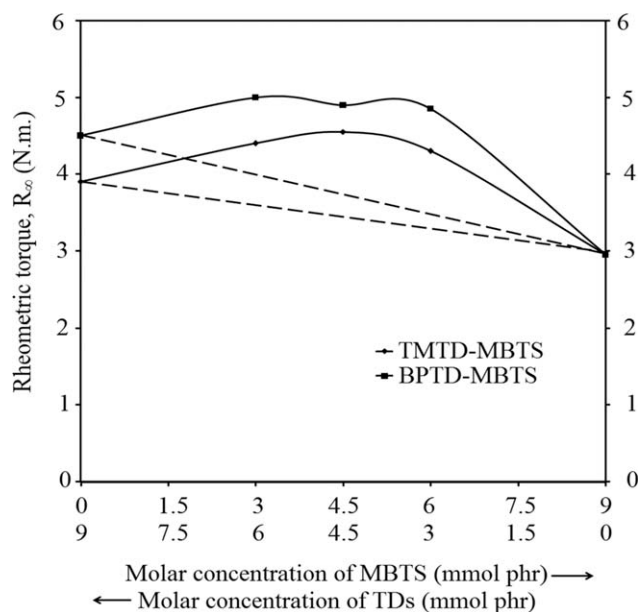


Figure 3 Effect of TD to MBTS milli molar ratio on the torque obtained from rheographs.

TMTD-MBTS accelerated system, the maximum value is obtained at the equimolar concentration of the accelerators, but the results are much higher in case of BPTD-MBTS accelerated system than TMTD-MBTS accelerated system (Table II).

It needs mentioning here that the elongation at break (%) values for BPTD-MBTS accelerated vulcanizate is low when compared with TMTD-MBTS accelerated vulcanizate (Table II). It is also clear from Table II that R_∞ values of TD-MBTS systems follow the order.

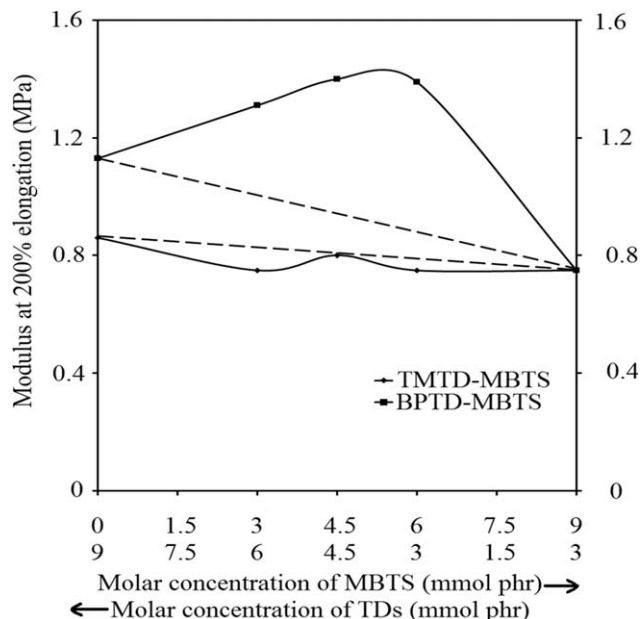
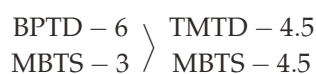
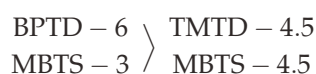


Figure 4 Effect of TD to MBTS milli molar ratio on the modulus at 200% elongation (MPa).



Tensile value also follows the same order for the combinations:



The results discussed so far clearly indicates that positive synergism is prominent in the BPTD-MBTS system. The cure and physical data of which established the supremacy of this system over TMTD-MBTS system used in this study.

