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Formulation for Passenger Tread Tire Compound Based on Styrene Butadiene Rubber/*cis*-Butadiene Rubber/Natural Rubber Blend and Semi-Dispersible Silica/Carbon Black Filler System

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Effects of silica/silane/carbon black reinforcement system in styrene butadiene rubber and its blend with *cis*-butadiene rubber and natural rubber were investigated with the help of experimental design. An optimized formulation with outstanding failure properties were calculated based on styrene butadiene rubber/natural rubber/*cis*-butadiene rubber blend in presence of semi-dispersible silica. The governing mechanisms on failure properties, tear resistance, crack growth and abrasion were also studied in details.

Key Words: Semi-dispersible precipitated silica, Dissipating mechanisms, Chain blunting, Tear resistance, Dimattia crack growth, Abrasion.

INTRODUCTION

Besides carbon black, silica is the other important and economical reinforcing filler which has been used in the rubber industry[1-4]. These white reinforcement fillers are prepared by precipitation from water soluble silicates and also chemical reaction between a sodium silicate solution and sulphuric acid and they possess siloxane and silanols surface chemical groups. These functional groups are so polar and incompatible with non-polar rubber domains such as natural rubber, *cis*-butadiene rubber or styrene butadiene rubber[5,6]. Therefore, silica compared with carbon black having similar specific surface area, provides lower degree of reinforcement[5,6].

The silica surface modifications using bifunctional organosilanes, have some great advantages which have lead to market competition, taking precedence over carbon black, particularly in tread passenger tire compound[7,8].

This is due to better balances in magic triangle properties of tread (rolling resistance, traction and wear) in the presence of silica/silane compared to carbon black. This superiority is owing to the different filler-filler and polymer-filler interactions[9]. A well dispersed surface-modified silica particles decreases filler-filler interactions and increases the filler-polymer interactions compared with carbon black. Hence, the loss factor (tangent delta) increases in low temperature and decreases in high temperature. Furthermore, the ultrafine silica particles which are well dispersed in rubber domain, would indicate better abrasion resistance[10,11].

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There are many publications in the field of silica/silane systems in tire tread compound. The better dispersion of silica in rubber domain to achieve the better balances between "on the road" properties of tire" abrasion, rolling resistance and traction" is the goal of the most of them[3,7,8,10-12]. However the potential of semi-dispersible conventional silica in super improving of failure properties (tear resistance, crack growth and abrasion) of the tire tread has been a little notation and detailed studies on the governing mechanisms are sparse. The other interesting domain in silica technology is also the improvement of sulphur curing rate with novel curing agents. However it is possible to achieve the same curing rate with rubber blending as it has been studied here.

In this study a detailed research on the failure properties of silica/silane/carbon in styrene butadiene rubber and its blends with *cis*-butadiene rubber and natural rubber has been conducted with the help of experimental design. A formulation with superior failure properties for passenger tread compound are suggested based on styrene butadiene rubber/*cis*-butadiene rubber/natural rubber blend rubber and semi-dispersible silica/silane/carbon black.

EXPERIMENTAL

All mixing ingredients were used as received. Natural rubber, SMR20, (MV=88, density = 0.910, PRI = 59.9) was supplied by Marub Co., Malaysia. *cis*-Butadiene rubber (BR), (MV = 45, density = 0.908) and styrene butadiene rubber (SBR), (MV = 48, density = 0.954) were obtained from Arak Petrochemical, Iran and Bandare Emam Petrochemical, Iran, respectively. Carbon black N330 (density = 1.8, pH = 8.68, iodine number = 81.7, DBP = 101.4) and N234 (density = 1.78, pH = 8, iodine number = 122.5, DBP = 120.3) were obtained from Iran Carbon Co. and Korea DC Chemical Co., respectively. Silica, Mansil1165, (BET surface = 170, density = 2.052, pH = 6.8) and silane coupling agent (Si69) are supplied by Degussa. Aromatic oil was used as a processing aid obtained from Behran Oil Co. Zinc oxide, stearic acid, sulphur and accelerator (CBS) were also included as curing agents, was supplied by Pars oxide Co., Iran, Acid chem. Co., Iran, Tesdak Co. and Nocil Co., respectively. Other chemicals including antioxidants and antiozonants were supplied from Bayer, Germany.

