# Investigation on Synergic Activity of *N*-Benzylimine Aminothioformamide Binary Accelerator System in Sulfur Vulcanization of Natural Rubber

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**ABSTRACT:** This study explored the possibility of preparing a new thio accelerator, *N*-benzylimine aminothioformamide to investigate its synergic accelerator activity in three conventional binary accelerator systems, *N*-cyclohexyl benzothiazyl sulfenamide, mercapto benzothiazyl disulfide, and tetramethylthiuram disulfide in the sulfur vulcanization of natural rubber. Each system was found effective in reduction of cure time as a further proof of the nucleophilic mechanism suggested in the earlier reports. The vulcanizates of the mixes of the three systems were experimented for evaluating their physicomechanical properties. Most of the properties were found better than those of the reference mixes. Crosslinks were also evaluated for correlating the properties. Based on the evaluated properties, optimum dosage of the new binary systems were derived. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 2976–2981, 2010

**Key words:** natural rubber; binary accelerator; synergism; vulcanization; physicomechanical properties

## INTRODUCTION

The use of binary accelerator systems in rubber vulcanization has received considerable attention because of the improved efficiency of such systems in the vulcanization process by virtue of synergism between them. Reports[1,2–5] reveal better cure and improved physicomechanical properties of the vulcanizates obtained by using such accelerator systems. Accelerators in which sulfur is combined as S—S, C—S—C, and C—S—N are generally inactive at lower temperatures due to increased thermal stability of the sulfur bonds. Thiourea (TU) and its derivatives are reported to have advantageous properties especially in the sulfur vulcanization of natural rubber (NR) and neoprene lattices.[1]

Philpot[6] showed that sulfur-containing nucleophiles enable accelerators, such as tetramethylthiuram disulfide (TMTD) to operate at lower vulcanization temperatures. He suggested an ionic mechanism for vulcanization reactions in which the S—S bond in TMTD is cleaved by the nucleophile generated from TU as represented in the Scheme 1.

Kuriakose et al.[4,7,8] investigated this further and found that the rate of vulcanization increased with nucleophilicity of TU derivatives. Recent studies by Susamma et al.[7] and Marykutty et al.[5,9] also support the same fact. Inspired by these studies and with a view to develop more effective binary accelerator systems we prepared a new thio compound *N*-benzylimine aminothioformamide (BIAT; Scheme 2), which is expected to be less toxic than the reported TU derivatives as a secondary accelerator in the sulfur vulcanization of NR along with *N*-cyclohexyl benzothiazyl sulfenamide (CBS), mercapto benzothiazyl disulfide (MBTS), and TMTD.

The structural features of BIAT can facilitate the polarization of C=S to create a nucleophilic sulfur. Also, steric reasons may have considerable role in the increased nucleophilicity.

In this study, different mixes were prepared using varying molar concentrations of BIAT along with CBS, MBTS, and TMTD separately. The control mixes were prepared using the primary accelerators only. Better cure characteristics of the vulcanizates clearly support nucleophilic mechanism in the sulfur vulcanization of NR. In the evaluation of physicomechanical properties of the vulcanizates, it was found that most properties are better than or comparable with the reference mixes. Aging properties were not evaluated in this study. Total crosslinks were estimated using Flory–Rhener equation[10] to correlate the variation in properties.

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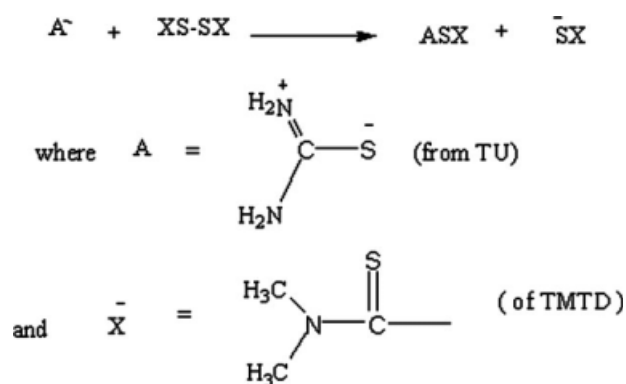
Scheme 1 General representation of synergism between primary and secondary accelerators.
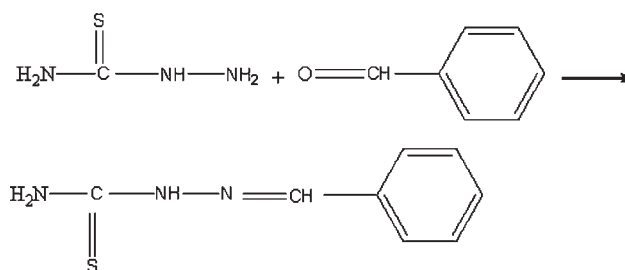


Scheme 3 Reaction route for the preparation of BIAT.