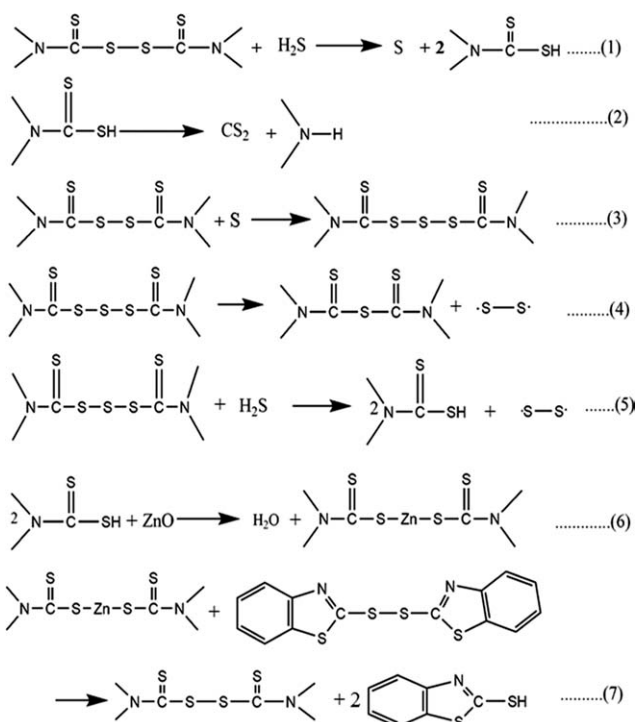
It is observed from Table II that highest t_2 value is obtained from BPTD-MBTS accelerated stock rather than TMTD-MBTS. This is due to the lower basicity¹⁰ of *N*-benzyl piperazine than dimethyl amine. The t_{90} values of BPTD-MBTS accelerated stocks in all the above two system (Table II) are also higher. This is probably due to the steric hindrance¹⁰ offered by the bulky amine moiety of BPTD.

It is now an established fact that MBTS decompose in the rubber medium and have been transformed into MBT.¹¹ It has been shown by the previous workers^{1,2} that MBT-TMTD system provides mutual activity. The synergistic effect is observed in MBTS-TMTD system thus arises from the generation of MBT. To understand the mutual activity between TD-MBTS system, the following proposed reactions scheme is presented (Scheme 1).

The scheme depicts the probable paths (steps 1–7) for the transformation of zinc dithio carbamate (ZDC) under the influence of MBTS in the presence of H_2S that is formed¹² during the process of vulcanization. Step 1, 3, 4, and 5 leads to the formation of crosslinking¹¹ of rubber, whereas step 6 and 7 indicates the regenerative path for TMTD¹³ in presence of MBTS. Step 2 is the destructive path of thiocarbamic acid, whereas step 6 and 7 produces thiuram disulfide from thiocarbamic acid in presence of ZnO and MBTS,¹³ which is responsible for synergistic effect. It needs mentioning¹³ here that MBT formed in the medium produces higher amount of TMTD from zinc dithiocarbamate than that obtained with MBT added to the system as such.

The effect of cure temperature on thiuram-MBTS system

As the temperature is increased modulus, tensile strength, torque etc. of the vulcanizates decreases.¹⁴ Hence, retention of these mechanical properties for the vulcanizates obtained at an elevated temperature is considered to be a measure of heat resistant¹⁴ of the cured products. The data at higher temperature are recorded in Table III.



Scheme 1 Mutual activity of TD-MBTS system during sulfur vulcanization of NR.

It is well known that as the cure temperature is raised, the efficiency of vulcanization decreases.^{15,16} The thiuram disulfide-MBTS systems show exactly the same decrease in efficiency, i.e., loss of rheometric torque which is directly related to crosslink density¹⁶ with increasing the cure temperature. This decrease in efficiency with increasing of cure temperature is considered to be partly due to an increase in the rate of breakdown of crosslink precursors, which are accelerated moiety attached to the rubber through polysulfidic linkages before they have reacted to form crosslinks.^{17–19} According to Coran model^{20,21} for sulfur vulcanization, before crosslinking there occurs crosslinking precursor with the combination of active sulfurating agent which then decomposes into radical called activated precursor. After the formation of activated precursor, crosslinking reaction takes place. We believe that when vulcanization occurs at higher temperature, the activated precursor can also reacts with the active sulfurating agent, giving rise to a nonactivated precursor or can even decomposes into inactive side products may be responsible for the decrease in efficiency of the accelerators at higher temperature. For this reason, lower amount of crosslinks forms during high temperature vulcanization. This can be understood from the decrease in the maximum rheometric torque at higher temperature.

For studying the efficiency of vulcanization at higher temperature, TMTD-MBTS and BPTD-MBTS

systems of milli molar ratio 6 : 3 are taken, and there vulcanization efficiency are measured in respect of torque, modulus, tensile strength, and elongation at break at 140, 160, and 170°C. These data are recorded in Table III. The results indicate that with increase of temperature as expected cure rate increases (Table III) for all the stocks. However at the same time, there occurs considerable shortfall in torque, scorch safety, and optimum cure time. The decrease of modulus values at 200% elongation as is evident from Table III up to the temperature 170°C for BPTD-MBTS (mix 7). A sharp increase in the modulus value as we are observe for TMTD-MBTS (mix 2) system up to temperature 160°C and beyond this temperature a little loss of modulus value occurs. This is an exception in the TD-MBTS vulcanizates. The decrease of rheometric torque (R_∞) and tensile strength are not very much regular for all the system. TMTD- accelerated stocks (mix 2, Table III) show regular decrease of torque (R_∞) and tensile strength. However, the regular diminishes of torque value occurs for the case of BPTD- accelerated systems with rise in temperature, but we see that a sudden fall of tensile strength occurs at 160°C temperature of vulcanization and again increase in tensile strength at 170°C but the overall a small loss in tensile strength is happened with rise in temperature from 140 to 170°C (Fig. 5).