Preparation and testing of rubber compounds: A laboratory-sized internal mixer (Pomini MIX32) was employed to prepare the rubber compounds. The mixing conditions were set as follows; fill factor: 0.75, rotor speed: 40 rpm, initial champer temperature: 50 ºC, mixing time: 5 min.

After mixing, the compounds were sheeted out using the two-roll mill(MCCIN 152 X 305 R - E). Vulcanization ingredients were added 24 h later on two-roll mill. The base formulation for a radial passenger tread compound consists of styrene butadiene rubber1712 (100 phr), a blend of N234/N330 (50 phr/20 phr), oil (5.5 phr), Zno (4.7), stearic acid (1.4), CBS (1.7 phr), sulphur (1.2 phr), other chemicals (7 phr). In this study we have substituted some per cent based styrene butadiene rubber with natural rubber and *cis*-butadiene rubber rubber and the substitution of N330 with silica.

Nine formulations were designed according to the Taguchi statistical method (Table-1). In all formulations the total of rubber (styrene butadiene rubber + natural rubber + *cis*-butadiene rubber) was kept at 100 phr. Cure characteristics were determined using an ODR rheometer, alpha technology. Delta torque is obtained by the subtract of maximum torque (MH) and minimum torque (ML). Scorch time (Ts_2) is the time to reach 2 units above minimum torque (ML) and optimum cure time (TP90) is the time to achieve 90 % of delta torque above minimum. Sheets and test specimens were vulcanized by compression molding in and experimental curing press at 145 ºC according to optimum curing time.

TABLE-1
FORMULATIONS, ACCORDING TO THE TAGUCHI DESIGN

	Refrence	BR, Silica	BR, Silica	NR, Silica	BR, NR, Silica	BR, NR	NR, Silica	BR, NR	BR, NR, Silica
Comp. No.	1	2	3	4	5	6	7	8	9
SBR1712	100	90	80	90	80	70	80	70	60
BR *cis*	0	10	20	0	10	20	0	10	20
NR	0	0	0	10	10	10	20	20	20
N234	50	50	50	50	50	50	50	50	50
N330	20	0	0	0	0	20	0	20	0
Silica	0	15	20	15	20	0	20	0	15
Silane	0	1.5	2	1.5	2	0	2	0	1.5
Oil	5.5	5.5	5.5	5.5	5.5	5.5	5.5	5.5	5.5
Chemicals	12.88	12.88	12.88	12.88	12.88	12.88	12.88	12.88	12.88
Total	188.38	184.88	190.38	184.88	190.38	188.38	190.38	188.38	184.88

BR: *cis*-Butadiene rubber, NR: Natural rubber.

Testing of rubber vulcanizates: Tensile stress-strain properties and tear resistance were determined according to ASTM D 624 , The Die-C specimen used for tear, DIN abrasion as per ISO 4649 and resilience and hardness according to ASTM D1054 and ASTM D 2240, respectively. Crack growth was determined using De Mattia crack growth tester in accordance with ASTM D 813. The dispersion index was determined in dispergrader according to ISO 11345 and resilience and hardness according ASTM D1054 and ASTM D 2240 , respectively. Data analysis of the main results were processed using statistical software, Minitab.

RESULTS AND DISCUSSION

The rheometry and physical-mechanical properties of formulations have been presented in Tables 2 and 3, respectively.

Curing characteristics: The main effect plots for optimum curing time, curing rate and delta torque are presented in Figs. 1-3, respectively. Although the silanization reaction between organosilane and silanol groups of silica surface, significantly

TABLE-2
RHEOMETRY PROPERTIES OF RUBBER COMPOUNDS (145 °C)

Comp. No.	ML (lb-in)	MH (lb-in)	Delta torque (lb-in)	PR Curing rate (lb-in/min)	Scorch time (min)	TP90, optimum curing time (min)
1	7.49	27.99	20.50	3.8	10.2	19.59
2	7.61	30.53	22.92	3.0	10.2	24.12
3	8.17	33.8	25.63	3.4	9.4	23.25
4	7.23	30.42	23.19	3.0	9.55	24.31
5	7.70	32.37	24.67	3.1	9.42	24.33
6	9.63	37.18	27.55	6.2	9.16	17.56
7	7.79	32.43	24.64	3.4	9.16	23.13
8	8.53	34.63	26.10	6.1	9.06	17.41
9	7.57	33.28	25.71	4.0	9.41	22.03

