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Study of Governing Mechanisms on Failure Properties of Filled Rubber Compound in Different Sulfur Crosslink Densities and Types

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The effect of crosslink density changes on failure properties of SBR and NR/BR based compounds, tear behaviour, crack growth, tensile and abrasion, are investigated. The governing mechanisms on each behaviour are discussed. It is concluded that in lower crosslink densities, the presence of stronger bonds has a dominant role on failure behaviour and an increase of crosslinking specially within monosulfidic bonds is useful, so efficient curing system delivers better properties than conventional ones. However at moderate and high crosslinks, the failure properties diminish significantly because of governing of chain movement ability mechanism. In this situation no significant change has been observed between efficient and conventional curing systems. At very high corsslinks, where chain movement ability mechanism is governed, the longer polysulfidic crosslinks with dissipating capability of break-down and reforming deliver better dematia crack growth. The same behaviour observed in NR based compounds but the differences were diminished with induced-crystallinity capability of NR rubber and super abrasion behaviour of BR rubber.

Key Words: Crosslink density, Efficient curing, Conventional curing, tear, Crack growth.

INTRODUCTION

Two common types of sulfur cures for diene elastomers are so-called conventional and efficient systems. Generally, high accelerator sulfur ratio and longer cure time increase the number of monosulfidic linkages at the expense of polysulfidic ones. Vulcanizates containing predominately monosulfidic crosslinks have better heat stability, set resistance and reversion resistance than those with polysulfidic links. This is attributed to a greater stability of C-S bonds compared to S-S bonds. However, because of the complexity of governing mechanisms, failure properties such as tear, crack growth and abrasion deliver complicated behaviour[1-8].

Indeed, several events occurring at the tip of a crack that are quite important in controlling it[9,10]. If an elastomeric network is capable of dissipating input energy into heat through irreversible molecular motions, less elastic energy will be available

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to break network bonds apart and fracture energy will increase. Principally, if upon deformation, stress concentrations within a network were absent (or somewhat eliminated), all load bearing chains would carry the same force. Fracture would occur by a catastrophic dissociation of backbone bonds at a very high, critical stress.

It is widely thought that the polysulfidic links results in higher tear strength, tensile strength and fatigue cracking resistance compared to compositions with dominant amounts of monosulfidic links, when vulcanizates are compared at the same crosslink density. This is thought to be due to the ability of S-S bonds in polysulfidic linkages to break reversibly, thereby relieving locally high stresses that could initiate and prograte failure[1,11,12].

However the contrary results[13-15] show that this mechanism is one of the several mechanism governing on failure behaviour. Also special mechanism introduced by nature of elastomer could affect the results significantly.

In this study the failure behaviour of rubber compounds has been investigated in different crosslink types and densities and different elastomer types for two different formulations. The governing mechanisms for each behaviour outlined.

EXPERIMENTAL

Natural rubber (SMR-20), SBR-1502 and BR *cis* products of Marub, Lanxess and Komho Co., were used as base polymer in this study. Carbon black N330 and N234 were obtained from Iran Carbon Co. and Korea DC Chemical Co., aromatic oil was used as a processing aid and zinc oxide, stearic acid, free sulphur and accelerator (OBTS and TMTD) were also included as curing agents. They were obtained from Behran oil Co., Pars oxide Co. Acid chem. Co., Iran Tesdak Co., Nocil Co. and Bayer Co., respectively. PVI was used as a retarder and was prepared of Nocil Co.

Compound formulations: Two series of formulation were used in this study. The first series were prepared based on master of radial tread formulation. All compositions contained (in phr): SBR 1712, 100; carbon black N234, 68; ZnO, 4.7; stearic acid, 1.47; coresin, 1.19; wax, 1.21; IPPD, 1.2; PVI, 0.2; other components (sulphur and accelerator) are given in Table-1.

Second series were prepared based on the master of bias truck tread formulation. SMR-20, 75; BR, 25; carbon black N330, 45; ZnO, 4; stearic acid, 3; anox-HB, 1; wax, 2; IPPD, 1.5; other components (sulphur and accelerator) are given in Table-2. The physico-mechanical properties of NR/BR and SBR compounds are given in Table-3.

