

## Statistical Analysis, Modeling and Optimiziton of Silica, Rubber Ratio and Sulfur Levels in Truck Tire Tread Compound

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A Box-Behnken response surface approach has been made to study the possibility of decrease of natural rubber/butadiene rubber ratio in truck tire tread compound with the assistance of silica/silane reinforcement filler. A mathematical modeling has been carried out to investigate the dependency of tear resistance, crack growth, abrasion, resilience, hardness and curing properties on NR/BR ratio, silica/N330 ratio and sulfur levels. The governing mechanisms have been discussed in details with the help of statistical results and surface plots. Improvement effect of silica on tear and crack growth behaviour has been attributed to the lower filler-rubber interactions in silica filled domains that led to less elastic input energy and more consumption of input energy *via* hysteresis deformations. But a significant drop in abrasion and hardness has been observed in silica substituted compounds, However, when content of BR increases, the negative effect of silica on abrasion decreases. The significant effects of sulfur are the drop in the tear and crack growth resistance. On the other hand, in high silica domains increase of sulfur content has no significant negative effect on tear and crack growth. An optimum formulation with lower ratio of NR/BR in presence of silica has been calculated.

**Key Words:** Response surface methodology, Surface plot, Silica, Butadiene rubber.

### INTRODUCTION

Precipitated silica as one of the novel fillers in almost all tread compound formulations with different behaviours comparing to carbon black and its modification with silanes call for a wide study domain in rubber compounding<sup>1-8</sup>.

The overall behaviour of an untreated precipitated silica in rubber compounds relative to carbon black is a decrease of hardness, modulus, abrasion and tensile, but a significant increase of tear and crack growth behaviour<sup>1,6</sup>. Drop in the first series properties was known to be related to different surface chemistry of silica and its high surface energy that made silica incompatible in non-polar rubber networks<sup>9-11</sup>. The high silica agglomeration has a negative effect on modulus, abrasion

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and tensile. However, modification with silanes reduces the surface energy and agglomeration trend and hence, it improves bound rubber and the properties mentioned above<sup>12,13</sup>.

However, with conventional silane-modified-silicas, it is not possible to achieve the best balances between physical and mechanical properties tire tread compound without significant changes in other variables.

Indeed, there is a abstruse relation between the physical and mechanical properties (in particular failure properties such as tear, crack growth, fatigue and abrasion) and compounding variables because of the abstruse governing mechanisms<sup>14-18</sup>. Determination and demonstration of these relationships are essential. Here experimental design and related techniques such as response surface method (RSM) could be a suitable tool<sup>19</sup>.

Modeling and analyzing engineering problems can be done through response surface methodology (RSM) which is a collection of statistical and mathematical methods. Optimizing the response surface as the main objective in this technique, is influenced by variable process parameters. The relationship between the controllable input parameters and the obtained response surface can be quantified *via* RSM<sup>20</sup>.

Response surfaces methods are commonly encountered in elastomer science and technology that falls fairly well into two categories: (i) contour and surface plots for illustration and prediction; (ii) modeling and optimization.

Weissert and Cundiff<sup>21</sup> made extensive use of contour plots according to the central composite design to elucidate relationships among compounding variables affecting properties of NR/BR blends for truck tire. They also optimized truck tire treads performance. Sarbach *et al.*<sup>22</sup> employed a central composite design to elucidate the nature of SBR/BR blends and filler/oil blends. They also optimized BR compounds for tread wear. Derringer employed a five-variable central composite design to study the levels of silica, oil, accelerators and sulfur<sup>23</sup>. Kukreja *et al.*<sup>24</sup> employed a two-variable (five level) central composite rotatable design to study the effect of vegetable oil and black in rubber formulations. They also fitted a two variable second order equation to their results.

Literatures discussed the role of silica in rubber compounds a little has been employed the experimental design and RSM method<sup>25,26</sup>. No significant attempt has been made to employ the conventional silica to improve the failure properties while keep the price of the compound as low as possible and the study of governing mechanisms on the failure properties are sparse.

In this study a special use of conventional silica in truck tire compound based on NR/BR has been studied. The main objective is to decrease the NR/BR ratio due to economic consideration while deliver the better failure properties. It is clear that, the low tearing and crack growth behaviour of BR rubber due to the low strain-crystallinity and highly elastic nature of this rubber is a critical factor that would confine the NR/BR ratio in truck tire tread compounds<sup>14</sup>. A Box-Behnken experimental design has been chosen and all properties has been statistically analyzed and modeled. The governing mechanisms on failure properties has been studied according to the statistical analysis conclusions and surface plots.