TABLE-3
PHYSICAL AND MECHANICAL PROPERTIES OF RUBBER COMPOUNDS

Comp. No.	Hardness (shore A)	Reselience (%)	Density (g/cm^3)	Abrasion (mm^3)	Dispersion	Tensile (Mpa)	Elongation	M300 (Mpa)	Tear (KN/m)	CG4000 (mm)
1	64	15.1	1.165	117.6	6.6	16.5	431.8	10.3	33.9	13.6
2	63	18.2	1.167	97.1	4.5	18.5	494.3	10.03	79.3	10.9
3	66	19.0	1.174	93.7	4.4	17.3	419.1	11.5	72.2	14.0
4	63	17.3	1.170	99.7	5.8	18.3	460.9	10.5	57.6	11.4
5	66	18.3	1.176	104.8	5.3	17.0	425.6	11.2	69.2	10.4
6	68	17.0	1.163	91.7	6.0	17.1	372.5	13.4	61.1	21.0
7	65	17.9	1.178	118.8	5.2	17.3	434.5	10.9	69.6	10.7
8	68	17.9	1.163	92.0	6.1	17.2	384.8	12.5	60.4	15.4
9	65	20.0	1.156	83.9	4.8	17.5	437.4	10.7	68.0	10.6

improves the sulphur curing behaviour, silica substitution shows a negative effect on the curing characteristics *i.e.*, lower curing rate and longer curing time. However no significant change is observed in delta torque. As the torque difference is directly proportional to the degree of crosslinking, it could be plausible that chemical crosslinks between silica surface and rubber chains has been formed during mixing and curing. On the other hand, changing of rubber domain has a significant positive effect on vulcanization behaviour. Both natural rubber and *cis*-butadiene rubber substituting, has been enhanced vulcanization, *i.e.*, increase of cure rate, delta torque and decrease of optimum curing time. So it could be predictable that substituted formulations have the same curing rate and the curing time and the higher crosslink density rather than the reference formulation.

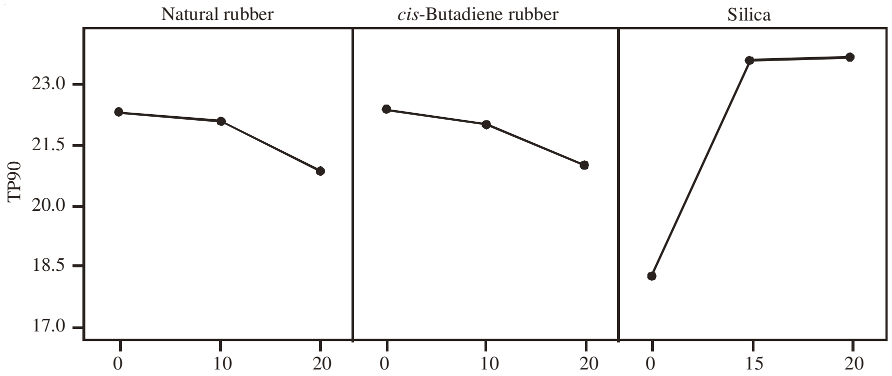

Fig. 1. Main effects plot-data means for optimum curing time (min)

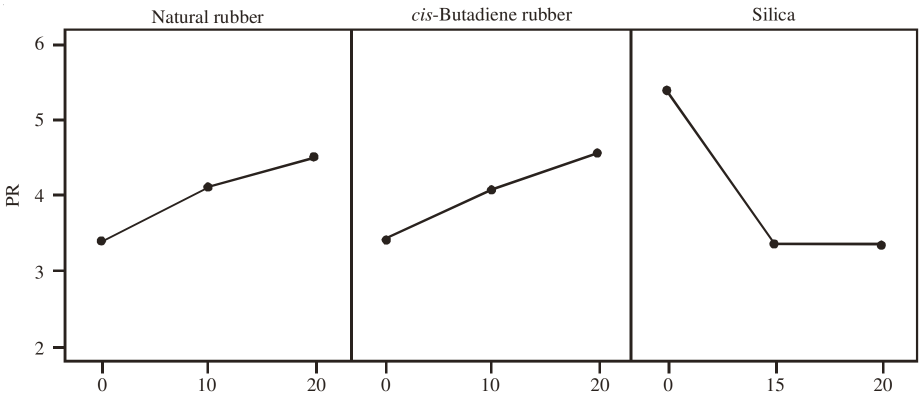

Fig. 2. Main effects plot-data means for curing rate (lb-in/min)