The experimental design carried out with Minitab software for each series. The sulfur and accelerator levels in two series cover broad level of crosslink densities (from very low to very high crosslink densities)

Compound preparation: Master compound series were similar for all formulations in each series. Master compounds were prepared in a Banbury internal mixer having a total volume of 220 L. A filled factor of 0.7 was used and the mixing speed

TABLE-1
EFFECT OF DIFFERENT SULFUR AND ACCELERATOR LEVELS ON CURING BEHAVIOUR OF NR/BR BASED COMPOUNDS

	Sulphur (phr)	OBTS (phr)	MH-ML (Lb-in)	Scorch time at 185 (°C)	Curing rate (Lb-in/min)	T.P. 90 185 (°C)	Reversion (%)
B1	0.5	0.5	9.55	93	4.8	208	0.70
B2	1.0	0.5	14.31	72	8.3	173	3.90
B3	1.5	0.5	18.17	62	11.7	158	7.60
B4	2.0	0.5	21.51	57	15.0	149	10.80
B5	0.5	1.0	15.08	78	10.3	168	2.25
B6	1.0	1.0	21.09	64	16.9	141	5.50
B7	1.5	1.0	24.34	57	20.7	133	8.95
B8	2.0	1.0	30.91	48	29.1	122	11.00
B9	0.5	1.5	21.13	72	15.1	162	1.80
B10	1.0	1.5	27.12	58	25.7	129	3.50
B11	1.5	1.5	31.85	51	33.9	177	6.70
B12	2.0	1.5	35.08	49	39.9	112	9.30
B13	0.5	2.0	24.90	75	18.1	166	1.40
B14	1.0	2.0	30.37	64	29.7	137	2.80
B15	1.5	2.0	34.28	55	39.3	119	4.80
B16	2.0	2.0	37.96	52	47.6	110	7.60

TABLE-2
EFFECT OF DIFFERENT SULFUR AND ACCELERATOR LEVELS ON CURING BEHAVIOUR OF SBR BASED COMPOUNDS

	Sulphur (phr)	CBS (phr)	MH-ML (Lb-in)	Scorch time at 185 (°C)	Cure rate (Lb-in/min)	T.P. 90 185 (°C)
R1	0.5	0.5	5.08	161	2.0	265
R2	1.0	0.5	10.75	119	4.5	253
R3	1.5	0.5	15.70	103	6.9	248
R4	2.0	0.5	19.82	91	9.0	244
R5	0.5	1.0	9.14	117	5.8	216
R6	1.0	1.0	15.55	97	11.9	196
R7	1.5	1.0	28.24	84	16.8	185
R8	2.0	1.0	24.90	78	19.8	184
R9	0.5	1.5	13.00	110	12.0	180
R10	1.0	1.5	18.14	95	22.0	165
R11	1.5	1.5	23.55	82	30.2	153
R12	2.0	1.5	27.37	78	34.8	151
R13	0.5	2.0	13.49	105	16.1	166
R14	1.0	2.0	20.58	90	31.9	146
R15	1.5	2.0	25.40	84	41.2	141
R16	2.0	2.0	28.87	79	46.9	136

was 40 rpm. The first rubber was masticated in the Banbury for 1 min before adding the carbon black and mixing for another minute; then, ingredients, except for the curatives were added and mixing continued for another 5 min before dumping.

TABLE-3
PHYSICO-MECHANICAL PROPERTIES OF NR/BR AND SBR COMPOUNDS IN DIFFERENT SULFUR AND ACCELERATOR SYSTEMS

Codes f NR/BR based comp.	OBTS	S	S/OBTS	MH-ML	Modulus 200 (%)	Tear resistance	CG Rate	Tensile strength	Abrasion	Elongation at break	Scorch time at 185 °C	Optimum curing time at 185 °C	Crosslink density	Crosslink type
B5	1.0	0.5	0.50	16.31	5.4	48.1	0.37	24.05	92.7	564.85	76	170.0	Low	E
B2	0.5	1.0	2.00	16.33	5.6	48.1	0.39	23.60	93.9	550.00	69	171.0		C
B9	1.5	0.5	0.33	21.52	6.6	42.5	0.44	24.20	77.3	500.75	72	157.5	Medium	E
B6	1.0	1.0	1.00	21.98	7.0	43.0	0.48	24.90	80.3	488.90	65	144.5		SE
B13	2.0	0.5	0.30	24.74	7.0	32.7	0.46	24.75	69.7	490.99	76	171.0	Medium	E
B10	1.5	1.0	0.67	27.59	8.6	33.9	0.95	24.98	80.3	435.09	59	132.0		E
B7	1.0	1.5	1.50	25.59	8.6	32.2	1.04	24.65	75.7	431.61	57	133.5		C
B14	2.0	1.0	0.50	29.35	9.0	37.8	1.22	23.03	84.8	392.13	67	142.0	High	E
B11	1.5	1.5	1.00	31.98	10.3	34.6	1.52	23.35	86.4	368.69	52	119.5		SE
B8	1.0	2.0	2.00	31.09	10.1	35.2	1.52	22.10	84.8	353.06	51	125.0		C
B15	2.0	1.5	0.75	34.16	11.4	33.8	1.95	21.80	92.4	325.75	56	120.0	Very high	E
B12	1.5	2.0	1.33	34.98	11.7	33.2	1.86	21.80	89.4	319.16	50	115.0		C
R9	1.5	0.5	0.3	11.6	4.40	39.0	1.1	16.4	103.8	572	110	180	Low	E
R5	1.0	0.5	0.5	9.1	3.57	38.5	1.0	13.2	121.5	625	117	216		E
R2	0.5	1.0	2.0	10.8	4.53	32.9	1.4	15.8	141.2	570	119	253		C
R6	1.0	1.0	1.0	15.6	5.90	33.3	2.2	18.1	122.9	491	97	196	Medium	SE
R3	0.5	1.5	3.0	15.7	6.27	32.5	1.9	18.3	116.5	476	103	248		C
R14	2.0	1.0	0.5	20.6	7.80	27.0	4.0	18.0	112.3	379	90	146	Medium	E
R7	1.0	1.5	1.5	20.7	8.57	27.6	4.8	17.6	112.2	351	84	185		C
R4	0.5	2.0	4.0	19.8	8.00	30.4	4.0	18.0	121.5	383	91	244		C
R15	2.0	1.5	0.8	25.4	10.60	21.2	5.6	16.8	122.9	292	84	141	High	E
R8	1.0	2.0	2.0	24.9	10.70	24.8	3.8	18.2	127.1	308	78	184		C
R16	2.0	2.0	1.0	28.9	12.93	16.7	5.8	16.8	137.7	250	79	136	Very high	SE
R12	1.5	2.0	1.3	27.4	12.40	16.0	4.7	15.9	133.5	245	78	151		C

