

N-Benzoyl-*N'**N'*-Disubstituted Thioureas—A New Binary Accelerator System and Its Effect of Nucleophilicity in Sulfur Vulcanization of Natural Rubber

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ABSTRACT: The effect of several new binary accelerator systems were studied with special emphasis to the relationship of nucleophilicity to their rheological and mechanical properties. In this study, dialkyl/azacycloalkyl substituted benzoylthioureas (BTU 1-5) were used as secondary accelerators (SA) along with three different primary accelerators (PA) viz., Cyclohexylbenzothiazylsulfonamide (CBS), Mercaptobenzothiazole (MBT) or Zincdithiocarbamate(ZDC) in the sulfur vulcanization of natural rubber. The effect of these secondary accelerators on the rheological and mechanical properties was found to be improved when compared

to the reference mixes. It is noted that the *N*-benzoyl-*N'**N'*-piperidinylthiourea (BTU 4) is more effective as a secondary accelerator due to the higher nucleophilicity of the same when compared with the test compounds. The ZDC-BTU gives the best result as binary accelerator system in natural rubber. Chemical characterization was carried out by determining the total crosslink density. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 978–984, 2012

Key words: BTU; natural rubber; vulcanization; cure; nucleophilic mechanism; mechanical properties

INTRODUCTION

Binary accelerator systems are widely used in rubber industry.^{1–9} Mixed system can effectively prevent pre vulcanization, permit the vulcanization to be carried out at a lower temperature in a shorter time and can produce a vulcanizate with superior qualities. Small amount of secondary accelerators can effectively reduce the quantity of primary accelerator to be used and there by reducing the cost of production.⁶ In binary accelerator system a small amount of secondary accelerators are enough for the vulcanization along with primary accelerator. Hence the study of vulcanization of natural rubber will have a direct impact on rubber industry which plays a major role in automobile industry.

The C–S–C, S–S, or S–N bonding in accelerators is inactive at temperatures less than 100°C because of the high thermal stability of the sulfur bonds. Study by Philpott¹⁰ reveals that sulfur-containing nucleophiles like thiourea (TU) enables such accelerators to become active even at lower temperatures. Different thiourea derivatives such as dithiobiurets

and phenyl-substituted amidinothioureas can act as secondary accelerators based on their nucleophilic reaction mechanism.^{11–14} *N*-Amidino-*N'*-phenylthiourea (APT) was found to be effective for vulcanization in dry rubber.^{6,15}

In this study, several *N*-benzoyl-*N'*,*N'*-dialkyl/azacyclosubstituted thioureas(BTU 1-5) were investigated in the vulcanization of natural rubber along with primary accelerators such as CBS, MBT and ZDC. In rubber compounding, it is beneficial to use a combination of two or more accelerators to enhance the physical and mechanical properties of the products.¹⁶ This study contributes a relationship between nucleophilicity of BTU and their rheological as well as mechanical properties. The optimum dosage of BTU required to achieve maximum cure and mechanical properties for the vulcanisate was also derived. Tensile properties like tensile strength, elongation at break, modulus, etc., were evaluated and compared with the control. The chemical characterization of the vulcanizates was studied to correlate the variation of physical properties with the crosslink density.

EXPERIMENTAL

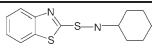
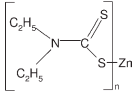
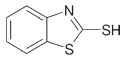
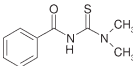
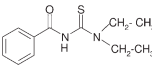
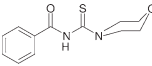
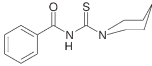
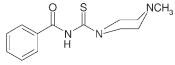
Synthesis of *N*-benzoyl-*N'*,*N'*-disubstitutedthiourea (BTU 1-5)

A solution of benzoylchloride(7.5 mmol) in 4 mL benzene was stirred well in presence of

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TABLE I
List of Chemical Compounds Used in Vulcanization Study

