Synergic Effect of *N*-Benzylimine Aminothioformamide Secondary Accelerator During Sulfur Vulcanization of a Styrene-Butadiene-Natural Rubber Blend

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ABSTRACT: In this study we reported synergic activity of a novel secondary accelerator *N*-Benzylimine aminothioformamide (BIAT) along with tetramethylthiuram disulfide (TMTD) in improving cure and mechanical properties of gum and filled mixes of Styrene-Butadiene Rubber (SBR). The feasibility of application of BIAT in sulfur vulcanization of an ideal blend of SBR and natural rubber (NR) has also been investigated. The mechanical properties like **t**ensile strength, tear resistance, hardness, compression set, and abrasion loss were measured. Swelling values were also determined as a measure of crosslink densities of the vulcanizates. The binary accelerator system BIAT-TMTD was found very effective in improving cure properties of the mixes of pure SBR and a 50/50 blend of SBR and NR.There was also found simultaneous improvement in mechanical properties of vulcanizates of both pure and blend. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 2257–2263, 2011

Key words: styrene-butadiene rubber; binary accelerator system; synergism; vulcanization; mechanical properties

INTRODUCTION

Reports[1–3] indicate that use of binary accelerator systems in rubber vulcanization provides better acceleration and improved mechanical properties of natural rubber (NR) vulcanizates. Thiourea (TU) and its derivatives are reported to have advantageous properties especially in sulfur vulcanization of NR and neoprene lattices.[4] Philpot[5] suggested an ionic mechanism for vulcanization reactions in which *S*-S bond in TMTD is cleaved by the nucleophile generated from TU as in Scheme 1

Recent studies[6–9] further show that rate of vulcanization increases with nucleophilicity of TU derivatives.

In an earlier study, Thomas and Ettolil[10] reported the preparation and characterization of a novel secondary accelerator, *N*-Benzylimine aminothioformamide (BIAT) and its synergic activity with conventional primary accelerators like *N*-cyclohexyl benzothiazyl sulfenamide (CBS), mercapto benzothiazyl disulfide (MBTS) and tetramethylthiuram disulfide (TMTD) in sulfur vulcanization of NR. The structure of BIAT is shown in Scheme 2. BIAT has been reported as an effective accelerator that improves cure and mechanical properties like tensile strength, tear resistance, hardness, compression set, and abrasion resistance. This could serve as further proof for nucleophilic mechanism already suggested for binary accelerator systems in rubber vulcanization.

In the vulcanization of diene rubber using sulfur and accelerators, efficiency of sulfur intake during crosslink formation mainly depends on the type of accelerator systems, structure of the base polymer and temperature of vulcanization.[11] Unlike NR, vulcanization of SBR, a copolymer, is relatively slower and therefore requires higher amounts of accelerator. This is attributed mainly to the less number of double bonds, which are responsible for crosslinking with sulfur.[12–14] The nonlinear molecular structure in SBR is responsible for the lower percentage of crosslinking. In addition to this, the trace amount of resinous substances or fatty acids left over in emulsion polymerized SBR can also contribute to retarding the process of vulcanization. The retarding effect can be overcome by the use of binary accelerator systems.[12,15,16] Binary accelerator systems enhance the efficiency of sulfur intake during crosslinking, which leads to improvement of mechanical properties of the finished rubber articles.

Sombatsompop et al. reported[17] that overall mechanical properties of NR/SBR blend vulcanizates progressively increased up to NR: SBR blend