## 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) was obtained from Arak Petrochemical, Iran. Carbon black N330 (Density = 1.8, pH = 8.68, iodine number = 81.7, DBP = 101.4) was obtained from Simorgh Carbon Co. Silica, Iran. Silica, Mansil 1165, (BET surface = 170, density = 2.052, pH = 6.8) and silane coupling agent (Si69) are supplied by Degussa. Zinc oxide, stearic acid, sulfur and accelerator (OBTS) 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.

**Methods:** The reference formulation is the truck tire tread compound (natural rubber = 75, butadiene rubber = 25, N330 carbon black filler = 50, sulfur = 1.17, accelerator (OBTS) = 0.82 Phr).

In order to statistical investigation and modeling of the compounding ingredient effects, a Box-Behnken response surface experimental design has been used with three variables and three levels: NR/BR: 75/25, 65/35, 55/45; silica/N330: 0/50, 10/40, 20/30; sulfur: 1, 1.17, 1.34.

Fifteen formulations have been designed based on Box-Behnken design. The center point has been repeated three times.

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 chamber temperature: 50 °C, mixing time: 5 min.

After mixing, the compounds were sheeted out using the two-roll mill (MCCIN 152 × 305 R-E). Vulcanization ingredients were added 24 h later on a two-roll mill.

Test compounds were cured on a hydraulic press at 151 °C to an optimum state of cure (t<sub>90</sub>) as determined by rheometer measurement.

### Determination of physical and mechanical properties

**Tensile properties:** Dumbbell-shaped test samples were punched out from the moulded sheets and the tests were carried out in stress/strain tester machine according to ASTM D412. Three samples of each compound were tested. The 100 and 300 % modulus, tensile strength and elongation at break were reported.

**Tear strength:** The punched samples (Die C) were measured on a stress/strain tester machine according to ASTM-D-624 form C or DIN 53515. Both of tensile and tear tests are run at ambient temperature at a crosshead speed of 500 mm/min.

**Hardness:** It was tested on a Shore A durometer according to ASTM-D-2240.

**Resilience:** A rebound tester was used to measure the compound rebound at room temperature (DIN 53512/ISO 4662).

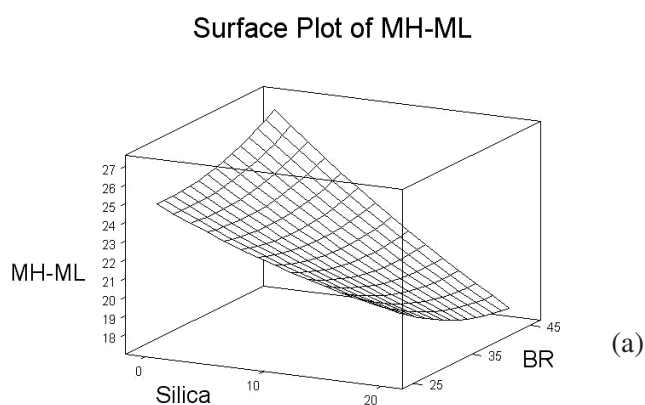
**Crack growth rate:** The compound crack growth rate was measured using a DeMatia crack growth tester. The slope of the crack growth (mm) - kcycle plot was reported.

**Abrasion:** The abrasion loss was determined according to ISO4649. The volume loss of the samples after test in abrasion machine has been reported.

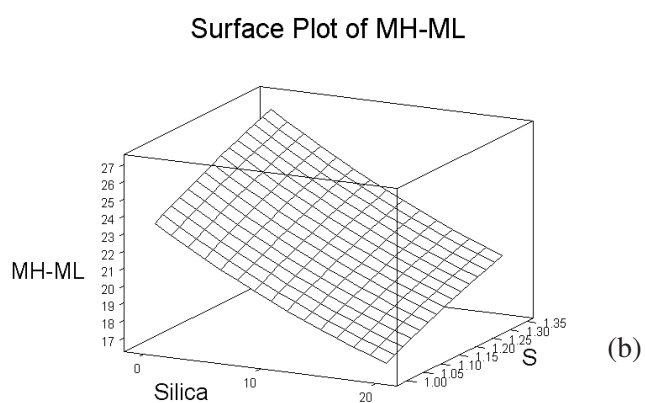
**Rheometry characteristics:** TP90 (time to 90 % of maximum torque development) and delta torque (the differences between maximum and minimum torque) are determined in an ODR rheometer (151 °C).

## RESULTS AND DISCUSSION

The formulation, the rheometry and the physical and mechanical properties have been presented in Tables 1 and 2. The surface plots for delta torque, tensile, modulus, crack growth rate, tear resistance, abrasion, hardness and resilience have been shown in Figs. 1-8.