Chemical name	Structure	Abbreviations
N-cyclohexyl-2-benzothiazolsulfenamide		CBS
Zincdithiocarbamate		ZDC
Mercaptobenzothiazole		MBT
N-benzoyl-N'N'-dimethyl thiourea		BTU 1
N-benzoyl-N'N'-diethyl thiourea		BTU 2
N-benzoyl-N'N'-morpholinyl thiourea		BTU 3
N-benzoyl-N'N'-piperidinyl thiourea		BTU 4
N-benzoyl-N'N'-(N-methylpiperazinyl) thiourea		BTU 5

tetrabutylammonium¹⁷⁻¹⁹ bromide(TBAB 0.2 g). To this mixture, aqueous solution of potassium thiocyanate (33%, 5.5 mL) was added in drops during 15 min. The aqueous layer was extracted with benzene and diethyl amine (7.5 mmol) was added. The work up and recrystallization from ethanol water system afforded yellow microcrystalline powder of N-benzoyl-N'N'-diethylthiourea(BTU 2). By using the same synthetic strategy four more BTU's were prepared and characterized. Thin layer chromatography was performed using silica gel-G (E. Merck, India) coated on glass plates and the spots were visualized under

UV-light. The spectra were recorded on Systronics UV-Vis Double beam Spectrophotometer-2201 for absorption studies. The infrared spectrum of the samples were recorded between 4000 cm⁻¹ and 400 cm⁻¹ on a JASCO 400 FTIR spectrometer, which was calibrated using polystyrene bands. The samples were prepared as a KBr disc. Bruker WM- 400 (400 MHz) was used for ¹H-NMR and JEOL GSX (125 MHz) for ¹³C-NMR spectra. Physical and spectral data of BTU 1-5 are as follows:

BTU 1

Yield 75%; m.p 138°C; IR (K Br) cm⁻¹ 3263.25, 3059.36, 3021.05, 2934.75, 2056.60, 1652.22, 1600.60, 1578.29, 1531.28, 1494.17, 1309.26, 1286.54, 1232.72, 1026.93, 1000.90, 943.35, 919.43, 792.30, 710.65, 687.47, 654.20, 612.72, 583.28, 529.18; δ_H(400 MHz; DMSO-d₆) 1.35 (6H, s), 3.95 (1H, s), 7.32-7.89 (5H, m); δ_C(125 MHz, DMSO - d₆) 42.0 (2), 113.0, 128.2, 129, 136, 136.2, 169, 173.0 and 180.7.

BTU 2

Yield 78%; m.p 110°C; IR (K Br) cm⁻¹ 3267.86, 3064.39, 3024.05, 2934.75, 2056.60, 1652.22, 1600.60, 1579.29, 1533.19, 1494.17, 1309.26, 1286.54, 1232.72, 1026.93, 1000.90, 943.35, 919.43, 792.30, 710.65, 687.47, 654.20, 612.72, 583.28, 534.10; δ_H(400 MHz; DMSO-d₆) 1.15-1.35 (6H, t, J 6.7), 3.55-3.75 (4H, q, J 6.7), 3.95 (1H, s), 7.32-7.89 (5H, m); δ_C(125 MHz, DMSO - d₆) 42.0 (2), 54 (2), 113.0, 128.2, 129, 136, 136.3, 169, 173.0 and 180.7.

BTU 3

Yield 75%; m.p 152°C; IR (K Br) cm⁻¹ 3297.16, 3243.23, 3035.48, 3015.21, 2969.28, 2924.04, 2892.62, 2847.38, 2755.99, 2700.57, 2056.17, 1822.02, 1665.93, 1602.31, 1580.86, 1521.82, 1455.28, 1357.09, 1269.04, 1223.15, 1200.10, 1148.74, 1062.36, 957.21, 918.82, 876.06, 791.42, 657.69, 588.45; δ_H (400 MHz;

TABLE II
Formulation of the Mixes Containing BTU 1-5

Ingredients	A	A1	A2	A3	A4	B	B1	B2	B3	B4	C	C1	C2	C3	C4
Natural rubber	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
Sulfur	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
CBS	1	1	1	1	1	-	-	-	-	-	-	-	-	-	-
MBT	-	-	-	-	-	1	1	1	1	1	-	-	-	-	-
ZDC	-	-	-	-	-	-	-	-	-	-	1	1	1	1	1
BTU1(a)	-	0.5	1	1.5	-	-	0.5	1	1.5	-	-	0.5	1	1.5	-
BTU2(b)	-	0.5	1	1.5	0.25	-	0.5	1	1.5	-	-	0.5	1	1.5	-
BTU3(c)	-	0.5	1	1.5	-	-	0.5	1	1.5	0.25	-	0.5	1	1.5	-
BTU4(d)	-	0.5	1	1.5	-	-	0.5	1	1.5	-	-	0.5	1	1.5	-
BTU5(e)	-	0.5	1	1.5	-	-	0.5	1	1.5	-	-	0.5	1	1.5	0.25