Master compounds were cooled to reach room temperature, within 8 h, before mixing with curatives. Curatives were mixed into master compounds on a two-roll mill. In this study, The curatives were slowly added to two-roll mill on master compound and the samples were stored at room temperature up to 24 h before vulcanization. Then sample sheets were cut and cured by compression molding according to optimum curing time (TP90) and 145 °C.

Testing: Compounds were characterized for vulcanization properties in a rheometer (ODR 2000E). Stress strain and tear properties of the vulcanizates were measured by using a dinamometer in accordance to ASTM D 624. Abrasion was measured through using Zwick testing machine based on ISO 4649. Resilience was measured by using Dunlop Tripsometer in accordance to ASTM D 2240. Crack growth was determined by using Demattia crack growth tester accordance to ASTM D 813.

RESULTS AND DISCUSSION

Crosslink density characteristics: As shown in Anova interaction plots, Figs. 1 and 2 there is a direct relationship between delta torque and sulphur content in different accelerator levels and accelerator contents in different sulfur levels in both SBR and NR/BR based compounds. Every change in sulfur and accelerator content affects crosslink density and reflected in delta torque. In this study, we discussed three regimes according to crosslink density *i.e.*, (i) Low crosslinks, 0.5 phr of sulfur or accelerator), (ii) moderate crosslinks (1.0 and 1.5 phr of sulphur or accelerator) and (iii) high crosslinks (2 phr of sulphur or accelerator).