Hold values: S: 1.17



Hold values: BR: 35.0

Fig. 1. Effect of NR/BR ratio, silica/N330 ratio and sulfur levels on delta torque

TABLE-1  
FORMULATIONS AND MIXING CONDITIONS

Compound code	Formulations			Rheometry properties	
	BR	Silica	S	Delta torque (lb-in)	Tp90 (min:s)
1	25	10	1.34	23.16	17:12
2	35	0	1.00	23.64	17:58
3	45	0	1.17	26.00	18:05
4	35	20	1.00	16.55	22:54
5	45	10	1.00	20.73	21:26
6	35	10	1.17	21.22	19:17
7	45	10	1.34	23.5	19:43
8	35	10	1.17	22.10	18:38
9	35	10	1.17	21.15	19:26
10	25	10	1.00	20.36	20:12
11	35	20	1.34	19.72	21:07
12	45	20	1.17	17.65	23:04
13	25	0	1.17	24.93	15:58
14	35	0	1.34	27.12	16:03
15	25	20	1.17	21.40	21:11

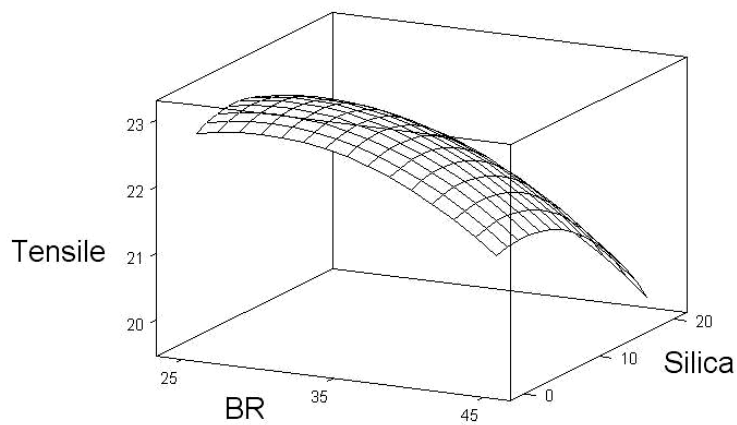
TABLE-2  
PHYSICAL AND MECHANICAL PROPERTIES

Compd. code	Tensile (Mpa)	M300 (MPa)	Tear (KN/m)	Dematia crack growth (mm/Kcycle)	Hardness (Shore A)	Resilience (%)	Abrasion (mm <sup>3</sup> )
1	21.9	7.30	44.8	0.457	52	24.3	90.8
2	22.3	7.60	55.9	0.513	54	23.5	62.7
3	21.3	8.03	26.6	0.848	55	24.0	65.4
4	20.2	5.40	52.6	0.384	45	21.4	86.9
5	20.7	6.80	47.7	0.544	49	21.9	63.7
6	22.4	7.03	40.8	0.577	51	23.8	94.4
7	22.4	8.20	25.4	0.682	54	24.5	63.8
8	22.3	7.70	37.9	0.635	52	24.2	78.8
9	23.0	7.02	38.4	0.520	51	24.2	88.3
10	23.1	6.60	52.6	0.402	48	22.0	93.9
11	22.3	6.60	52.3	0.515	51	24.0	75.3
12	19.4	5.70	52.1	0.514	47	23.5	69.6
13	23.1	8.90	41.6	0.590	55	24.2	76.7
14	22.4	8.30	29.0	0.600	56	25.0	63.0
15	21.6	5.60	51.1	0.493	48	23.9	111.1

The experimental results (Table-1) were also fitted to a full quadratic second order polynomial equation by applying multiple regression analysis. The delta torque, tear resistance, crack growth rate, modulus, abrasion, hardness, resilience and tensile are used as response parameters.

$$\text{Property} = a * \text{BR} + b * \text{Silica} + c * \text{S} + d * \text{BR}^2 + e * \text{Silica}^2 + f * \text{S}^2 + g * \text{BR} * \text{Silica} + h * \text{BR} * \text{S} + i * \text{Silica} * \text{S}$$

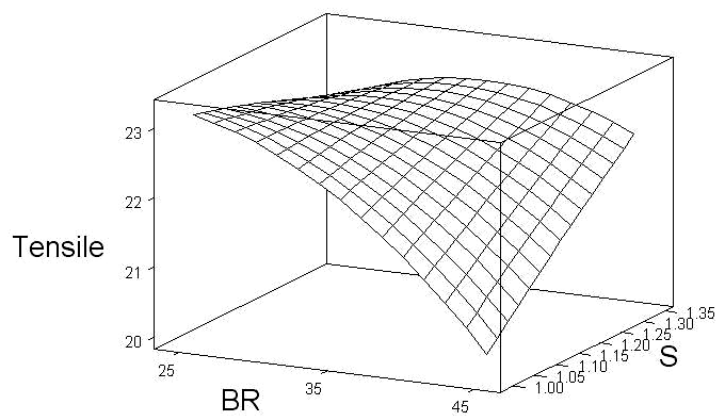
Surface Plot of Tensile



Hold values: S: 1.17

(a)