TABLE III
Cure Characteristics of CBS Alone and CBS-BTU Mixes

Mixes	Minimum torque	Maximum torque	t_5	t_{10}	t_{90}	Cure rate index $100/t_{90}-t_{10}$
A	3.6	14.2	1.11	1.78	14.64	7.78
A _{1a}	0.11	5.94	0.85	1.27	6.13	20.57
A _{2a}	0.14	6.10	0.76	0.82	7.34	15.33
A _{3a}	0.34	6.74	1.02	1.89	8.43	15.29
A _{1b}	0.11	5.94	0.74	0.91	6.12	19.19
A _{2b}	0.14	6.10	0.69	1.04	6.92	24.27
A _{3b}	0.34	6.76	0.82	1.09	7.07	16.72
A _{4b}	0.14	5.76	0.62	1.03	6.34	18.83
A _{1c}	0.12	5.83	0.71	1.09	7.21	16.34
A _{2c}	0.14	6.13	0.97	1.12	7.96	14.62
A _{3c}	0.33	6.69	1.03	1.78	8.76	14.33
A _{1d}	0.11	5.94	0.88	1.11	5.43	23.15
A _{2d}	0.14	6.10	0.99	1.13	5.98	20.61
A _{3d}	0.34	6.76	1.02	1.89	6.07	23.92
A _{1e}	0.09	5.82	0.91	1.10	6.28	19.31
A _{2e}	0.14	6.15	0.98	1.09	7.12	20.24
A _{3e}	0.33	6.86	1.04	1.91	7.33	18.45

DMSO- d_6) 3.60-3.75 (4H, t, J 7.7), 3.82-3.89 (4H, t, J 7.7), 3.95 (1H, s), and 7.39-7.98 (5H, m); δ_C (125 MHz, DMSO - d_6) 23.0 (2), 49.0 (2), 113.0, 123.2, 125.0, 129.5, 136.0, 152.5, 172.0 and 184.2.

BTU 4

Yield 81%; m.p 115°C; IR (K Br) cm^{-1} 3168.72, 3061.61, 3030.78, 2998.86, 2958.79, 2932.64, 2858.70, 2056.76, 1960.95, 1650.57, 1600.87, 1581.29, 1531.60, 1468.46, 1447.85, 1437.64, 1370.40, 1278.55, 1181.29, 1161.09, 1088.69, 1019.39, 950.11, 854.62, 835.10, 794.56, 656.17, 570.69; δ_H (400 MHz, DMSO- d_6) 2.69(2H, q, J 7.8), 3.56-3.61 (4H, t, J 5.0), 3.66-3.80 (4H, t, J 5.0), 3.95(1H, s) and 7.39-7.98 (5H, m); δ_C (125 MHz, DMSO - d_6) 23.8, 37.2(2) 49.0 (2), 121.9, 128.1, 136.2, 152.9, 165.0, 169.2, 174.3 and 184.8.

BTU 5

Yield 74%; m.p 143°C; IR (K Br) cm^{-1} 3267.86, 3064.39, 3024.05, 2934.75, 2056.60, 1652.22, 1579.29, 1494.17, 1309.26, 1286.54, 1026.93, 943.35, 919.43, 792.30, 710.65, 687.47, 654.20, 612.72, 583.28; δ_H (400 MHz, DMSO- d_6) 3.21(3H, s), 3.51-3.66 (4H, t, J 5), 3.69-3.80 (4H, t, J 5), 3.95(1H, s) and 7.39-7.98 (5H, m); δ_C (125 MHz, DMSO - d_6) 37.8(2) 49.4 (2), 121.9, 128.1, 136.2, 152.9, 165.0, 169.0, 171.5 and 184.8.