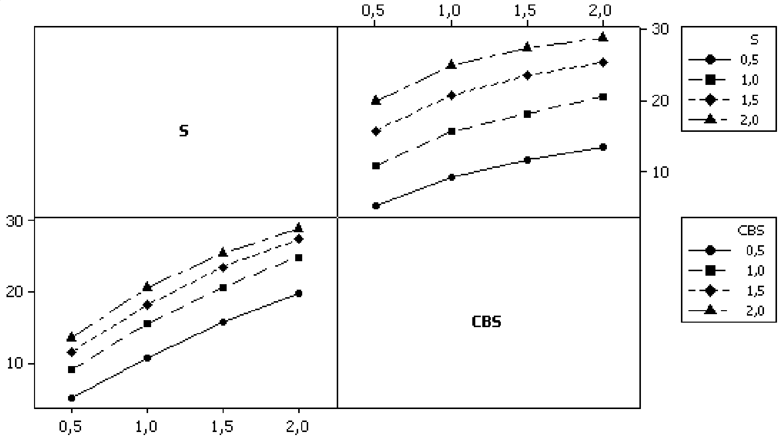

Fig. 1. Interaction plot for delta torque based on SBR compounds

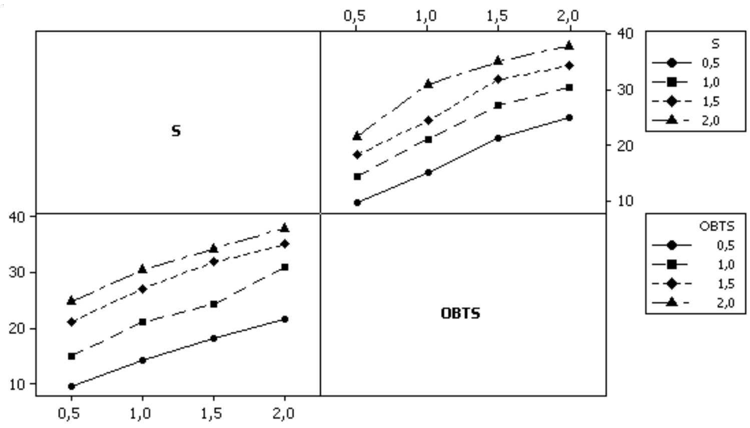

Fig. 2. Interaction plot for delta torque based on NR/BR compounds

Modulus: The Anova interaction plots for modulus 200 % (Figs. 3 and 4) show the same behaviour both in SBR and NR/BR based compounds, modulus increases as sulfur or accelerator increases.

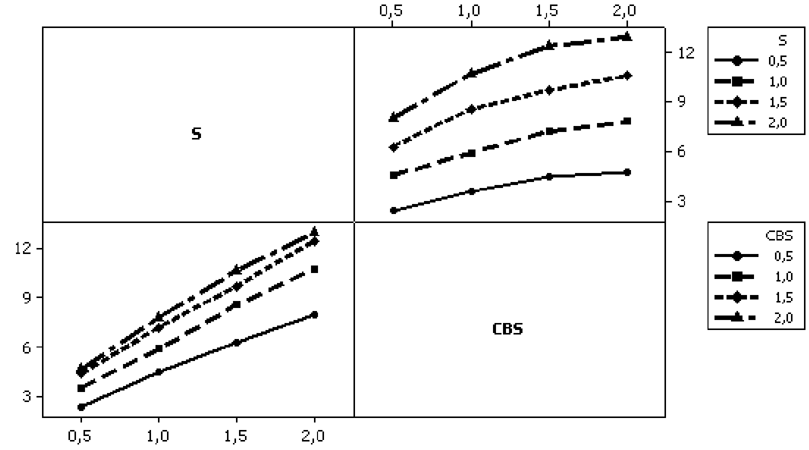

Fig. 3. Interaction plot for modulus 200 % based on SBR compounds

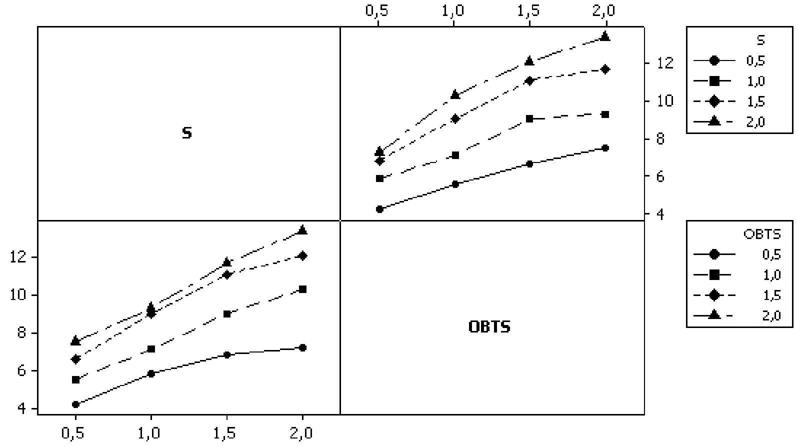

Fig. 4. Interaction plot for modulus 200 % based on NR/BR compounds

Reversion: A Monsanto Rheometer, model ODR 2000 has been used to test the rubber compound since the rheometer torque was found to be suitable as an indicator of reversion behaviour. Percentage reversion (R) is defined as: $R = (T_{max} - T_t)100/(T_{max} - T_{min})$, where T_{max} = maximum torque, T_t = torque at min and T_{min} = minimum torque on the rheometer.

Fig. 5 shows that low sulphur/accelerator ratio improves the resistance to reversion in NR/BR based compound, that indicating the formation of more stable crosslink *i.e.*, less polysulfidic type. Desulfuration process decreases due to less polysulfidic crosslink and leads to reduction of reversion.Two types of crosslinks presented in rubber domain *i.e.*, rubber-rubber crosslinks and filler -rubber crosslinks or attachments. Increase of crosslink density enhances rubber-rubber and rubber-filler interactions, hence reflected in modulus.