Surface Plot of Tensile

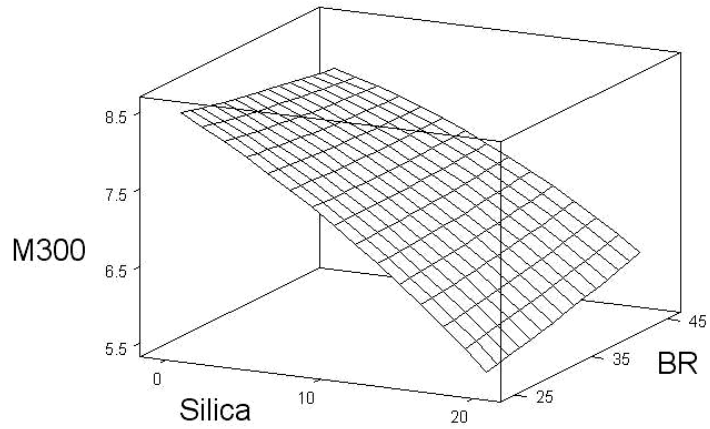


Hold values: Silica: 10.0

(b)

Fig. 2. Effect of NR/BR ratio, Silica/N330 ratio and sulfur levels on tensile strength

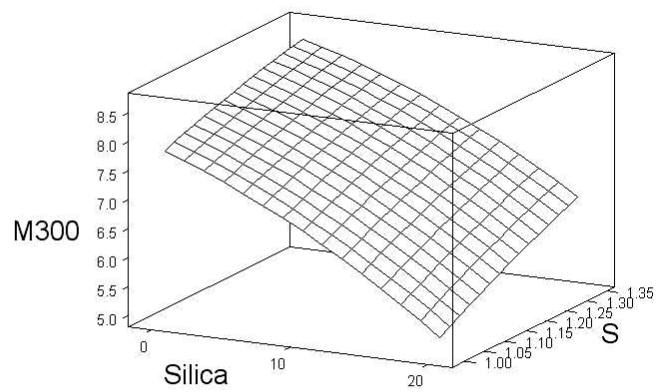
### Surface Plot of M300



Hold values: S: 1.17

(a)

### Surface Plot of M300

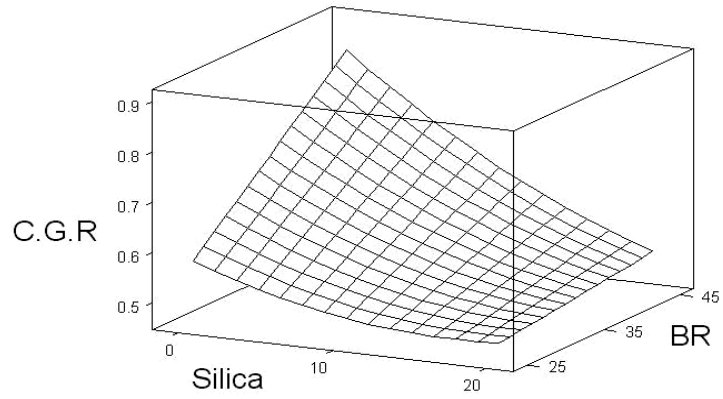


Hold values: BR: 35.0

(b)

Fig. 3. Effect of NR/BR ratio, Silica/N330 ratio and sulfur levels on modulus

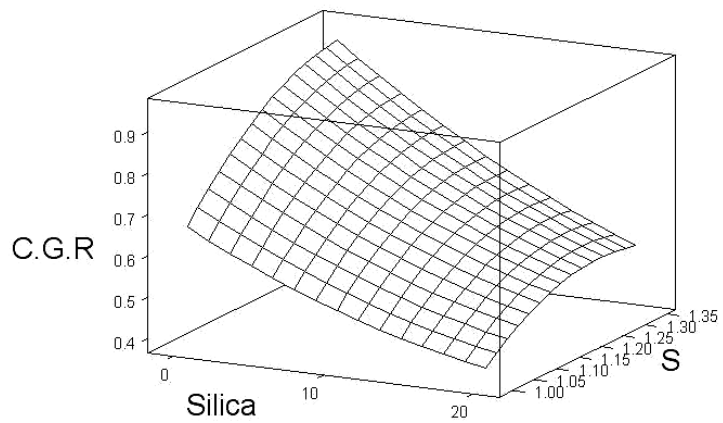
Surface Plot of C.G.R



Hold values: S: 1.17

(a)