Rheological and mechanical properties

The natural rubber (ISNR-5) used in the study had a mooney viscosity (ML 1 + 4, 100°C) of 85 and was obtained from Rubber Research Institute of India, Kottayam. The CBS, ZDC, and MBT were supplied by Bayer India, Bombay and the rubber additives

TABLE IV
Cure Characteristics of MBT Alone and MBT-BTU Mixes

Mixes	Minimum torque	Maximum torque	t_5	t_{10}	t_{90}	Cure rate index $100/t_{90}-t_{10}$
B	1.98	10.24	3.65	3.86	20.54	5.99
B _{1a}	0.11	5.94	0.85	1.01	9.83	20.57
B _{2a}	0.14	6.10	0.96	1.12	10.34	15.33
B _{3a}	0.34	6.76	1.02	1.39	10.43	15.29
B _{1b}	0.11	5.94	1.08	1.21	10.50	10.76
B _{2b}	0.14	6.10	1.09	1.24	10.92	8.78
B _{3b}	0.34	6.76	1.02	1.89	11.07	10.89
B _{1c}	0.12	5.83	0.99	1.19	12.21	9.07
B _{2c}	0.14	6.13	1.07	1.22	12.96	8.52
B _{3c}	0.33	6.69	1.13	1.28	13.76	8.01
B _{4c}	0.28	5.93	1.11	1.36	12.84	8.71
B _{1d}	0.11	5.94	0.98	1.11	8.93	12.78
B _{2d}	0.14	6.10	0.99	1.13	9.18	12.42
B _{3d}	0.34	6.76	1.02	1.89	9.77	12.69
B _{1e}	0.09	5.82	1.03	1.29	11.78	9.53
B _{2e}	0.14	6.15	1.01	1.31	11.92	9.43
B _{3e}	0.33	6.86	1.04	1.91	12.14	9.77

TABLE V
Cure Characteristics of ZDC Alone and ZDC-BTU Mixes

Mixes	Minimum torque	Maximum torque	t_5	t_{10}	t_{90}	Cure rate index $100/t_{90}-t_{10}$
C	1.98	2.43	1.67	2.07	10.45	11.93
C _{1a}	0.11	5.94	0.85	1.27	5.13	25.91
C _{2a}	0.14	6.10	0.87	1.32	5.34	24.87
C _{3a}	0.34	6.76	0.92	1.39	5.43	24.75
C _{1b}	0.11	5.94	0.78	1.01	5.09	24.51
C _{2b}	0.14	6.10	0.99	1.04	5.22	23.92
C _{3b}	0.34	6.76	1.02	1.69	5.37	27.17
C _{1c}	0.12	5.83	0.91	1.09	6.21	19.53
C _{2c}	0.14	6.13	1.07	1.12	6.36	19.08
C _{3c}	0.33	6.69	1.03	1.28	6.76	18.25
C _{1d}	0.11	5.94	0.89	1.11	4.93	26.18
C _{2d}	0.14	6.10	0.99	1.13	5.18	24.69
C _{3d}	0.34	6.76	1.02	1.89	5.39	28.57
C _{1e}	0.09	5.82	0.79	1.10	5.78	21.37
C _{2e}	0.14	6.15	0.98	1.19	6.12	20.28
C _{3e}	0.33	6.86	1.04	1.91	6.32	22.67
C _{4e}	0.31	6.75	1.02	1.63	6.24	21.69

ZnO, stearic acid, and sulfur were of rubber grade. The different rubber mixes were prepared on a laboratory size two-roll mixing mill according to ASTM D 3182-89. The cure characteristics of the mixes were determined at 150°C using a Goettfert elastograph (Model 67.85) according to ASTM D 2084-88. The tensile strength (ASTM D 412-83), % strain at break (ASTM D 412-83), abrasion loss (ASTM D5963-04) and hardness (ASTM D2240-05) were determined. A list of compounds used in this study is given in Table I along with their chemical structures and abbreviations.

The rheological measurements of BTU 1-5 were done after compounding the mixes and matured the composites at room temperature for 24 h. The systems containing optimum dosage of BTU and the corresponding references were used for this study. The formulations of the different mixes used in the study are given in Table II. The mixing was done in an electrically heated hydraulic press at 150°C and a pressure of 120 kg cm⁻². After determining the cure characteristics of the vulcanizates, the tensile and tear resistance were calculated from the dumbbell shaped and angular strips cut from the compression molded sheets.