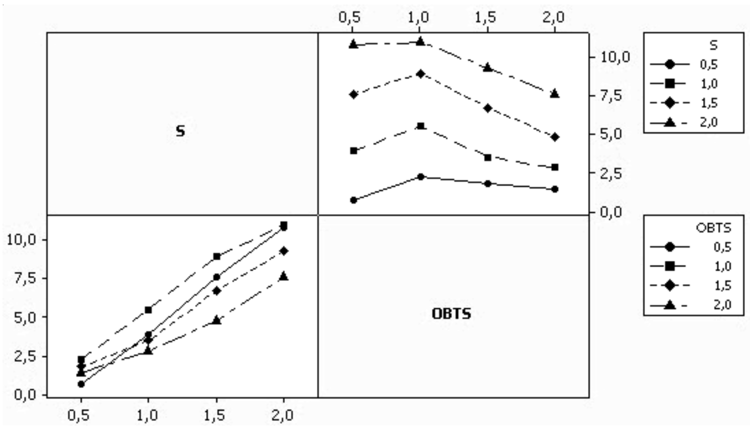

Fig. 5. Interaction plot for reversion based on NR/BR compounds

Failure properties: As shown in Figs. 6 and 7, the crack growth rate increases as sulfur or accelerator increases, there are two exceptions, in very high amounts of crosslink density and in low amount of sulfur (0.5 phr), increasing accelerator content has no significant effect on crack growth rate. The overall crack growth behaviour is similar for both SBR and NR/BR based compounds.

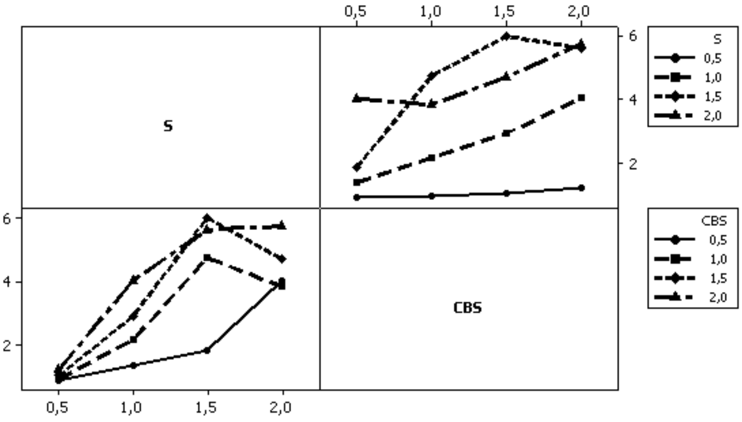

Fig. 6. Interaction plot for crack growth rate based on SBR compounds

Tear resistance: The anova interaction plots for tear resistance have been presented in Figs. 8 and 9 for SBR and NR/BR based compounds, respectively. Tear resistance of SBR based compounds decreases sharply in moderate and high crosslink domains with increasing sulphur or accelerator (increasing of crosslink density), but it has a reverse behaviour in low crosslinks, especially with increasing accelerator in 0.5 phr sulphur.

There is the same tear behaviour in NR/BR based compound, *i.e.*, decreasing tear resistance with increasing crosslink density, but in comparison to SBR based compounds even in low crosslinks the tear resistance decreases, also the tear curves in NR/BR compounds are not as smooth as SBR based compounds.

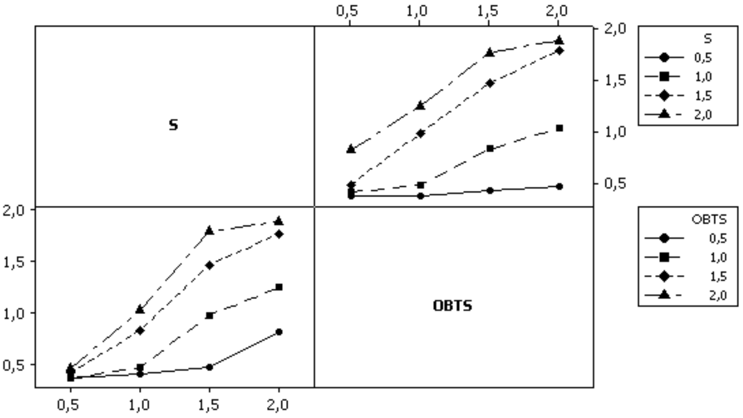

Fig. 7. Interaction plot for crack growth rate based on NR/BR compounds

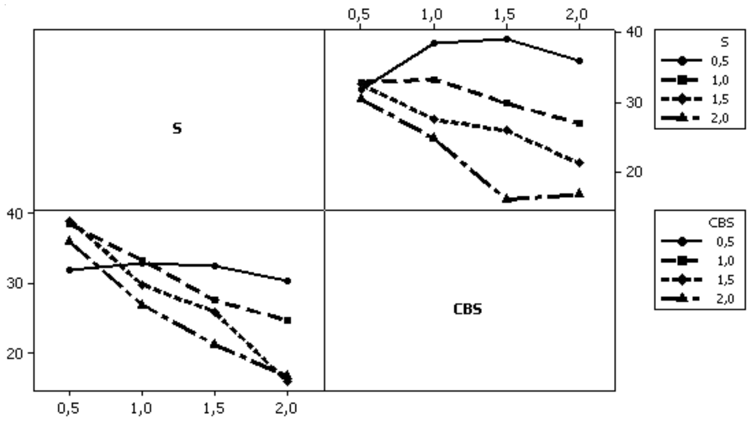

Fig. 8. Interaction plot for tear resistance based on SBR compounds

Tensile behaviour: Fig. 10 shows that tensile behaviour are not affected by crosslink densities, only in low crosslink levels the increasing of sulphur or accelerator could improve tensile. But from Fig. 11 (anova interaction plot for tensile behaviour of NR/BR based compound) it can be concluded that the crosslink density has significant and complicated effect on tensile and in general increasing crosslink density has a negative effect on tensile.