## EXPERIMENTAL

### Rubber and ingredients

NR: ISNR-5 of Mooney viscosity (ML.1 + 4,100°C) equal to 85 supplied by rubber Research Institute of India, Kottayam was used. Zinc oxide, stearic acid, CBS, MBTS, TMTD, and sulfur used were of rubber grade. Chemicals used for the preparation of BIAT, benzaldehyde, and thiosemicarbazide were of analar grade.

### Preparation of BIAT

Thiosemicarbazide (0.2 mol) was stirred well with 75 mL water. To this hot suspension, 0.2 mol fresh benzaldehyde was poured initially in thin stream with vigorous shaking. After complete addition of benzaldehyde, continued shaking for 15 min when pale yellow mass separates out (Scheme 3). Crushed the mass and washed several times with hot water to remove the unreacted reagents and any benzoic



**(a)**



**(b)**

Scheme 2 (a) The new secondary accelerator BIAT. (b) The proposed BIAT nucleophile.

acid formed. Recrystallised from water-ethanol mixture, collected, and dried. (m.p. 149°C). The compound was characterized by IR, NMR, and elemental analysis.

Elemental analysis (%): C = 53.60 (expt.), 53.63 (caltd), H = 5.01 (expt.), 5.03 (caltd), N = 23.41 (expt.), 23.46 (caltd), S = 17.80 (expt.), 17.88 (caltd).

IR (cm$^{-1}$), with KBr: 3397( NH str.), 3151( Aromatic C—H str.), 2342 (CN str.), 1365(CS str.)1519 (NH def.), 808–938(CH def.) $^1$H-NMR (δ, ppm from TMS in CDCl$_3$): 7.9 (NH proton, 1H), 7.6 (NH$_2$ protons, 2H), 7.2–7.4 (Aromatic protons, 5H), 6.5 (CH=, 1H).
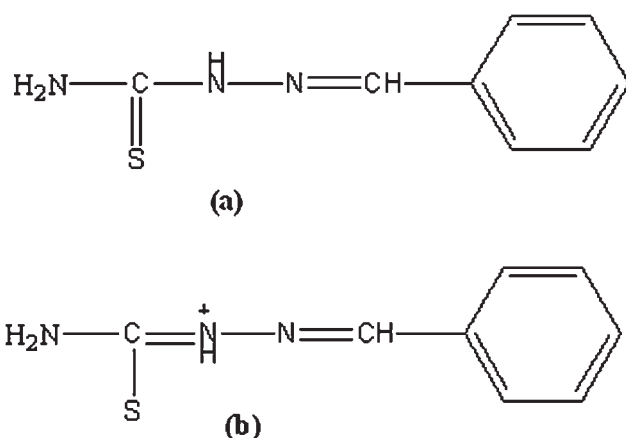
### Formulations of NR

Different mixes were prepared by varying the concentrations of BIAT ranging from 0.005 to 0.015 mequiv of BIAT as shown in the Table I. The reference mix $C_R$ contains CBS equivalent to the sum of mequiv of BIAT and 0.00175 mequiv of CBS. The NR mixes were prepared for BIAT-CBS, BIAT-TMTD, and BIAT-MBTS. The reference mix $T_R$ contains 0.0137 mequiv of TMTD and $M_R$ 0.009 mequiv of MBTS as in the case of CBS. The mixes were prepared on a laboratory size two-roll mixing mill (15.3 × 30.5 cm) as per ASTM designation D 3182-89.

### Evaluation of cure properties

The optimum cure time ($t_{90}$) of the mixes (time to reach 90% of the maximum torque) was determined on a Goettfert elastograph, model 67.85 at 150°C. The cure properties were obtained directly and the values are given in the Table II.