Cure characteristic of various accelerator in NR gum

In this study, the binary systems containing BPTD-MBTS and TMTD-MBTS at 6 : 3 milli molar ratio, whose maximum rheometric torque (R_∞) shows a moderately high value at 140°C are considered for studying their kinetics. Cure characteristics data are

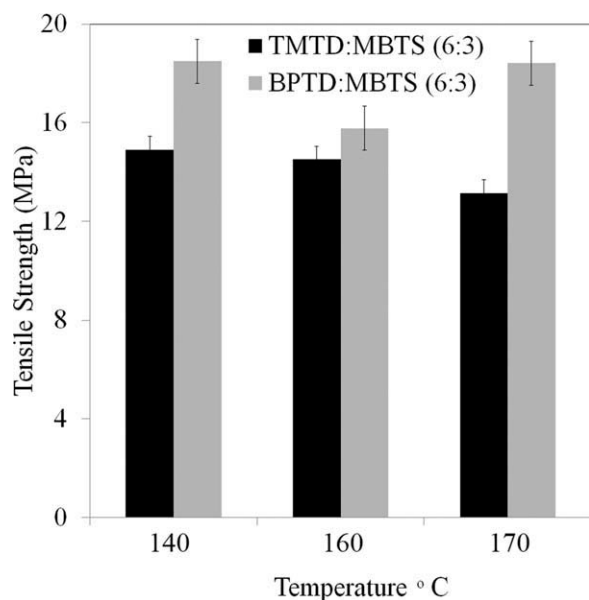


Figure 5 Effect of temperature on tensile strength.

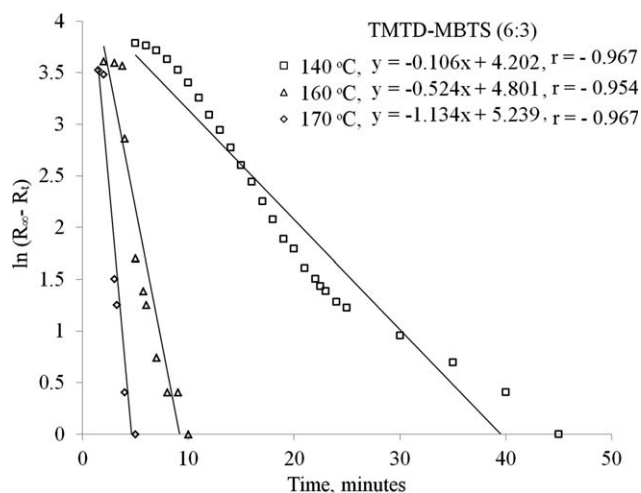


Figure 6 Plot of $\ln(R_\infty - R_t)$ at different time of curing of TMTD-MBTS (6 : 3) system.

recorded in Table IV. It is seen from the table that maximum torque (R_∞), scorch time (t_2), and optimum cure time (t_{90}) decreases with increase in temperature. This decrease in efficiency with increasing of cure temperature is considered to be partly due to an increase in the rate of breakdown of crosslink precursors, which are accelerator moiety attached to the rubber through polysulfidic linkages before they have reacted to form crosslink.¹⁷⁻¹⁹ It is also seen from the Table IV that CRI and rate constant increases with increase in temperature (Table IV, Figs. 6 and 7). The increase is very much higher for TMTD-MBTS system rather than BPTD-MBTS accelerated system (Table IV, mix 2 and 7) may be due to larger amino group for the latter than the former. Although CRI and rate constant is higher for TMTD-MBTS (mix 2) than BPTD-MBTS (mix 7) but high