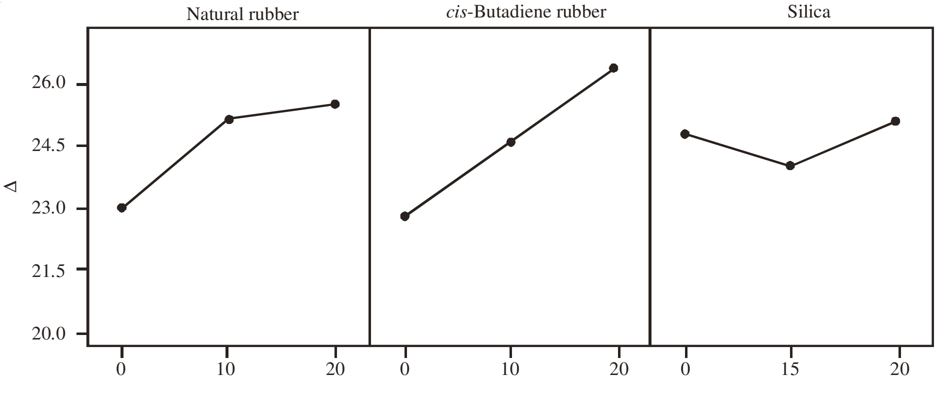

Fig. 3. Main effects plot-data means for delta torque (lb-in)

Failure properties: Fig. 4 indicates that the tear behaviour of rubber compounds increases significantly in presence of natural rubber, *cis*-butadiene rubber and silica (silane). In other words, all substituted formulations deliver excellent tear resistance

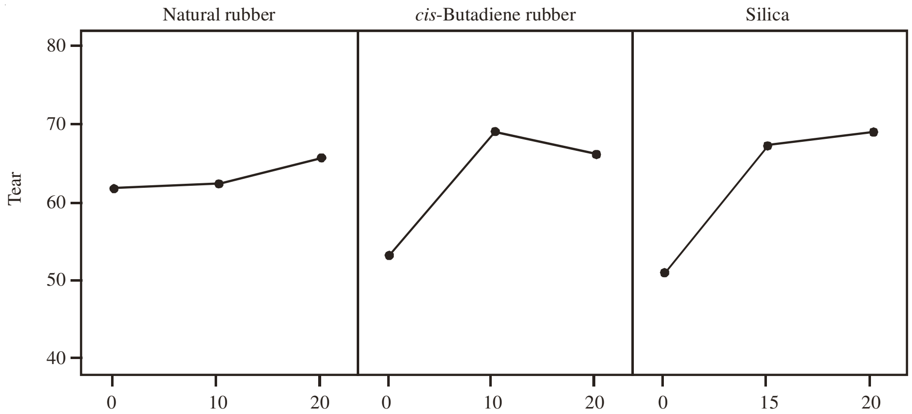

Fig. 4. Main effects plot-data means for tear behaviour (KN/cm)

with respect to the reference compound as shown in Table-3. Here Silica containing compounds show super effects than the others.

Fig. 5 shows excellent crack growth behaviour in the presence of silica (silane), while *cis*-butadiene rubber effect is relatively negative. Here silica shows better behaviour than natural rubber.

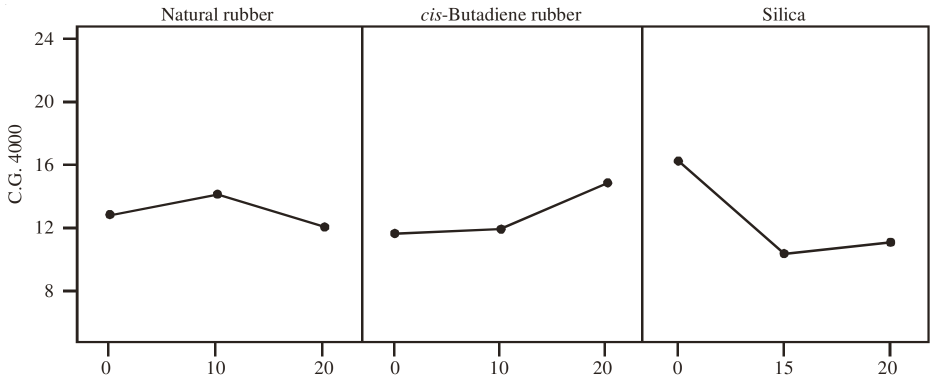

Fig. 5. Main effects plot-data means for crack growth (mm in 4 kcycle)

The abrasion behaviour presented in Fig. 6 shows the better behaviour of natural rubber and *cis*-butadiene rubber and the weaker behaviour of silica (silane). Here *cis*-butadiene rubber substituting leads to super abrasion improvement.