Induction time( $t_5$) is the time required for one unit(1.0 dNm) to raise above minimum torque(i.e., about 5% vulcanization). Elastographic scorch time ($t_{10}$) is time required for two units to raise above the minimum torque( about 10% vulcanization).The cure rate index is reported as $100/(t_{90}-t_{10})$.The compounds were then vulcanized up to the optimum cure time in an electrically heated laboratory

### TABLE I
### NR Mixes Containing CBS-BIAT for $C_1$–$C_R$, MBTS-BIAT for $M_1$–$M_R$, and TMTD-BIAT for $T_1$–$T_R$

| Ingredients phr[a] | Mixes | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $C_1$ | $C_2$ | $C_3$ | $C_4$ | $C_R$ | $M_1$ | $M_2$ | $M_3$ | $M_4$ | $M_R$ | $T_1$ | $T_2$ | $T_3$ | $T_4$ | $T_R$ |
| NR | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| ZnO | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| Stearic acid | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| CBS | 1.32 | 1.32 | 1.32 | 0.462 | 3.147 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| MBTS | 0 | 0 | 0 | 0 | 0 | 1.66 | 1.66 | 1.66 | 0.6308 | 3.3158 | 0 | 0 | 0 | 0 | 0 |
| TMTD | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1.2 | 1.2 | 1.2 | 0.6 | 3.285 |
| BIAT | 0.895 | 1.3425 | 1.79 | 2.685 | 0 | 0.895 | 1.3425 | 1.79 | 2.685 | 0 | 0.895 | 1.3425 | 1.79 | 2.685 | 0 |
| S | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |

[a] Parts per hundred parts of rubber (g).

type hydraulic press at 150°C at a pressure of 120 kg cm$^{-2}$.

### Tensile Properties and Tear resistance

The tensile properties of the vulcanized samples were determined on a Universal Testing Machine, Instron Corp., series IX model 1034, using a cross-head speed of 500 mm min$^{-1}$ as per ASTM D 412-87, using dumbbell specimen.

Angular specimens were used to determine tear strength on the same machine.

### Hardness

Hardness (Shore A) was measured as per ASTM D 2240-86.

### Compression set

Compression set was determined as per ASTM D 395-89(method B)

### Abrasion loss

Abrasion Loss was measured using DIN abrader (DIN 53516)

### Crosslink density

Samples of approximately 1 cm diameter and 0.2 cm thickness and 0.2 g weight were punched out from the central portions of the vulcanizate and allowed to swell in toluene for 24 h. The swollen samples were taken out and weighed after removing the solvent on the surface of the samples using blotting paper. The solvent was removed in vacuum and the weight of solvent swollen samples was taken. The volume fraction of rubber $V_r$ in the swollen network was calculated by the method[11,12] and using the equation:

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

where $T$ is the weight of the test specimen, $D$ is the weight of deswollen test specimen, $F$ is the weight fraction of the insoluble components, $A_s$ is the weight of absorbed solvent corrected for the swelling increment, $\rho_r$ is the density of test specimen, and $\rho_s$ is the density solvent. From $V_r$, the total crosslink density $1/2M_c$ was calculated using Flory–Rhener[10] equation as:

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

### TABLE II
### Cure Properties of CBS-BIAT, MBTS-BIAT, and TMTD-BIAT NR Mixes

| Cure properties | $C_1$ | $C_2$ | $C_3$ | $C_4$ | $C_R$ | $M_1$ | $M_2$ | $M_3$ | $M_4$ | $M_R$ | $T_1$ | $T_2$ | $T_3$ | $T_4$ | $T_R$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Minimum torque (dNm) | 0.03 | 0.22 | 0.21 | 0.23 | 0.22 | 0.07 | 0.37 | 0.15 | 0.28 | 0.37 | 0.30 | 0.25 | 0.36 | 0.54 | 0.39 |
| Maximum torque (dNm) | 10.70 | 7.15 | 7.10 | 6.23 | 9.58 | 6.39 | 3.31 | 8.13 | 7.12 | 7.75 | 6.33 | 8.40 | 7.82 | 7.22 | 9.88 |
| Optimum cure time ($t_{90}$ min) | 2.56 | 2.20 | 2.20 | 2.05 | 11.13 | 4.03 | 3.31 | 2.34 | 2.13 | 17.52 | 1.41 | 1.17 | 1.10 | 1.17 | 3.55 |
| Elastograph scorch time ($t_{90}$ min) | 0.41 | 0.47 | 0.44 | 0.40 | 6.43 | 2.01 | 1.58 | 1.01 | 0.50 | 10.03 | 1.03 | 0.41 | 0.37 | 0.36 | 2.06 |
| Induction time ($t_5$ min) | 0.41 | 0.50 | 0.47 | 0.44 | 6.45 | 1.48 | 1.22 | 0.55 | 0.42 | 8.29 | 0.56 | 0.37 | 0.33 | 0.31 | 1.44 |
| Cure rate index (CRI) | 46.5 | 57.8 | 56.8 | 60.6 | 21.3 | 38.37 | 43.67 | 55.25 | 57.47 | 13.35 | 111.11 | 123.46 | 128.21 | 113.64 | 46.95 |