Abrasion: According to the anova plots, Figs. 12 and 13, the abrasion behaviour of SBR and NR/BR based compounds in different sulphur and accelerator contents obey the following behaviour. In low crosslink densities (0.5 phr sulphur or 0.5 phr accelerator levels) the abrasion decreases as sulfur or accelerator increases and with increasing crosslink levels the slope of curves decreases so that in higher crosslinks levels, if becomes positive (1.5 and 2.0 phr) and completely inverse behaviour is observed. This behaviour could be observed in both SBR and NR/BR based compounds.

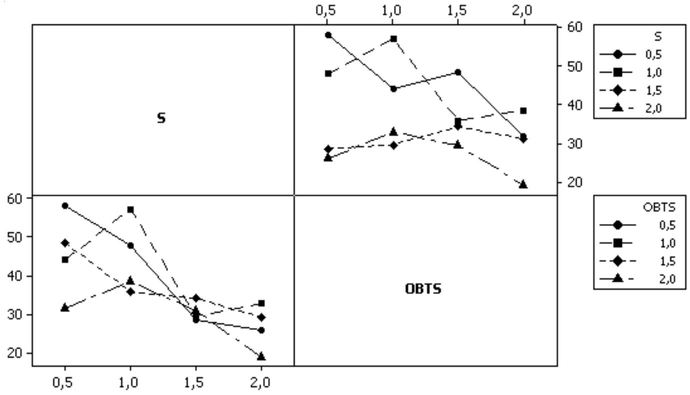

Fig. 9. Interaction plot for tear resistance based on NR/BR compounds

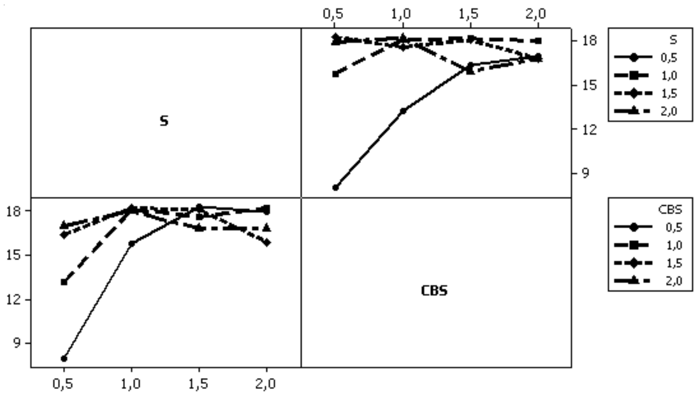

Fig. 10. Interaction plot for tensile strength based on SBR compounds

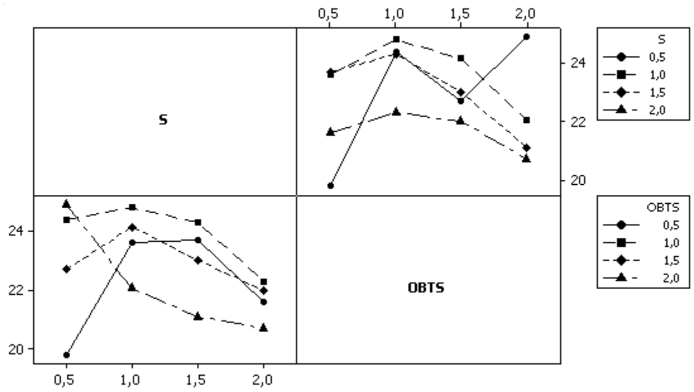

Fig. 11. Interaction plot for tensile strength based on NR/BR compounds

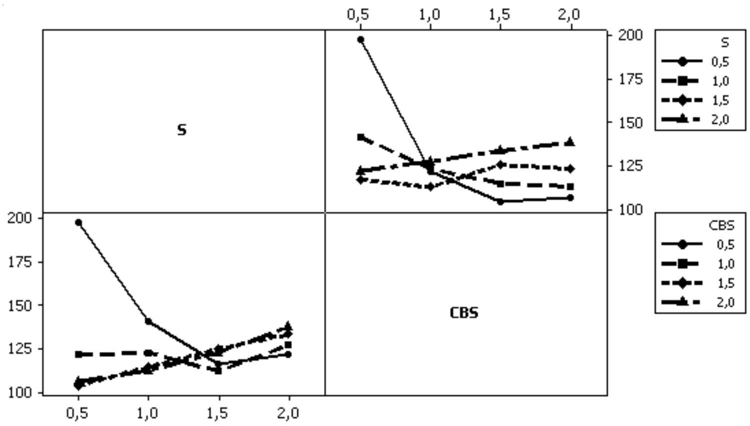

Fig. 12. Interaction plot for abrasion based on SBR compounds

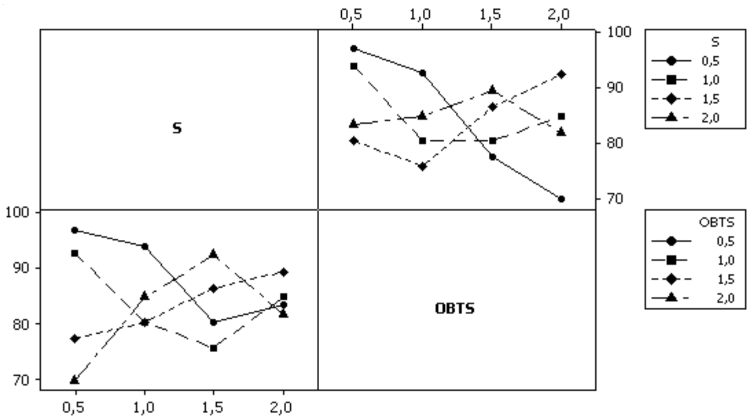

Fig. 13. Interaction plot for abrasion based on NR/BR compounds

The overall overview of crosslink densities on tear, crack growth, tensile and abrasion, presented in Figs. 14 and 15.