Effects of different levels of natural rubber, *cis*-butadiene rubber and silica on tensile strength, have been presented in Fig. 7. They showed no significant effect for natural rubber and *cis*-butadiene rubber substitutions. A little increase is observed in 15 phr substituted-silica compounds. Finally, elongation curves presented in Fig. 8 show a decrease for natural rubber and *cis*-butadiene rubber substitution and an increase for silica substitution.

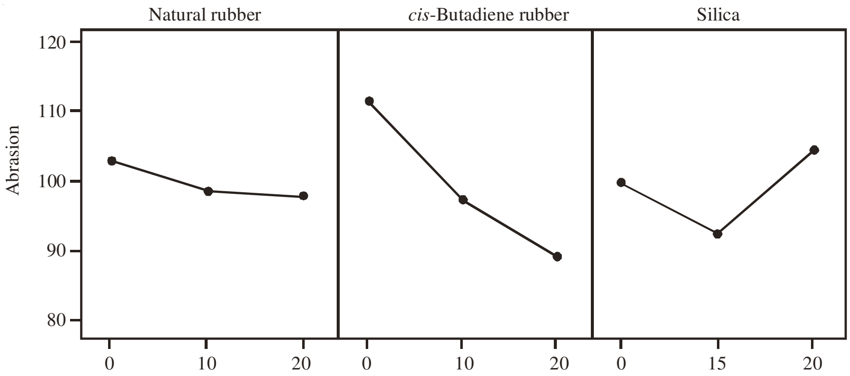

Fig. 6. Main effects plot-data means for abrasion (mm^3)

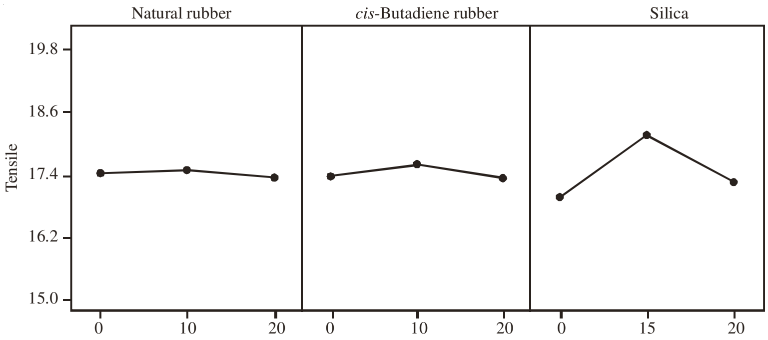

Fig. 7. Main effects plot-data menas for tensile (Mpa)

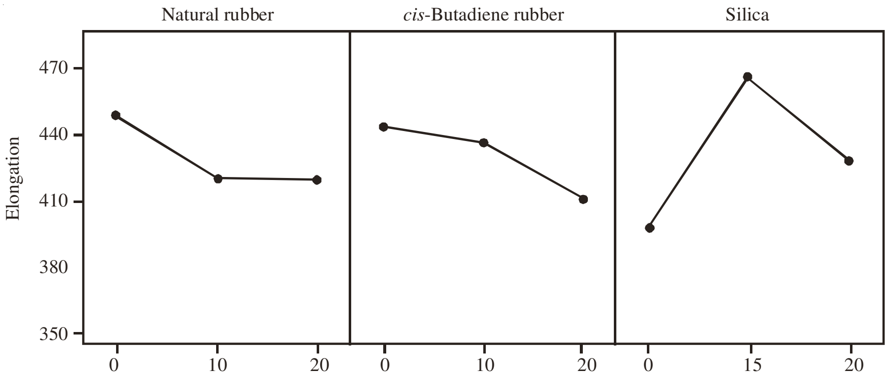

Fig. 8. Main effects plot-data means for elongation

Hardness, modulus and resilience: Fig. 9 indicates that the hardness of the rubber compounds increases in presence of natural rubber, *cis*-butadiene rubber and decreases in the presence of silica (silane). The same behaviour is observed for modulus 300 % (Fig. 10). The effect of natural rubber and *cis*-butadiene rubber on the resilience is the same as hardness and modulus, however, the silica substituting has an increase in resilience.