## TABLE III
### Tensile Properties of CBS-BIAT, MBTS-BIAT, and TMTD-BIAT NR Vulcanizates

| Mix No. | Tensile strength (MPa) | 100% modulus (MPa) | Elongation at break (%) |
|---|---|---|---|
| $C_I$ | 1.73 | 0.92 | 159.8 |
| $C_2$ | 21.71 | 0.35 | 705.06 |
| $C_3$ | 18.75 | 0.35 | 696.67 |
| $C_4$ | 9.26 | 0.20 | 648.45 |
| $C_R$ | 1.10 | 0.69 | 162.37 |
| $M_1$ | 10.19 | 0.10 | 691.70 |
| $M_2$ | 11.88 | 0.45 | 685.40 |
| $M_3$ | 14.13 | 0.42 | 562.70 |
| $M_4$ | 17.02 | 0.33 | 680.00 |
| $M_R$ | 1.44 | 0.29 | 390.80 |
| $T_1$ | 12.93 | 0.31 | 665.76 |
| $T_2$ | 1.99 | 0.71 | 236.72 |
| $T_3$ | 3.25 | 0.76 | 320.03 |
| $T_4$ | 14.13 | 0.55 | 632.57 |
| $T_R$ | 1.15 | 0.91 | 127.47 |

where $V_s$ is the molar volume of the solvent (toluene $V_s = 106.2$ cm$^3$ mol$^{-1}$), $\chi$ is the interaction parameter for NR-solvent[12] ($\chi$ for NR-toluene = 0.42), and $M_c$ is the number average molecular weight of the rubber chains between crosslinks.

## RESULTS AND DISCUSSION

The synergic activity of the new accelerator BIAT is evident from the results shown in the Table II. There is almost 1/3rd reduction in the vulcanization time for the three binary systems when compared with the respective single accelerator systems. Considerable increase in the cure rate is a further proof for the nucleophilic mechanism suggested in the earlier reports.[2–15,16–18] Poor scorch safety[19,20] may cause processing problems, which is expected to be remedied in the future studies.

In the BIAT-CBS binary system, all the vulcanizates of the mixes have higher preaging tensile properties compared with the reference mix $C_R$ (Table III). All the vulcanizates except $C_1$ have better elongation at break percent, which is true for tear resistance also (Table IV). The mixes have almost comparable hardness. Compression set percent is minimum for $C_3$. The physicomechanical properties of test samples are in accordance with the crosslink density values of the samples. Considering the cure characteristics and the physicomechanical properties of the mixes, the dosage corresponding to $C_2$ (Table I) is derived as the optimum dosage (1.32 phr CBS and 1.3425 phr BIAT).

In the BIAT-MBTS binary system, all the vulcanizates of the mixes have higher preaging tensile properties compared with the reference mix $M_R$, but maximum for $M_4$ (Fig. 1). Elongation at break percent values are higher for other mixes than the reference mix $M_R$ (Fig. 2). Tear resistance values are better for the vulcanizates of the mixes except for $M_1$ than that of the reference (Fig. 3). Hardness values are comparable. Compression set % values are found comparable with the reference mix. Better abrasion loss values are found for $M_3$ and $M_4$ (Table IV). The physicomechanical properties of test samples are in accordance with the crosslink density values of the samples. Based on the cure scorch safety and other physicomechanical properties, the dosage of the mix $M_3$ is taken as the optimum dosage of binary accelerators (1.66 phr MBTS and 1.79 phr BIAT).