Determination of chemical crosslinks by equilibrium volume swelling measurements

Circular-shaped strips cut from the center of the sheets were immersed in toluene at room temperature and allowed to swell for 48 h. The swollen samples were taken out and weighed in every 10 min intervals for the first one hour and then weighed in every half an hour till constant weight was obtained. Finally the strips were weighed after swelling for 48 h.

The chemical crosslink density of the different vulcanizates were determined from the equilibrium swelling measurements and calculated according to the following Flory- Rehner Equation.²⁰

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

Where, M_c = molar mass between crosslinks, ρ_p = density of polymer, V_s = molar mass of solvent (for toluene $V_s = 106.2 \text{ cm}^3 \text{ mol}^{-1}$), V_r = molar volume of rubber, χ = interaction parameter²¹ ($\chi_{(\text{NR-Toluene})} = 0.42$). The term V_r was calculated by using the relation,

$$V_r = \frac{W_1/\rho_1}{(W_1/\rho_1 + W_2/\rho_2)}$$

where, W_1 = weight of rubber, W_2 = weight of solvent, ρ_1 = density of rubber, and ρ_2 = density of solvent. The crosslink densities ($1/2M_c$) were calculated from the above data.

RESULTS AND DISCUSSION

Cure characteristics and tensile properties

In this study, BTU 1-5 were used as secondary accelerators along with three primary accelerator CBS, MBT, and ZDC in the ratios SA: PA as 0.5 : 1, 1 : 1, and 1.5 : 1, respectively. Cure characteristics of different mixes containing BTU-CBS, BTU-MBT, or BTU-ZDC systems are given in Tables III-V respectively. In all these cases the amount of PA is constant and as the amount of secondary accelerator varied, the lowest cure time was obtained for the 0.5 phr mixes. This may be due to the greater

TABLE VI
Tensile Properties of Mixes Containing CBS-BTU,
ZDC-BTU, and MBT-BTU Systems

Mix No.	Tensile strength (MPa)	% strain at break	300% modulus (MPa)
A1a	21.15	471.23	1.13
A2 a	20.38	412.24	1.01
A3a	19.16	409.28	0.87
A1b	22.17	473.86	1.23
A2b	22.03	427.25	1.14
A3b	21.26	414.12	1.03
A4b	21.34	466.21	1.15
A1c	18.52	464.19	1.04
A2c	17.15	403.11	0.76
A3c	17.11	389.26	0.64
A1d	23.35	489.45	1.28
A2d	23.18	456.34	1.21
A3d	21.76	434.23	1.18
A1e	19.76	431.43	1.22
A2e	19.13	413.76	1.02
A3e	19.14	412.78	0.98
B1a	14.74	365.16	0.77
B2a	12.31	317.52	0.71
B3a	12.16	302.31	0.67
B1b	14.87	371.83	0.73
B2b	13.34	346.12	0.62
B3b	12.72	331.45	0.48
B1c	13.12	312.32	0.59
B2c	12.68	303.87	0.59
B3c	11.96	247.44	0.48
B4c	12.29	305.12	0.53
B1d	16.13	379.67	0.87
B2d	15.78	351.24	0.79
B3d	15.12	347.78	0.73
B1e	13.67	331.23	0.75
B2e	12.33	311.16	0.67
B3e	12.11	278.81	0.62
C1a	23.13	558.69	1.21
C2a	23.02	526.12	1.17
C3a	22.61	517.12	1.12
C1b	24.25	586.82	1.23
C2b	23.68	554.17	1.21
C3b	22.23	533.72	1.05
C1c	22.34	463.34	1.11
C2c	22.16	445.81	1.06
C3c	22.14	440.68	0.94
C1d	26.12	643.51	1.32
C2d	25.25	637.21	1.31
C3d	24.13	584.72	1.27
C1e	23.18	512.37	1.21
C2e	22.73	486.79	1.08
C3e	22.14	463.64	0.98
C4e	22.86	493.12	1.05

availability of sulfur for the vulcanization purpose in the optimum dosage. We observed an increase in cure time for mixes (A₄b, B₄c, and C₄e) containing still lower amount of SA say 0.25phr. From this we understand that an insufficient amount of accelerator may cause under curing (i.e., incomplete vulcanization), which can reduce the characteristic properties of the sample. An increase in amount of accelerator may causes over curing (i.e., degradation after com-

plete crosslinking) which results in the early break and poor mechanical properties of the sample. The tensile strength values of the experimental mixes containing BTU are found to be better than those of the reference mixes. The mixes containing 0.5 phr. of BTU exhibits the best tensile properties, so this can be considered as the optimum dosage for effective vulcanization.