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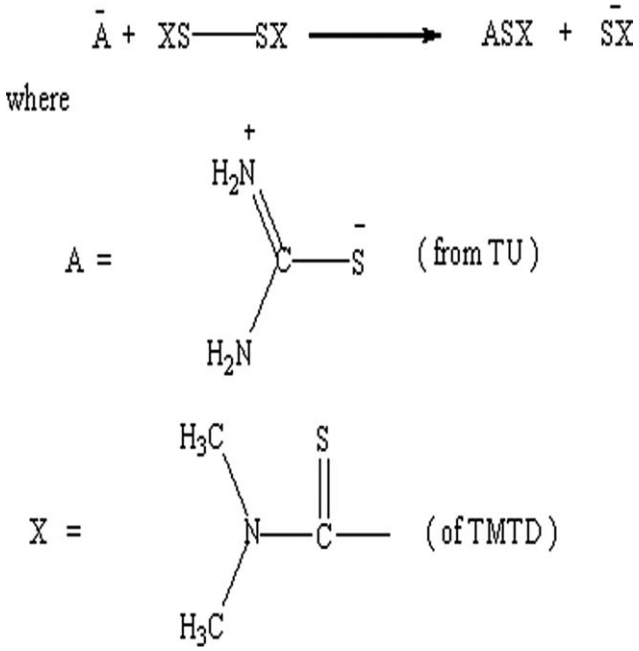


Scheme 1 General representation of synergism between a primary and secondary accelerator.

ratio 1 : 1(50 : 50 phr) and then decreased. According to him the decrease in mechanical properties of the blend with increase in the NR content is due to (i) NR has more reactive sites to form crosslinks during vulcanization than SBR (ii) molecular structure of NR is simpler and more flexible making the crosslinks in NR more feasible (iii) SBR has benzene rings imparting steric hindrance to the crosslinking reaction.

In this study we prepared gum and filled mixes of pure SBR and also mixes of a 50/50 NR-SBR blend using our BIAT-TMTD binary accelerator system and other conventional ingredients as shown in Table I.The study also includes determination of optimum cure time of each mix and curing of the rubber compounds at 150°C to investigate important mechanical properties, as further proof of nucleophilic mechanism already suggested. Optimum dosage of BIAT for vulcanization of pure SBR and NR-SBR blend has also been derived.

EXPERIMENTAL

Rubber and ingredients

Styrene-Butadiene rubber (of grade 1502) was supplied by Ceynar Rubber Chemicals, Kottayam. Rubber grade Zinc oxide, stearic acid, TMTD, Diethylene glycol (DEG), naphthenic oil, sulfur, and precipitated silica were used in this study.

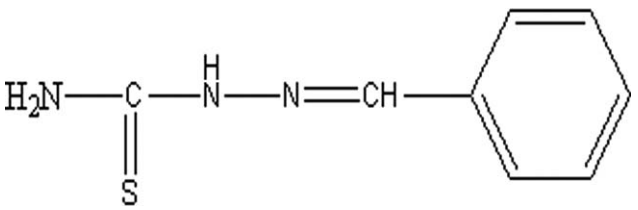
Formulations of pure SBR

Different SBR gum mixes were prepared varying the concentrations of BIAT ranging from 0.005 to 0.01*M* equivalents of BIAT, taken in gram along with 0.005 mol of the primary accelerator TMTD (Table I).The mix S_1 contains 0.005 mol (0.895 g) of BIAT and 0.005 mol (1. 2 g) of TMTD, S_2 contains 0.0075 mol of BIAT, and 0.005 mol of TMTD and S_3 contains 0.005 mol of TMTD and 0.01 mol of BIAT. The control mix S_R contains 0.01 mol of TMTD only as accelerator. Since curing was done at 150°C, 1.5 g sulfur was taken in all the mixes. Conventional quantities of zinc oxide and stearic acid were used.

The filled mixes were also prepared as per the Table I. The mix SF_1 contains 0.005 mol of TMTD, and 0.005 mol of BIAT as the binary accelerator system. The mix SF_2 contains 0.005 mol ofTMTD, and 0.0075 mol of BIAT. The mix SF_3 contains 0.005 mol of TMTD, and 0.01 mol of BIAT. 0.01 mol of TMTD as the single accelerator was taken in the reference mix SF_R. The amount of all other ingredients remains the same. All the mixes contain 30 g precipitated silica as the filler. All mixes were prepared in a two roll mixing mill (15.3 × 30.5 cm^2, Indian Expeller) at a friction ratio 1 : 1.14 as per ASTM designation D3182-89, first by masticating SBR for 7 min and then mixing other ingredients in the order as shown in Table I. Mixing was continued for a further 3 min and the batch was homogenized by passing it in single direction to ensure orientation of chains and to preserve mill direction before molding.