Surface Plot of C.G.R



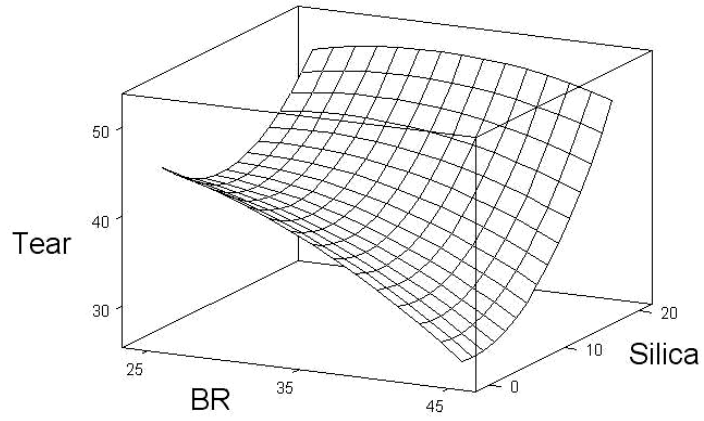
Hold values: BR: 45.0

(b)

Fig. 4. Effect of NR/BR ratio, Silica/N330 ratio and sulfur levels on crack growth rate



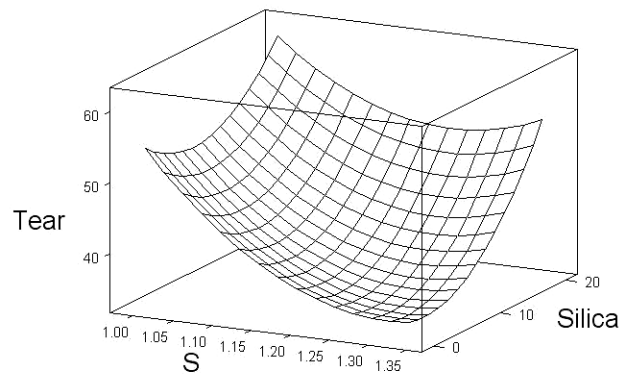
### Surface Plot of Tear



Hold values: S: 1.17

(a)

### Surface Plot of Tear

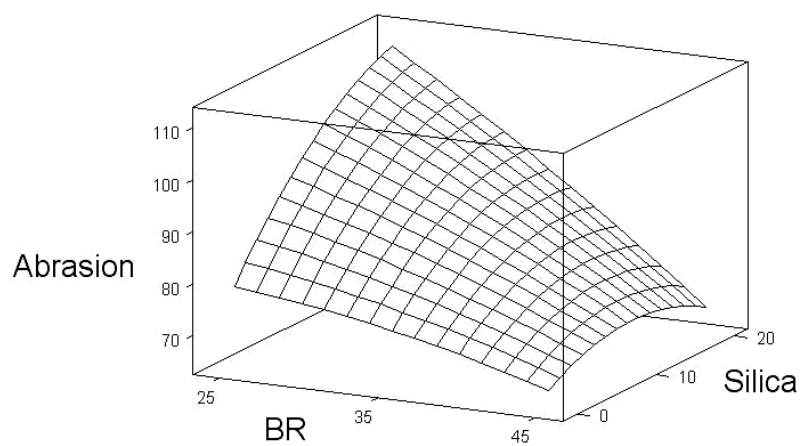


Hold values: BR: 35.0

(b)

Fig. 5. Effect of NR/BR ratio, Silica/N330 ratio and sulfur levels on tear strength

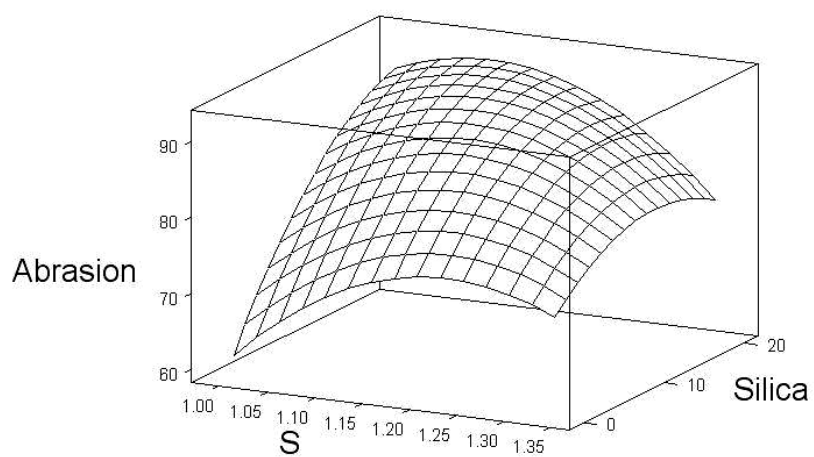
### Surface Plot of Abrasion



Hold values: S: 1.17

(a)