TABLE VII
Physical Properties of Mixes Containing CBS-BTU,
ZDC-BTU, and MBT-BTU Systems

Mix No.	Hardness (shore A)	Compression set (%)	Abrassion loss (mL/h)	Total crosslink density × 10 ⁵ (g/mol/mL)
A1a	42.7	23.86	1.92	4.1367
A2 a	40.3	21.25	2.31	4.0145
A3a	36.7	21.12	2.34	3.1287
A1b	44.6	24.23	3.23	4.2398
A2b	42.8	23.43	3.44	4.1434
A3b	42.1	23.28	3.57	4.0346
A4b	43.5	22.16	3.36	4.0437
A1c	39.2	21.19	1.87	3.9175
A2c	40.5	21.11	2.11	3.7656
A3c	39.1	19.26	2.21	3.645
A1d	46.7	25.45	3.12	4.2819
A2d	43.5	25.34	3.34	4.2186
A3d	43.4	24.23	3.56	4.1834
A1e	42.6	21.43	2.11	3.2224
A2e	42.1	20.76	2.13	3.2102
A3e	39.4	20.12	2.24	2.9821
B1a	34.4	20.16	1.94	3.7726
B2a	32.3	20.12	2.11	3.7134
B3a	32.1	18.31	2.14	2.6967
B1b	34.8	21.83	2.23	3.7483
B2b	33.4	21.12	2.34	3.6722
B3b	32.2	20.45	2.77	3.4853
B1c	28.7	16.32	1.89	2.5369
B2c	28.2	13.87	2.18	2.5923
B3c	27.9	13.44	2.21	2.4138
B4c	27.4	14.43	1.99	2.4672
B1d	36.1	22.67	2.27	3.8947
B2d	35.7	21.24	2.32	3.7921
B3d	35.2	21.18	2.74	3.7311
B1e	31.6	21.23	2.03	2.7895
B2e	31.3	21.16	2.11	2.6727
B3e	31.1	20.81	2.23	2.6212
C1a	43.3	24.69	2.91	4.2321
C2a	43.2	24.12	3.12	4.1787
C3a	42.6	24.21	3.34	4.1212
C1b	45.5	25.11	3.52	4.3431
C2b	44.6	24.34	3.56	4.2327
C3b	44.2	24.12	3.97	4.0522
C1c	42.3	23.82	2.87	4.1112
C2c	42.1	23.17	3.17	4.0613
C3c	41.4	21.72	3.25	4.0123
C1d	49.3	26.51	4.08	5.3622
C2d	49.1	26.21	4.14	5.3143
C3d	48.5	24.72	4.36	4.7542
C1e	43.5	24.37	2.91	4.2234
C2e	43.3	23.91	3.28	4.1875
C3e	42.1	23.64	3.36	4.0812
C4e	42.4	23.87	3.04	4.1421

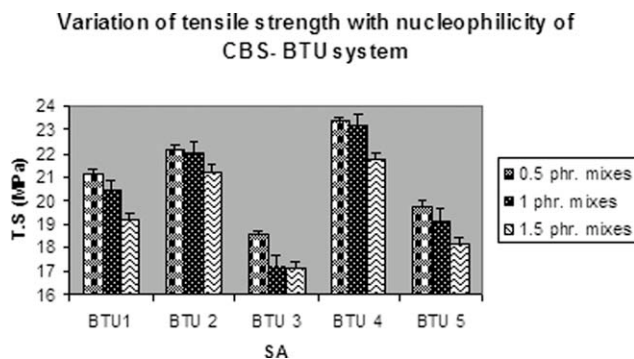


Figure 1 Variation of tensile strength with nucleophilicity of CBS-BTU system.