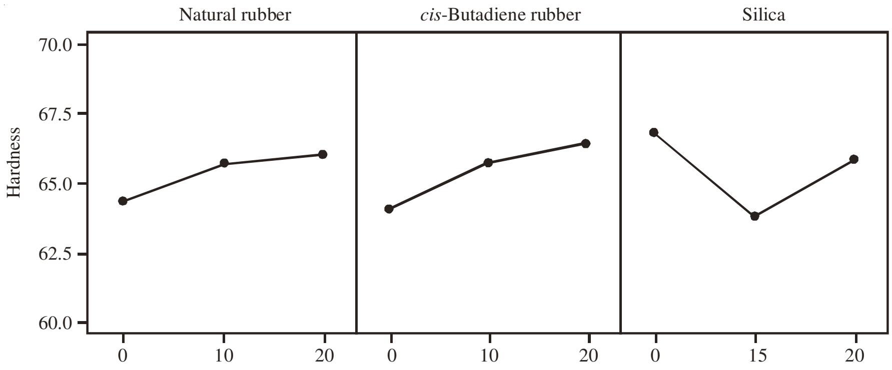

Fig. 9. Main effects plot-data means for hardness

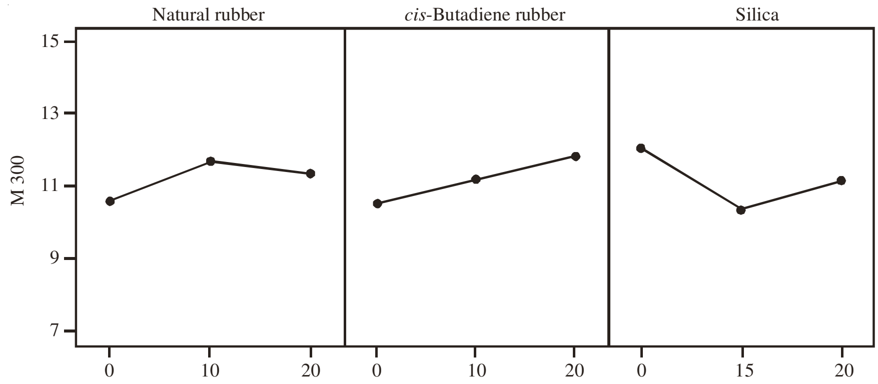

Fig. 10. Main effects plot-data means for modulus 300 %

Study of the governing mechanisms on the physical and the mechanical properties: For the basic study of the physical and the mechanical properties, it is necessary to determine the dispersion index of the compounds. The results are illustrated in Fig. 12. Silica/silane formulations show lower dispersion index. The surface energy measurements carried out on silicas and carbon blacks using inverse gas chromatography (IGC) show that the different components of the surface energy for silica and carbon black varied significantly[13-15]. At comparable surface areas and structures, reinforcing silica is characterized by lower dispersive component of surface the energy (*i.e.*, lower filler-polymer interaction). However, the specific component of the surface energy of silica is much higher than carbon black (higher filler-filler interaction). The silanization with silane can reduce both components of the surface energy, hence better compatibly of silica with rubber domain and better dispersion. However, the silanization reaction could not carried out completely even after modification of silica, the agglomeration trend of silica particles is more than carbon black. So it can be predictable that bound rubber content would decrease in silica/silane compound, hence lower filler-polymer interaction.

Another reason for lower filler-polymer interaction of silica compounds could be plausible from Figs. 3 and 9-11. The substitution of N330 with silica results in lower modulus 300 %, and hardness and higher resilience. Because the delta torque has not been changed in the presence of silica, the lower silica-rubber interaction could be concluded.