In order to cause a crack to grow, sufficient energy must be supplied to the crack front to meet the requirements of fracture[9,10]. In general, the supply energy can come from two sources; (1) stored strain energy released from the specimen as the crack grows and (2) that supplied directly by the testing machine. In turn, the energy that is supplied can be expanded in two main ways: (1) by breaking of bonds that were presented (before crack progration across the fracture plane), (2) *via* hysteretic losses due to irreversible deformation processes.

So, there are two counterpart mechanisms, reinforcement and chain movement. The decreasing dematia crack growth and tear resistance with increasing of crosslink density both in SBR and NR/BR based compound, clearly show that strong interactions, *via* increasing crosslink density, has a negative effect on tearing and dematia crack growth, two factors could contribute, here; increase of elastic energy introduced on

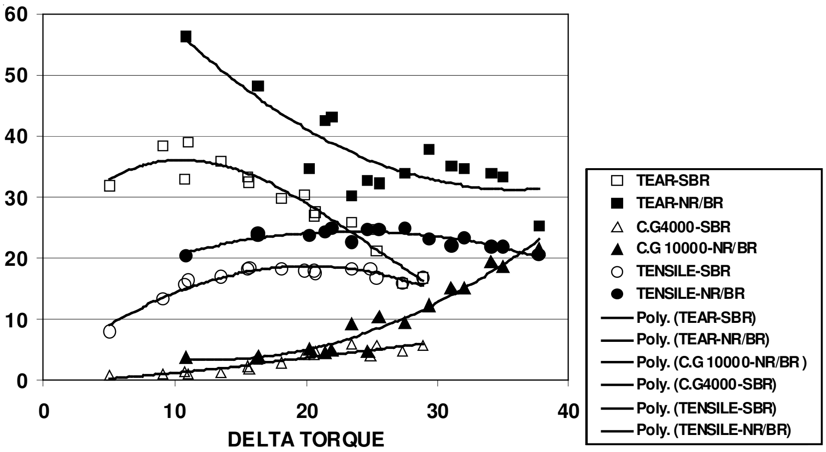

Fig. 14. Total torque-failure curves in one diagram

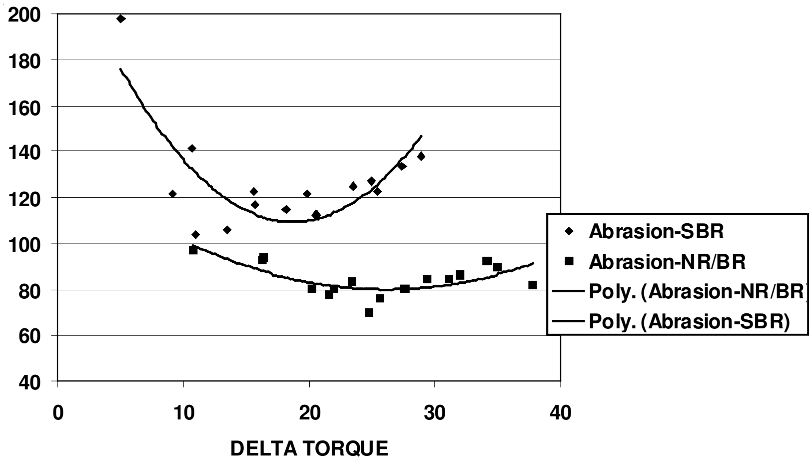

Fig. 15. Total torque-abrasion curves in one diagram

crack tip when crosslink density increases (increase of input energy on crack tip). Lower hysteresis chain deformations because of more restriction of chains movement by increasing crosslink density[16].