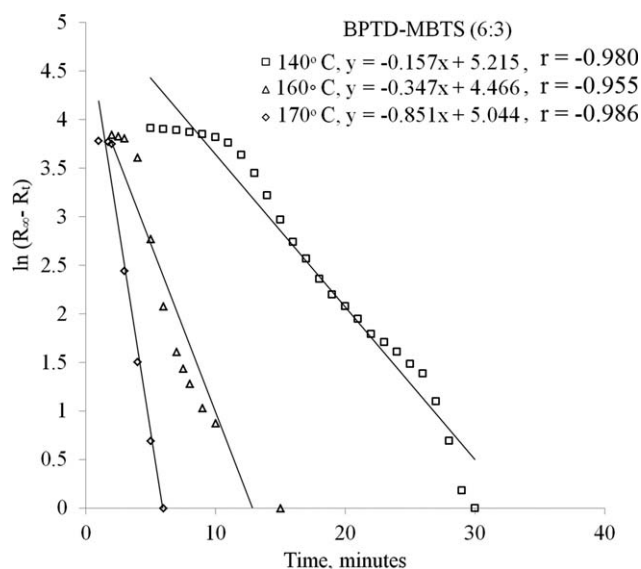


Figure 7 Plot of $\ln(R_\infty - R_t)$ at different time of curing of BPTD-MBTS (6 : 3) system.

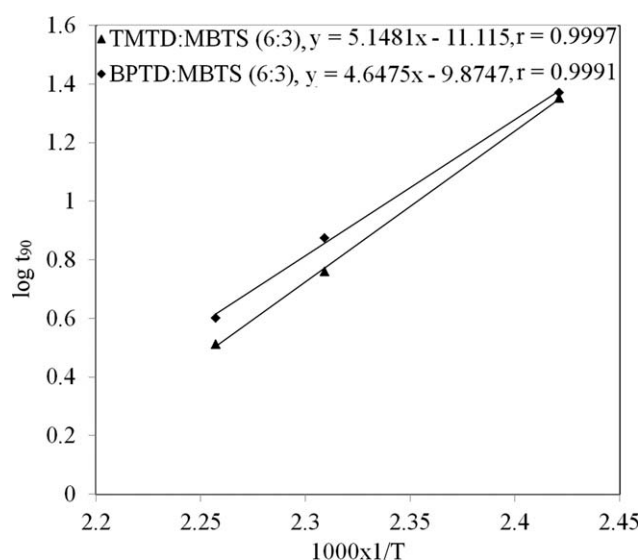


Figure 8 Plot for activation energy (E_a).

maximum rheometric torque (R_∞) for the later indicates the crosslinking efficiency is higher than that of former throughout all the temperature. At high temperature, break down of crosslinks occur due to increase the rate of formation of ZnS.¹⁵ However, the exact mechanism of ZnS formation has not been yet discovered. We believe that ZDC (zinc dithiocarbamate), which is formed as an intermediate in the accelerator chemistry (Scheme 1), may also responsible for the destruction of some of the polysulfidic linkages.¹³ Naturally both ZBPDC (Zinc *N*-benzyl piperazino dithiocarbamate) and ZDMC (Zinc dimethyl dithiocarbamate) have some effect to break down the crosslinks. Here, the conclusion may arise that ZDMC is more prone to destruction of the polysulfidic crosslinks rather than ZBPDC. Plot of $\log t_{90}$ vs. $1/T$ is shown in Figure 8. From the figure, we observe that a straight line occurs for TD-MBTS at various temperature from which we get slopes and calculates the activation energy of the vulcanizates. From Figure 8, it is clear that the slope of TMTD-MBTS and BPTD-MBTS systems are approximately same, i.e., the activation energy of TMTD-MBTS ($E_a = 96.22$ kJ/mol) and BPTD-MBTS ($E_a = 92.59$ kJ/mol) shows the comparable value at the same millimolar ratio (6 : 3), which may be indicates the same type of synergism for both the combined system.

CONCLUSIONS

Various combinations of safe amine-based thiuram disulfide with the safe MBTS and with other ingredients as ZnO, stearic acid, and sulfur in NR gum

vulcanizates are studied. Synthesized safe amine-based accelerator Bis (*N*-benzyl piperazino) thiuram disulfide (BPTD) combined with MBTS replaces the unsafe conventional TMTD with enhancement of mechanical properties in the vulcanization of rubber. A strong synergistic effect in the mechanical properties is found in the novel thiuram disulfide combined with MBTS in the gum vulcanization. Kinetic study reveals that TMTD-MBTS (6 : 3) poses slight high activation energy rather than BPTD-MBTS (6 : 3) system. Although rate constant values are low for BPTD-MBTS (6 : 3) compared to TMTD-MBTS (6 : 3) in the high temperature vulcanization, the crosslinking efficiency of former is very large compared to later. This may be responsible for improvement in heat resistance behavior of the novel accelerator in the combination with MBTS. From this study, we see that safe bis(*N*-benzylpiperazino) thiuram disulfide (BPTD) can successfully replaces unsafe rubber additives (TMTD) with very little loss of tensile strength but increase in modulus, high heat resistance property combination with MBTS.

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