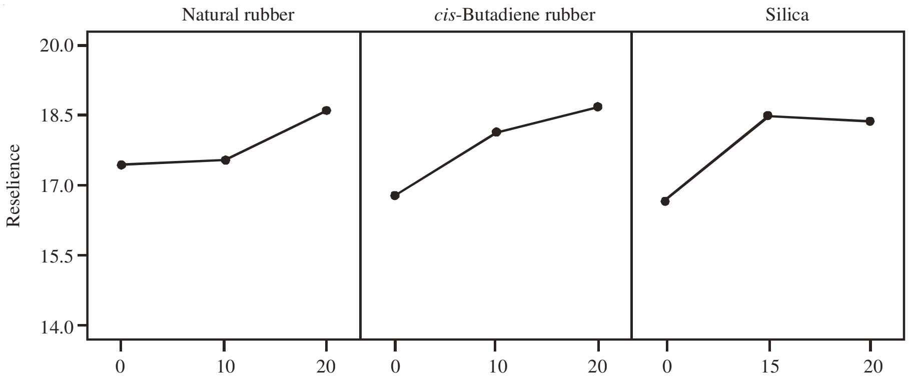

Fig. 11. Main effects plot-data means for resilience

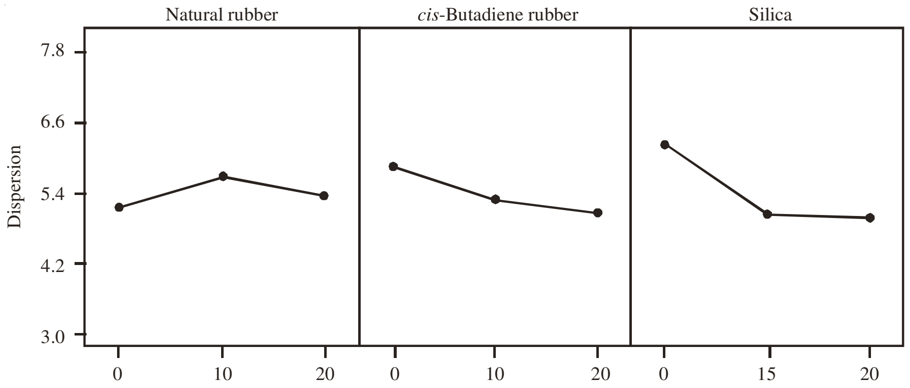

Fig. 12. Main effects plot-data means for dispersion

Failure properties: In order that a failure occur, sufficient energy must be supplied. In general, the energy supplied can come from two sources: (1) stored elastic energy and (2) that supplied directly by testing machine. In turn, the energy that is supplied can be expended in two main ways (1) by breaking of bonds that were present across the fracture plane and (2) *via* hysteretic losses due to irreversible deformation processes[16,17]. The latter is called catastrophic energy dissipation and the former is noncatastrophic energy dissipation.

Here the filler-polymer interaction can affect the failure behaviour in two counterpart aspects; (1) the stronger bonds need more energy for breaking and increasing fracture energy. (2) The lower interaction between filler-polymer *via* weaker bonds lead to better movement of rubber chains and also better surface slippage of rubber chains.

If an elastomer network is capable of dissipating input energy into heat through irreversible molecular motions, less elastic energy will be available to break network bonds apart and to increase fracture energy.

In addition, other aspects had to be considered; *e.g.*, strain-crystallization elastomers, most notably natural rubber, have high tensile strength without the addition of a particulate filler. The source of strengthening again is substantial dissipation energy which accompanies strain-crystallization. The improvement of tear resistance (Fig. 4) with increasing natural rubber content can be attributed to this natural rubber capability. The alignment of chains front crack tip can deviate the crack path, hence increasing tearing energy. This type of tearing is called knotty tearing[18-20]. The enhanced crack growth of the filled natural rubber in comparison to gum natural rubber is attributed to "super blunting" and enhanced strain-crystallization[21]. However, knotty tearing can occur in the presence of the filler, by filler agglomerates. Better tear behaviour of silica filled compound rather than carbon black may be attributed to more agglomeration tendency of silica particles in the rubber domain particularly in absence of silane.

The high tear resistance of *cis*-butadiene rubber rubber can be explained from dispersion main effect plot (Fig. 12); the dispersion index of filler decreases in presence of *cis*-butadiene rubber.