Preparation of the NR-SBR blend

NR and SBR were masticated separately in a laboratory size two- roll mixing mill (15.3 × 30.5 cm^2, Indian Expeller) at a friction ratio 1 : 1.14 as per ASTM designation D3182-89 for 10 min and then blended for 5 min, followed by mixing with various ingredients in the order as given in Table I. When silica filled mixes were prepared, the mixing process was continued for 15–20 min. After incorporating the ingredients, the batch was homogenized by passing it in single direction to ensure orientation of chains and to preserve mill direction before molding. The mixes SN_1 to SN_R represent gum mixes of SBR-NR blend and SN_1 to SN_3 contain varying concentration of BIAT ranging from 0.005 to 0.01 mol. All other ingredients were in the same quantity. The mixes SNF_1 to SNF_R represent filled mixes of the



Scheme 2 Structure of BIAT.

TABLE I
Formulations of Unblended and Blended SBR (Unfilled and Filled) Containing BIAT-TMTD Binary Accelerator System

Ingredients	Mixes															
Parts per hundred parts of rubber	S_1	S_2	S_3	S_R	SF_1	SF_2	SF_3	SF_R	SN_1	SN_2	SN_3	SN_R	SNF_1	SNF_2	SNF_3	SNF_R
SBR	100	100	100	100	100	100	100	100	50	50	50	50	50	50	50	50
NR	0	0	0	0	0	0	0	0	50	50	50	50	50	50	50	50
ZnO	5	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	2
TMTD	1.2	1.2	1.2	2.4	1.2	1.2	1.2	2.4	1.2	1.2	1.2	2.4	1.2	1.2	1.2	2.4
BIAT	0.895	1.3425	1.79	0	0.895	1.3425	1.79	0	0.895	1.3425	1.79	0	0.895	1.3425	1.79	0
Silica	0	0	0	0	30	30	30	30	0	0	0	0	30	30	30	30
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	1.5
DEG	0	0	0	0	2	2	2	2	0	0	0	0	2	2	2	2
Naphthenic oil	0	0	0	0	5	5	5	5	0	0	0	0	5	5	5	5

blend and SNF_1 to SNF_3 contain 0.005 to 0.01 mol of BIAT. Other ingredients were in the same quantity. The reference mix SNF_R contains 0.01 mol of TMTD only as the single accelerator.

Evaluation of the 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 Vario (German) at 150°C. The cure properties were obtained directly and the values are given in the Table II. Elastographic scorch time (TS_2) is the time required for two units to raise above the minimum torque (about 10% vulcanization). The compounds were then vulcanized up to the optimum cure time in an electrically heated laboratory type hydraulic press (Indian Expeller) 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 4411, using a crosshead speed of 500 mm min^{-1} as per ASTM D412-87, with dumbbell shaped specimen.

Hardness

Hardness (Shore A) was measured as per ASTM D2240-86 using a Zwick 3114 hardness tester on unstressed molded cylindrical samples (30 mm

TABLE II
Cure Properties of Unblended and Blended SBR (Unfilled and Filled) Containing BIAT-TMTD Binary Accelerator System

Mixes	T_{90} min	Elastographic scorch time (TS_2) min	Minimum torque, dNm	Maximum torque, dNm
Unblended and unfilled SBR				
S_1	6.5	1.8	3.43	19.91
S_2	5.8	1.9	3.37	18.79
S_3	3.7	1.5	2.75	15.80
S_R	13.6	2.5	1.26	11.66
Unblended and filled SBR				
SF_1	21	1.2	2.0	12.10
SF_2	20	1.1	2.58	15.13
SF_3	17	0.9	2.77	16.50
SF_R	22	1.8	2.23	14.92
Blended and unfilled SBR				
SN_1	15	1.2	0.52	12.2
SN_2	11	1.0	0.64	9.98
SN_3	12	0.8	0.46	9.57
SN_R	13	2.3	0.33	8.27
Blended and filled SBR				
SNF_1	18	1.3	2.91	14.25
SNF_2	16	0.8	2.26	13.64
SNF_3	17	0.7	2.84	13.96
SNF_R	21	1.7	1.98	11.08

diameter × 6 mm thick). For each vulcanized sample three measurements were taken and the result was reported as the average.