The tensile properties such as tensile strength, % strain at break and 300% modulus for the three different PA - BTU systems were given in Table VI. All these properties were improved considerably when compared with the reference mixes. The improvement in property of BTU-4 as an SA could be attributed to the more nucleophilic character in comparison to others. The presence of accelerator affects the structure of the rubber molecules, which will control the physical and mechanical properties of the product. When comparing the three different SA/PA systems, it is clear that ZDC-BTU system is more efficient in accordance with the cure and mechanical properties. This is due to the difference in the stability of complexes formed from ZDC/CBS/MBT with ZnO. The results of other physical properties such as hardness, compression set, abrasion loss etc. of the different systems are given in Table VII.

The chemical characterization of the vulcanizate samples was carried out using the equilibrium swelling method. Chemical crosslink density of natural rubber vulcanizates is a principal constitutive unit that governs mechanical properties of the rubber, i.e., tensile strength, tear strength, permanent set, and so forth. Therefore, it is quite important to determine crosslink density. The chemical crosslink density values of different mixes were given in Table VII. Mixes having 0.5 phr. samples are found to

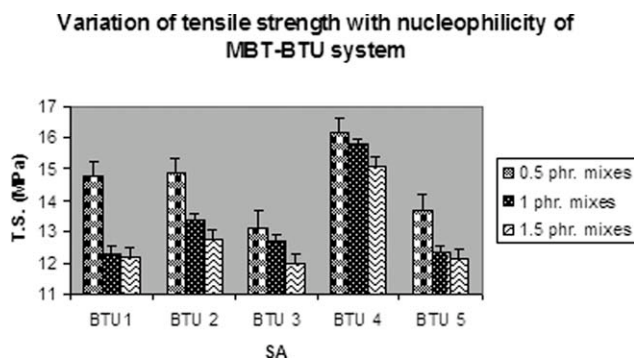


Figure 2 Variation of tensile strength with nucleophilicity of MBT-BTU system.

Variation of tensile strength with nucleophilicity of ZDC-BTU system

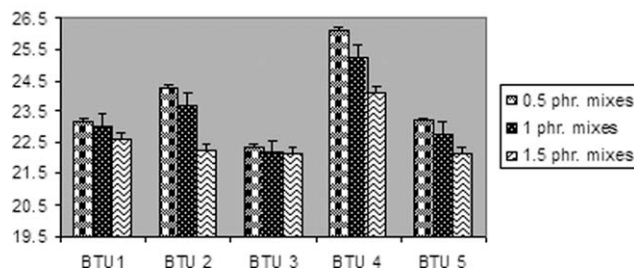


Figure 3 Variation of tensile strength with nucleophilicity of ZDC-BTU system.

have highest chemical crosslink density in support of the optimum dosage derived. The BTU 4-ZDC system is found to have highest crosslink density. This can be correlated to the better tensile and physical properties for the same system.

Effect of nucleophilicity of different BTU on physical and mechanical properties

We tried to compare the nucleophilic character of different BTUs with the cure and mechanical properties. We found that among the five BTUs examined, that with highest nucleophilicity viz BTU 4 shows the best cure and mechanical properties. The lower cure time obtained for the above can be due to the nucleophilic attack by the BTU, which promotes the S-S bond cleavage in the primary accelerator, leading to faster cure. The variations of tensile strength of different vulcanizates formed in presence of various BTU in correlation with their nucleophilicity are shown in Figures 1 to 3. It is clear from the figures that there is a correlation between nucleophilic character of the SA and their tensile strength for 0.5 phr., 1 phr. and 1.5 phr. mixes. We noticed that the highest nucleophilic BTU 4 containing system has the highest tensile strength. The nucleophilic character of the five different BTUs are in the order BTU 4 > BTU 2 > BTU 1 > BTU 5 > BTU 3. The same relation is found to be true for the various other properties studied, as shown in Tables VI and VII. This gives further evidence to support the suggestions made by Philpot that a nucleophilic mechanism is involved in the vulcanization process.

CONCLUSIONS

This study supports a nucleophilic reaction in the binary accelerator system as suggested by Philpot. Among the different benzoylthioureas investigated, BTU 4 which is more nucleophilic is found to be more effective for the vulcanization purposes. The systems containing optimum dosage of BTU give better results compared with the reference mixes. Among the three different binary accelerator systems studied, BTU-ZDC

system is found to be the best due to higher stability of complexes formed from that binary accelerator system. The newly introducing binary system involves the SA namely dialkyl/azacycloalkyl substituted benzoylthioureas, which are non toxic and reported to have various applications in pharmaceutical field.

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