### Surface Plot of Abrasion

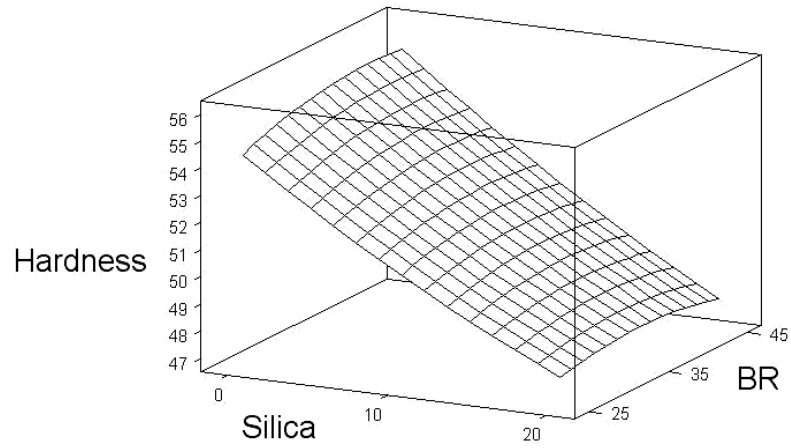


Hold values: BR: 35.0

(b)

Fig. 6. Effect of NR/BR ratio, Silica/N330 ratio and sulfur levels on abrasion loss

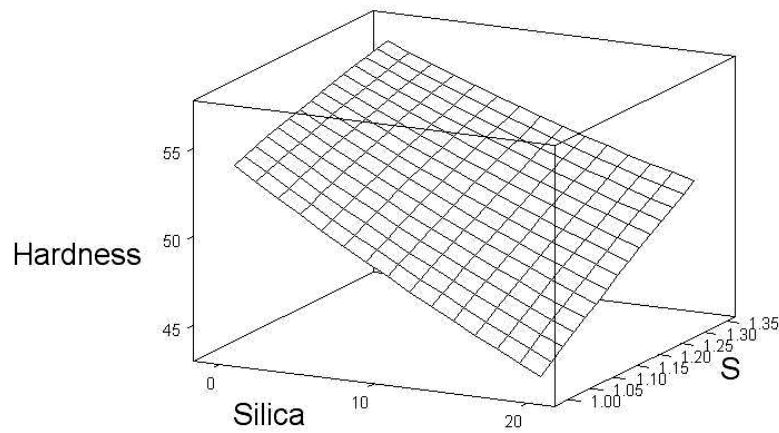
### Surface Plot of Hardness



Hold values: S: 1.17

(a)

### Surface Plot of Hardness

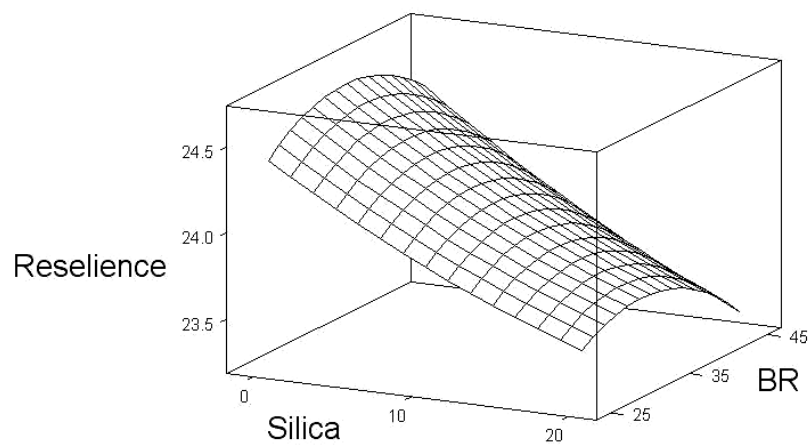


Hold values: BR: 45.0

(b)

Fig 7. Effect of NR/BR ratio, Silica/N330 ratio and sulfur levels on hardness

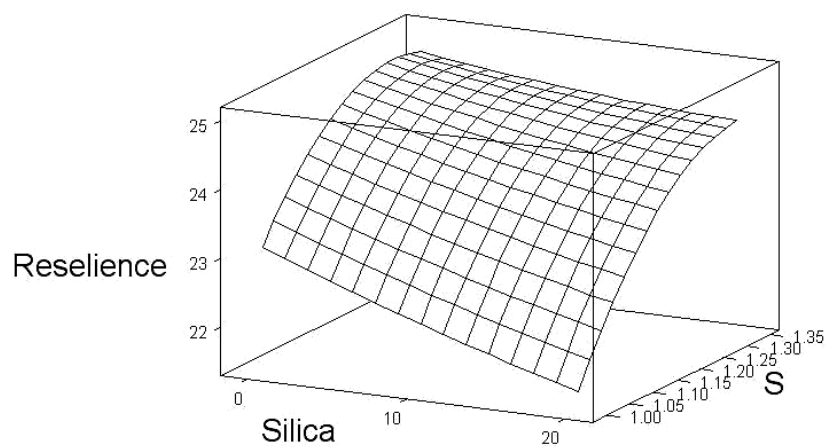
### Surface Plot of Reselien



Hold values: S: 1.17

(a)