Compression set

Compression set was determined as per ASTM D395-89 (Method B) using the apparatus manufactured by Prolific Engineers India Ltd. The molded samples (1.25cm thick and 2.8 cm diameter) in duplicate compressed to constant deflection (25%) were kept for 22 h at 27°C. The samples were taken out and after keeping for 30 min, final thickness was measured. The compression set % was calculated as in eq. (1)

$$\text{Compression set } \% = (t_0 - t_1) \times 100/t_0 - t_s \quad (1)$$

where t_0 and t_1 are the initial and final thickness of the specimen and t_s is the thickness of the space bar used.

For each molded sample, average of the duplicate measurements was reported as the final result.

Abrasion loss

Abrasion loss was measured using DIN abrader (DIN 53516). Molded sample having a diameter of 6 ± 0.2 mm and a thickness of 6 mm was inserted into the sample holder so that 2 mm of the sample remained exposed and allowed to move across the surface of an abrasive sheet mounted on a revolving drum. Weight of the test specimen was noted before and after the test. The difference in weight was converted into volume loss by dividing the weight loss with density of the specimen. Three molded samples of each mix were used for the determination of abrasion loss and the final result was expressed as the average of these results.

Swelling value (Q)

Circular samples of ~ 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 again after removing the solvent on the surface of the samples using blotting paper. The solvent was removed in vacuum and the weight of the deswollen sample was again noted to calculate the swelling value[18] for each sample as an indicator of crosslink density[19] of the vulcanizates using the eq. (2)

$$\text{Swelling value} = (W_s - W_d) \times W_R/W_1 \times 100 \quad (2)$$

W_s is the weight of solvent swollen samples, W_d is the weight of deswollen samples, W_1 is the weight of preswollen samples and W_R is the weight of recipe (total weight of all components in the mix including rubber).

RESULTS AND DISCUSSION

Cure properties of unblended SBR mixes (unfilled and filled)

For unblended and unfilled SBR mixes (formulations S_1, S_2, S_3, and S_R), the T_{90} value was highest for the reference formulation (S_R) not containing BIAT (Table II) and decreased with increasing dosage of the novel accelerator BIAT. All the unfilled SBR mixes had better cure properties than the reference mix S_R containing only the single accelerator TMTD. The mix S_3 was found to possess minimum cure time and the value was about $1/4^{th}$ of that of the reference mix S_R. T_{90} values of all test mixes were found much less than that of S_R. The scorch safety values were also better. The delta torque values were also higher for the test mixes than the reference, which could indicate better cure state of the test mixes.

Silica-filled SBR mixes containing the binary accelerator system (formulations SF_1, SF_2, SF_3, and SF_R) showed better cure properties (Table II) than the reference mix SF_R containing TMTD alone. Cure time was found minimum for the filled mix SF_3 containing maximum dosage of BIAT (1.79 phr). Because of the adsorptive nature of silica, higher quantity of BIAT was required to cause a considerable reduction of cure time as found for SF_3. There was found five units decrease of cure time for SF_3 when compared with the reference SF_R. The mix SF_3 had better cure state also. Cure properties of the mixes were improved by the synergic action between BIAT and TMTD.