However as shown in Anova interaction plot (Figs. 6 and 7) in both SBR and NR/BR based compound (0.5 phr), increasing of sulphur (hence crosslink density) has no negative effect on crack growth, at very low sulfur content. Introduction of covalent sulphuric bonds is still important, here, to keep crack growth.

This is true for tear behaviour of SBR based compounds too, in low crosslinks, increasing of interactions *via* crosslinks has a positive effect on tearing. However this exception couldn't be observed for NR/BR based compound and in all crosslinks the tear resistant decreased. It seems that the contribution of induced-crystallinity in NR chains has significant role beside dissipation mechanisms, so that increasing of crosslink densities interferes the induced-crystallinity and it has negative effect on tear behaviour of NR/BR based compounds in all crosslink densities[2,3].

The competitive behaviour of two main mechanisms, reinforcement and chain movement are also observed in tensile and abrasion behaviour of SBR and NR/BR based compounds in different crosslink densities. Because reinforcement is a govern mechanism at low crosslinks, the tensile approaches to the maximum and abrasion approaches to minimum. Because of restriction of chain movement at higher crosslinks, these properties have inverse effect. However, because of presence of BR rubber with superior abrasion behaviour, abrasion behaviour experiment lesser change in NR/BR based compound compare to SBR based compound.

Effect of type of sulphur crosslinks: An overview of anova and main effect plots show that the right and left curves obey the same behaviour in almost all cases. So it is observed to some extent that the ratio of sulphur/accelerator has no significant effect. However for better comparison of effect of sulphur/accelerator ratio the following procedure has been carried out: first of all, the points that have the same crosslink density are specified by Figs. 1 and 2. Then the physico-mechanical properties for these points are obtained from Figs. 1-13. The results are summarized in Table-3. The table is divided into five section according to the crosslink density ranging from low to very high both for NR/BR and SBR based compounds. In each sections the same crosslink density points compared with each other. These points have different ratios of sulphur/accelerator as called efficient (ratio lower of 1), semi efficient(ratio equal to 1) and conventional (ratio which are higher of 1).

Because of the same crosslink density, the points in each section would have the same modulus 200 %, which means the same input elastic energy is introduced when deformation or extension occurred. The comparison of points in each section show that in SBR based compounds at low crosslink density the efficient sulphur systems have better abrasion, tear and crack growth behaviour than conventional sulfur curing systems. The reason contributed to stronger monosulfidic (S-S) bonds presented in efficient systems, than polysulfidic (S-Sn-S) bonds in conventional systems. As mentioned above at low crosslink densities the stronger bonds has significant role. As crosslink density increased and reach to high levels the differences between properties diminish between points so that in medium to high crosslinks the relatively no change has been observed between conventional and effective properties. At high and very high crosslink density the reverse behaviour observed especially in crack growth, here, the chain movement capability is important and S-Sn-S bonds deliver better flexibility to chains[16].

Also the dissipation process of breakdown and reformation of polysulfidic S-Sn-S bonds in repetition processes like dematia crack growth could be responsible of better crack growth of conventional systems in very high crosslink densities.

In NR/BR based compounds the effect of crosslink type is relatively lesser than SBR based compound specially in tear behaviour where induced-crystallinity in NR chains has dominant role. The crack growth behaviour has the same behaviour of SBR but lesser differences is observed between results in each section of crosslinks.

Because of presence of BR with superior abrasion behaviour, the effect of crosslink type on abrasion of NR/BR based compound is low. However a little improvement has been observed in efficient NR/BR based compounds which shows the importance of S-S strong bonds.

Conclusion

The SBR and NR/BR based compounds used in this study are the tread formulation with moderate to some high crosslink density. As shown in this study the differences between efficient and conventional sulphur curing systems is significant in low and very high crosslinks. It is possible to move from conventional to efficient systems in moderate crosslinks. This would have some advantages, elimination of reversion in NR/BR based compounds and decreasing curing time in SBR based compounds. As shown in Table-3 the efficient systems in moderate crosslinks deliver lower optimum curing time at the same scorch time for SBR based compounds.

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