### Surface Plot of Reselien



Hold values: BR: 35.0

(b)

Fig 8. Effect of NR/BR ratio, Silica/N330 ratio and sulfur levels on resilience

The regression coefficients (a, b, c, ..., i) found for these equations and their significance levels are shown in Table-3. The coefficient of multiple determination,  $R^2$ , for tear resistance is found to be 96.7 % which means that the model could explain 96.7 % of the total variations in the system. The relatively high value of  $R^2$  for responses (crack growth rate: 92.7, modulus: 92.6, abrasion: 95.6, hardness: 98.1 %, tensile: 91.4, resilience: 94) indicates that the second order polynomial equations is capable of representing the system under the given experimental domain.

Additionally, an analysis of variance (ANOVA) table was constructed for a further check of the model adequacy (Table-4 and **Appendix**).

Computer software for regression analysis, aside from estimating the equation coefficients, usually provides statistics which indicate whether a model can be considered adequate. The most common diagnostic for detecting inadequacy is the F-ratio for lack of fit. The F-lack -of-fit value calculated by the computer is compared to a reference value to determine if it is statistically significant. If it is significant, then the equation must be modified until lack of fit diminishes to a point of insignificance, usually at the 5 % level of significance.

The P-values (significance of the lack-of-fit) according to the Table-3 for physical and mechanical properties are as follows: tear: 0.149, crack growth rate: 0.634, modulus: 0.378 abrasion: 0.975, hardness: 0.322, tensile: 0.315, delta torque: 0.267, that confirm the models.

In addition to the F-lack of -fit test, The F ratio for regression must be at the very least, statistically significant at the 5 or 1 % level of significance (Table-3).

**Delta torque:** Delta torque is determined from subtraction of maximum and minimum torque of rheometer curves could be a measure of crosslink density of vulcanizates. The dependency of delta torque to the understudy variable is shown in Fig. 1.

For better understanding of the behaviours, the results obtained from statistical analysis are presented in Table-3.

From Fig. 1a it is clear that silica has a decreasing effect on the delta torque or crosslink density. The calculated P-value for silica regression coefficient is 0.00 (Table-3). Although the silanization reaction between organosilane and silanol groups of silica surface, significantly improves the sulfur curing behaviour, silica substituting shows a negative effect on the curing characteristics.

The positive effect of sulfur on the delta torque is obvious from Fig. 1b and statistical analysis (calculated P-value for S regression coefficient is 0.003 according to the Table-3).

However, no significant change is observed for BR substitution (calculated P-value for BR regression coefficient is 0.409 according to the Table-3).

The square and interaction terms are not significant except BR\*silica term (P-value = 0.026).