Mechanical properties of unblended SBR vulcanizates (unfilled and filled)

Tensile properties

All the unblended and unfilled SBR mixes had higher tensile strength values than the reference mix S_R (Table III). Tensile strength was maximum for S_2 which was found in agreement with its delta torque value, indicating higher crosslink density. The 100% modulus was also higher for all the test mixes compared with S_R and maximum for S_2. Elongation at break percent values of the test mixes were almost comparable. Thus tensile properties of the unfilled mixes containing BIAT-TMTD binary accelerator system were found improved by the synergism between the accelerators. Tensile strength first increased with increasing dosage of BIAT up to S_2 and then showed a decreasing trend (Fig. 1). This was due to the attaining of maximum crosslinks between rubber chains by the suggested synergism

TABLE III
Mechanical Properties of Unblended and Blended SBR (Unfilled and Filled) Containing BIAT-TMTD Binary Accelerator System

Mixes	Tensile strength MPa	100% Modulus MPa	Elongation at break %	Tear resistance N/mm	Hardness (Shore A)	Compression set %	Abrasion loss cm^3/ hr	Swelling value
Unblended and unfilled SBR								
S_1	1.653	1.405	135	14.259	47	3.32	0.393	3.269
S_2	1.796	1.445	138	13.953	47	3.20	0.387	3.241
S_3	1.790	1.443	139	13.697	48	4.13	0.395	3.253
S_R	1.570	1.377	121	8.385	45	4.67	0.454	3.270
Unblended and filled SBR								
SF_1	3.685	1.511	260	27.910	55	5.99	0.286	3.669
SF_2	4.778	1.724	272	34.289	55	5.29	0.244	3.626
SF_3	5.040	1.732	275	40.631	56	5.68	0.210	3.613
SF_R	3.614	1.448	268	21.516	55	5.90	0.299	3.676
Blended and unfilled SBR								
SN_1	2.336	0.939	236	17.752	40	2.88	0.169	3.905
SN_2	2.399	1.184	227	17.245	41	2.81	0.169	3.784
SN_3	2.359	1.063	213	17.330	42	2.43	0.167	3.882
SN_R	1.690	1.170	150	12.650	42	2.18	0.177	3.993
Blended and filled SBR								
SNF_1	6.973	1.429	406	32.25	51	6.56	0.257	3.998
SNF_2	7.105	1.551	419	34.87	52	6.57	0.233	3.923
SNF_3	6.818	1.540	402	34.05	52	6.36	0.236	4.013
SNF_R	5.253	1.524	296	29.76	52	6.54	0.267	4.034

between BIAT and TMTD. Optimum dispersion of BIAT was at 0.0075 mols (1.3425 phr) of BIAT.

The same observations were repeated for the filled samples also. The filled samples were found exhibiting higher tensile strength and 100% modulus than the reference formulation SF_R containing no BIAT. This was also in agreement with their higher delta torque values. SF_3 was found to possess highest tensile properties due to maximum crosslink density. Tensile properties of filled samples were much higher than that of the unfilled samples (Table III), showing the ability of silica to increase crosslink density further. In the case of filled samples also, tensile strength first increased with increasing dosage of BIAT and then decreased (Fig. 1), which also could be attributed to the optimum dispersion of BIAT.

Tear resistance

Tear resistance was much improved for all the unfilled mixes (Table III), showing more than 5 units increase, compared with S_R. Similar improvement was seen for the filled samples also.SF_3 exhibited maximum tear resistance value in accordance with tensile strength. The silica filled mixes exhibited more tear resistance than the gum counterparts, indicating efficiency of silica in increasing crosslink density further.

Abrasion loss

Abrasion loss values were lower for the test mixes (both unfilled and filled) when compared with the corresponding reference mixes, showing higher abrasion resistance due to more crosslinking. Among the unfilled and unblended SBR mixes, S_2 possessed minimum abrasion loss in accordance with its tensile and tear properties. SF_3 had minimum abrasion loss compared to other test mixes and the reference mix. This observation also could support efficiency of silica in the present BIAT-TMTD system. Silica was found effective in reducing abrasion loss.