In the BIAT-TMTD binary system, all the vulcanizates of the mixes have higher preaging tensile

## TABLE IV
### Other Physicomechanical Properties of CBS-BIAT, MBTS-BIAT, and TMTD-BIAT NR Vulcanizates

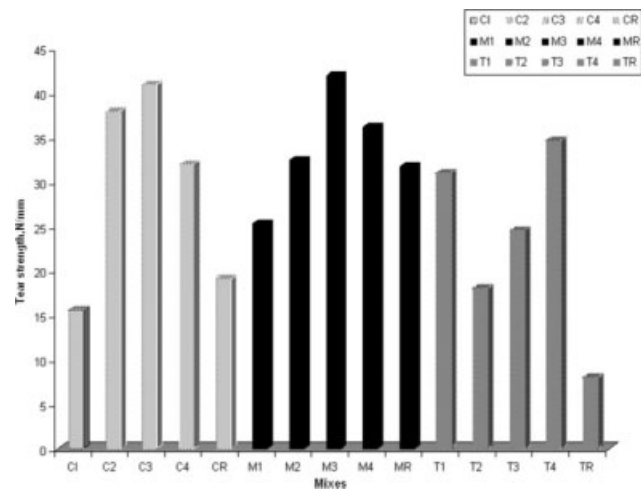| Mix No. | Tear resistance (Nm m$^{-1}$) | Hardness shore A | Abrasion loss (cm$^3$ h$^{-1}$) | Compression set (%) | Total cross link density $\times 10^4$ (g mol cm$^3$) |
|---|---|---|---|---|---|
| $C_I$ | 15.57 | 48 | 7.02 | 4.84 | 0.93 |
| $C_2$ | 37.87 | 39 | 6.63 | 4.97 | 1.26 |
| $C_3$ | 40.88 | 36 | 6.26 | 3.86 | 1.27 |
| $C_4$ | 31.93 | 34 | 6.49 | 5.20 | 1.03 |
| $C_R$ | 19.09 | 39 | 3.23 | 3.09 | 1.67 |
| $M_1$ | 25.29 | 32 | 11.40 | 4.00 | 0.95 |
| $M_2$ | 32.45 | 37 | 11.05 | 3.52 | 1.18 |
| $M_3$ | 41.90 | 42 | 4.79 | 4.53 | 1.38 |
| $M_4$ | 36.15 | 38 | 4.37 | 4.32 | 1.45 |
| $M_R$ | 31.72 | 40 | 7.12 | 4.10 | 1.22 |
| $T_1$ | 30.96 | 39 | 2.80 | 4.42 | 0.99 |
| $T_2$ | 18.03 | 45 | 3.13 | 4.67 | 1.55 |
| $T_3$ | 24.52 | 43 | 2.49 | 4.62 | 1.39 |
| $T_4$ | 34.60 | 42 | 2.25 | 2.01 | 1.87 |
| $T_R$ | 8.01 | 46 | 5.90 | 1.45 | 1.89 |
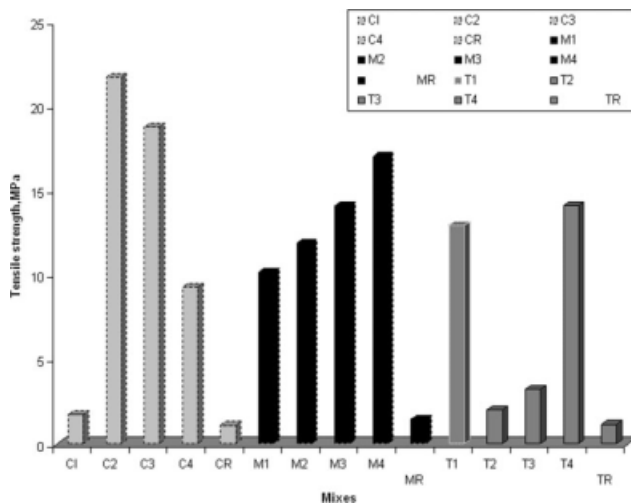
**Figure 1** Tensile strength of CBS-BIAT, MBTS-BIAT, and TMTD-BIAT NR vulcanizates.

properties compared with the reference mix $T_R$, but maximum for $T_4$ (Figs. 1 and 4).The mixes have better elongation at break percent values compared with the reference mix $T_R$ (Fig. 2). Tear resistance is maximum for $T_4$ (Fig. 3). Compression set % and abrasion loss are minimum for $T_4$.