In the filler domain other mechanisms may be introduced. It seems that the addition of filler should somewhat reduce, compared to unfilled case, the degree of stress magnification and hence the load on the chains, in particular at the tips of inherent or international flaws. For a given degree of macroscopic extension, the chains in a filled specimen, because, in part, of strain amplification, carry an average load that is greater an unfilled specimen. Indeed, it is implicit that the fact that a filled material has a higher resistance to deformation than an unfilled one. In spite of the increased average chain load in the presence of filler, noncatastrophic energy dissipating processes can apparently reduce stress magnification and allow the stress to be somewhat more evenly distributed throughout the network structure. Several dissipation processes may be considered, one is the possibility of attachment of a newly broken network chain to carbon black surface that would regain load-carrying capability rather than irreversibly transmitting its load to neighboring chains. (This hypothesis is consistent with the need for a high specific surface area in order to have substantial reinforcement with a particular filler.) Another dissipation mechanism involves the surface attachment of dangling chains only attached to the network at one end. Upon application of stress, these chains could bear load and reduce stress concentration. The other proposed mechanism is slippage capability of the chains on the surface of filler. A very strong interaction in which slippage is largely prohibited may be undesirable.

With the help of this information and experimental results from dispersion results, we can explain the better tear and crack growth of silica/silane relative to carbon black. The silica/silane deliver a moderate filler-polymer interaction compared to carbon-rubber interaction.

Due to silanization, the bonds between silica and the rubber chains are not so weak. In addition, during vulcanization strong covalent bonds are created between the silica surface and the rubber *via* the silane bridge[22,23]. It seems to be a desired balance between the two reinforcement mechanisms, presence of some strong bonds and better overall slippage of surface attached rubber chains, that expand more energy through dissipative processes.

Another important result is that irreversible motions and slippage dissipation mechanisms has larger contribution on de matia crack growth behaviour. The crack growth resistance of natural rubber is not as good as it's tear behaviour in this study. This can be explained from delta torque results. Higher crosslink density of natural rubber-substituted compounds restricts the rubber chain motions. The same behaviour is observed for *cis*-butadiene rubber-substituted compounds.

As shown in Fig. 6 the silica/silane system has negative effect on abrasion behaviour, it could be concluded that stronger bonds between filler-rubber are dominant and noncatastopic dissipating processes have secondary effects on abrasion behaviour.

TABLE-4
OPTIMIZATION PROCEDURE, THE PREDICTION OF THE RESULTS

Response optimization						
Parameters	Goal	Lower	Target	Upper	Weight	Import
Tensile	Target	17	17.5	19	1	1
Tear	Target	55	65.0	85	1	1
TP90	Target	19	23.0	24	1	1
Hardness	Target	62	65.0	69	1	1
Abrasion	Target	75	90.0	105	1	1
CG4000	Target	5	9.0	12	1	1
M300	Target	9	10.0	12	1	1
Global solution						
NR	=	19.9231				
BR	=	16.6483				
Silica	=	16.5661				
Predicted responses						
Parameters	=	17.5000; desirability = 1.00000				
Tensile	=	76.3749; desirability = 0.43125				
Tear	=	22.5056; desirability = 0.87640				
TP90	=	65.1978; desirability = 0.95055				
Hardness	=	19.6992; desirability = 0.15038				
Abrasion	=	93.1347; desirability = 0.79102				
CG4000	=	9.9750; desirability = 0.67499				
M300	=	10.7065; desirability = 0.64676				
Composite desirability = 0.60793						

Selection of best formulation: An optimized formulation has been calculated in Minitib software, response surface section. First, target the lower and upper limits for each property specified as shown in upper section of the Table-4. Then, the best amount for natural rubber, *cis*-butadiene rubber and silica/silane have been calculated by the software and the values for this condition have been predicted as shown in lower section of Table-4.

Conclusion

A blend of styrene butadiene rubber/*cis*-butadiene rubber/natural rubber in the presence of carbon black/silica/silane showed an excellent balance between the failure and the physico-mechanical properties of a tread formulation. The abrasion, tear, crack growth and resilience have been improved 20, 125, 26 and 30 %, respectively. Here the presence of silica/silane with moderate dispersion index beside a strain-crystalline elastomer, natural rubber, enhanced tear and crack growth, because of super-blunting of natural rubber rubber chains and dissipating mechanisms introduced in the presence of silica; also, blending with *cis*-butadiene rubber could maintain and even overcome the negative effects of silica on the abrasion.

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