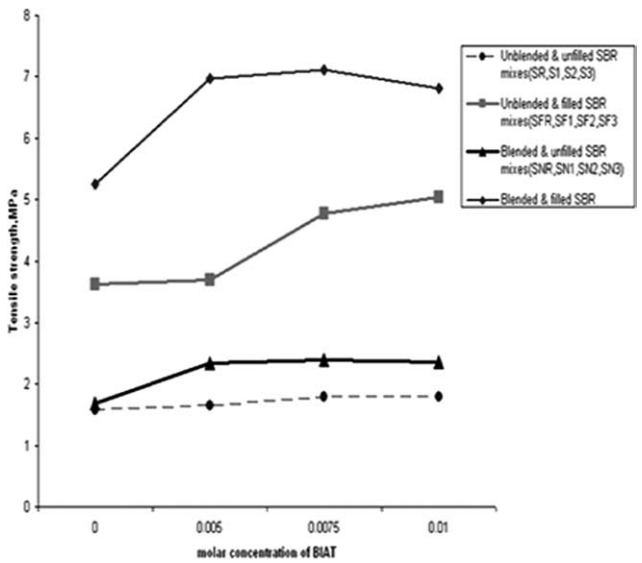


Figure 1 Variation of tensile strength with molar concentration of BIAT in unblended and blended SBR (unfilled and filled) systems.

Hardness and compression set

Hardness values were a little higher for the test mixes, for both unfilled and filled when compared with the corresponding reference mixes, indicating more crosslinks in them. As expected, the filled samples exhibited 7–8 units increase in hardness than the unfilled mixes.

The mixes showed lower compression set values than the reference. But the presence of filler could increase set values, due to the increase in stiffness.

Swelling values

Both the unfilled and filled SBR vulcanizates showed lower swelling values than the corresponding reference formulations. The reduction in swelling values could be attributed to the higher crosslink densities. The swelling values showed agreement with the mechanical properties studied. Among the unfilled and unblended SBR mixes, S_2 possessed minimum swelling value in accordance with its high tensile and tear properties. Similarly swelling value was minimum for SF_3 due to higher crosslink density.

Thus the improved cure and mechanical properties of the test samples indicated that efficient crosslinking occurred in unblended SBR mixes when BIAT-TMTD binary accelerator was used in sulfur vulcanization of SBR. This was further proof of nucleophilic mechanism of vulcanization reaction. Because of the faster formation of disulfide, trisulfide, and polysulfide, faster curing of the mixes occurred. There was enhancement in mechanical properties owing to the increase in the number of various sulfidic linkages including polysulfidic linkages between rubber chains. Thus synergism between BIAT and TMTD could improve mechanical properties of unfilled and filled SBR mixes by increasing the number of sulfidic crosslinks. The incorporated silica particles could form additional crosslinks causing further enhancement in mechanical properties when compared with the unfilled counterparts.

Though cure time was a little higher for the mix S_2 than S_3, its delta torque value and scorch safety were higher. Also, it possessed superior mechanical properties compared with other mixes. The excessive use of BIAT could be avoided if S_2 was taken as the ideal formulation. Similarly the dosage corresponding to SF_3 could be taken as ideal.

Cure properties of blended SBR (unfilled and filled)

In the case of 50/50 NR-SBR blend also, the above observations were repeated. Cure time was maximum for the blended reference formulation SN_R not containing BIAT and it decreased with increasing dosage of BIAT up to SN_2 corresponding to 1.3425 phr of BIAT (Table II). There was found 2 units reduction of cure time for SN_2 when compared with the unfilled reference mix SN_R. In the case of filled samples also, cure time first decreased with increase in dosage of BIAT and then increased. The mix SNF_2 exhibited 5 units decrease in cure time with respect to the filled reference mix SNF_R. The results could indicate that optimum dispersion of BIAT for NR-SBR blend was at 1.3425 phr. The test mixes of the blend (both unfilled and filled) showed higher delta torque values than their reference mixes, indicating higher state of cure. The mixes had comparable scorch safety.