The various vulcanizates have almost comparable properties. As scorch safety is much better for $T_1$, its dosage is taken as the optimum dosage (1.2 phr TMTD and 0.895 phr BIAT).

Applying the similar arguments for the BIAT-CBS system, it is evident that the dosage corresponding to $C_2$ is optimum. (1.32 phr CBS and 1.3425 phr BIAT)

In the three systems studied, there is an increase in tensile strength with crosslink density and among the systems it was found that the BIAT-CBS system has given the best physicomechanical properties.
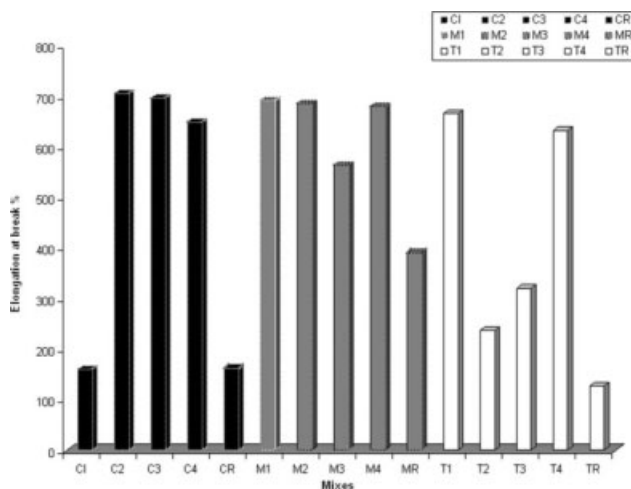


**Figure 2** Elongation at break % in CBS-BIAT, MBTS-BIAT, and TMTD-BIAT NR vulcanizates.



**Figure 3** Tear resistance in BIAT in CBS-BIAT, MBTS-BIAT, and TMTD-BIAT NR vulcanizates.

## CONCLUSIONS

BIAT can be used as a synergic secondary accelerator in the sulfur vulcanization of NR along with the conventional accelerators CBS, MBTS, and TMTD. The results obtained in this study can be considered as an evidence of nucleophilic mechanism of the vulcanization reaction. There is considerable improvement in many of the physicomechanical properties of the vulcanizates containing BIAT when compared with those containing CBS, MBTS, and TMTD primary accelerators alone.
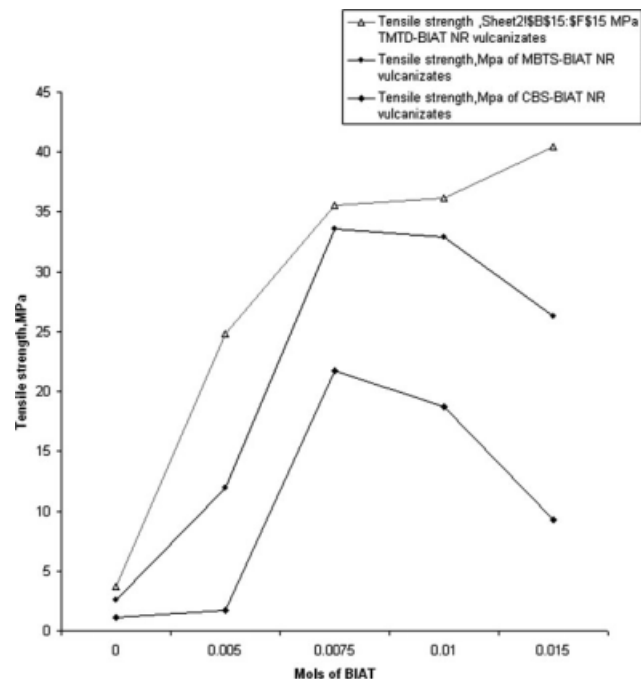


**Figure 4** Variation of tensile strength with molar concentration of BIAT in CBS-BIAT, MBTS-BIAT, and TMTD-BIAT NR vulcanizates.

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