Mechanical properties of blended SBR vulcanizates (unfilled and filled)

Tensile properties

Unfilled mixes of the blend exhibited higher tensile strength than the reference mix and the value was higher for SN_2, indicating higher crosslink density.!00% modulus value was also found higher for SN_2 (Table III). The elongation at break percent values were also better for the test mixes. Because of lack of sufficient dosage of BIAT, number of crosslinks was less in SN_1 with consequent lowering of tensile strength and modulus compared with SN_2 and SN_3. Tensile properties first showed an increase up to SN_2 and then decreased due to the optimum dispersion of BIAT at 1.3425 phr (Fig. 1).

In the case of filled samples, tensile strength was about 1 unit higher than the reference mix. There was an increase in tensile strength with increase in dosage of BIAT and then showed a decrease as for the gum mixes, indicating maximum crosslink density for SNF_2 due to optimum dosage of BIAT in it. The same trend was observed for 100% modulus values. The test mixes showed comparable elongation at break percent values.

Tear resistance

The unfilled mixes exhibited 5 units increase in tear resistance value with respect to the reference mix (Table III).This could also be due to their higher crosslink densities. The filled mixes also showed the same trend and the values indicated two-fold increase compared to the unfilled mixes due to the additional increase in crosslink densities by the filler action. SNF_2 exhibited higher tear resistance value due to the optimum dosage of BIAT.

Abrasion loss

Abrasion loss values of the blended mixes, both unfilled and filled (Table III), were lower than that of the reference mixes, indicating higher crosslink

densities. SNF_2 had minimum abrasion loss and hence maximum abrasion resistance.

Hardness and compression set

All the gum mixes showed comparable hardness (Table III). But there was found 10 units increase in hardness for the filled mixes compared to the unfilled mixes due to additional enhancement in crosslink density by filler action. Compression set percent values were higher for the filled mixes due to the increase in stiffness of rubber chains by filler incorporation.

Swelling values

Unfilled mixes of the blend exhibited lower swelling values than the corresponding reference mix SN_R (Table III). Swelling values were found to decrease from SN_1 to SN_2 and then found increasing, indicating that crosslink density follows the opposite trend. Swelling value was least for SN_2 showing maximum crosslink density for it. Filled mixes of the blend also exhibited the same trend. SNF_2 was found showing minimum swelling value due to higher crosslink density. The swelling values of both unfilled and filled mixes of NR-SBR blend were in agreement with their mechanical properties studied.

Analyzing the various properties studied for the NR-SBR blend system, the mixes SN_2 and SNF_2 could be derived as the ideal mixes of unfilled and filled systems respectively. The results could also support the finding that efficient crosslinking occurred in SBR-NR blend, both unfilled and filled samples, in presence of the new binary accelerator system. In this case also, synergism between BIAT and TMTD could lead to faster and easier formation of sulfides causing an increase in the number of sulfidic crosslinks between rubber chains as for the unblended SBR system. The incorporated silica particles could lead to the formation of additional crosslinks and thus caused additional enhancement in mechanical properties when compared with the unfilled counterparts.

CONCLUSIONS

N-Benzylimine aminothioformamide (BIAT) can be used as an effective secondary accelerator along with TMTD in sulfur vulcanization of unfilled and filled SBR systems to improve cure and mechanical properties when compared with the use of TMTD alone. Suitable blend can be prepared from SBR and NR and the resulting blend can be efficiently cured with BIAT-TMTD binary accelerator system with improvement in mechanical properties. Unlike in unfilled SBR mixes, high dosage of BIAT is necessary for effective action in improving cure and mechanical properties of filled SBR mixes. This may be due to additional consumption of accelerator by the highly adsorptive silica filler. Improvement in cure and mechanical properties of unfilled and filled unblended SBR mixes and the SBR-NR blend is further proof of the nucleophilic reaction mechanism of vulcanization reaction. The synergic action between BIAT and TMTD leads to faster and easier formation of di, tri and other polysulfides, thereby increasing the number of sulfidic crosslinks between rubber chains. This has enhanced mechanical properties of unblended SBR and a 50/50 blend of SBR and NR.

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