TABLE-3  
ESTIMATED REGRESSION COEFFICIENTS FOR THE PROPERTIES

Term	Estimated regression coefficients for delta torque				Estimated regression coefficients for tensile			
	Coeff. *	SE coeff.	T	P	Coeff.	SE coeff.	T	P
Constant	21.49	0.4468	48.098	0.00	22.5767	0.3061	73.748	0.000
BR	-0.24	0.2736	-0.90	0.409	-0.7375	0.1875	-3.934	0.011
Silica	-3.296	0.2736	-12.047	0.00	-0.7	0.1875	-3.734	0.014
S	1.527	0.2736	5.583	0.003	0.3375	0.1875	1.8	0.132
BR*BR	0.593	0.4027	1.471	0.201	-0.5	0.2759	-1.815	0.129
Silica × Silica	0.413	0.4027	1.024	0.353	-0.7258	0.2759	-2.63	0.047
S × S	-0.145	0.4027	-3.63	0.734	-0.0508	0.2759	-0.184	0.861
BR × Silica	-1.205	0.3869	-3.114	0.026	-0.1	0.2651	-0.377	0.722
BR × S	-0.007	0.3869	-0.019	0.985	0.725	0.2651	2.735	0.041
Silica × S	-0.078	0.3869	-0.200	0.849	0.5	0.2651	1.886	0.118
S=0.7739, R-Sq=97.4%, R-Sq(adj.)=92.8%					S=0.5302, R-Sq=91.4%, R-Sq(adj.)=76%			
Term	Estimated regression coefficients for modulus 300%				Estimated regression coefficients for dematia crack growth rate			
	Coeff.	SE coeff.	T	P	Coeff.	SE coeff.	T	P
Constant	7.250	0.2733	26.532	0.000	0.57733	0.03005	19.213	0.000
BR	0.041	0.1673	0.247	0.815	0.08075	0.01840	4.388	0.007
Silica	-1.191	0.1673	-7.119	0.001	-0.08063	0.01840	-4.381	0.007
S	0.500	0.1673	2.988	0.031	0.05138	0.01840	2.792	0.038
BR*BR	0.029	0.2463	0.117	0.912	0.02608	0.02709	0.963	0.38
Silica × Silica	-0.221	0.2463	-0.898	0.410	0.00783	0.02709	0.289	0.784
S × S	0.054	0.2463	-0.218	0.836	-0.08217	0.02709	-3.033	0.029
BR × Silica	0.242	0.2366	1.025	0.352	-0.05925	0.02602	-2.277	0.072
BR × S	0.175	0.2366	0.74	0.493	0.02075	0.02602	0.797	0.461
Silica × S	0.125	0.2366	0.528	0.620	0.01100	0.02602	0.423	0.690
S=0.4433, R-Sq=92.6%, R-Sq(adj.)=79.2%					S=0.05205, R-Sq=92.7%, R-Sq(adj.)=79.4%			
Term	Estimated regression coefficients for tear strength				Estimated regression coefficients for abrasion loss			
	Coeff.	SE coeff.	T	P	Coeff.	SE coeff.	T	P
Constant	39.033	1.775	21.994	0.000	87.17	3.002	29.035	0.000
BR	-4.788	1.087	-4.405	0.007	-13.75	1.837	-7.479	0.001
Silica	6.875	1.087	6.326	0.001	9.39	1.837	5.106	0.004
S	-7.163	1.087	-6.591	0.001	-1.79	1.837	-0.972	0.376
BR*BR	-0.504	1.6	-0.315	0.765	-0.20	2.706	-0.072	0.945
Silica × Silica	4.321	1.6	2.701	0.043	-6.27	2.706	-2.317	0.068
S × S	4.096	1.6	2.560	0.051	-8.92	2.706	-3.297	0.022
BR × Silica	4.000	1.537	2.603	0.048	-7.55	2.6	-2.904	0.034
BR × S	-3.625	1.537	-2.359	0.065	0.8	2.6	0.308	0.771
Silica × S	6.650	1.537	4.327	0.008	-2.98	2.6	-1.144	0.304
S=3.074, R-Sq=96.7%, R-Sq(adj.)=90.8%					S=5.2, R-Sq=95.6%, R-Sq(adj.)=87.6%			
Term	Estimated regression coefficients for hardness				Estimated regression coefficients for resilience			
	Coeff.	SE coeff.	T	P	Coeff.	SE coeff.	T	P
Constant	51.33	0.4410	116.413	0.000	24.0667	0.2462	97.755	0.000
BR	0.250	0.2700	0.926	0.397	-0.0625	0.1508	-0.415	0.696
Silica	-3.625	0.2700	-13.424	0.000	-0.4875	0.1508	-3.234	0.023
S	2.125	0.2700	7.869	0.001	1.1250	0.1508	7.462	0.001
BR*BR	-0.417	0.3975	-1.048	0.343	-0.2333	0.2219	-1.051	0.341
Silica × Silica	0.333	0.3975	0.839	0.440	0.0667	0.2219	0.3	0.776
S × S	-0.167	0.3975	-0.419	0.692	-0.6583	0.2219	-2.967	0.031
BR × Silica	-0.250	0.3819	-0.655	0.542	-0.0500	0.2132	-0.235	0.824
BR × S	0.250	0.3819	0.655	0.542	0.0750	0.3132	0.352	0.739
Silica × S	1.000	0.3819	2.619	0.047	0.2750	0.3132	1.29	0.254
*CODED	S=0.7638, R-Sq=98.1%, R-Sq(adj.)=94.6%				S=0.4264, R-Sq=94%, R-Sq(adj.)=83.1%			

## Appendix: The analysis of variance

Analysis of Variance for MH-ML						
Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	9	113.877	113.877	12.6530	21.13	0.002
Linear	3	106.073	106.073	35.3578	59.04	0.000
Square	3	1.972	1.972	0.6572	1.10	0.431
Interaction	3	5.832	5.832	1.9441	3.25	0.119
Residual Error	5	2.994	2.994	0.5989		
Lack-of-Fit	3	2.434	2.434	0.8113	2.89	0.267
Pure Error	2	0.561	0.561	0.2803		
Total	14	116.872				

Analysis of Variance for Tensile						
Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	9	15.0108	15.0108	1.6679	5.93	0.032
Linear	3	9.1825	9.1825	3.0608	10.89	0.012
Square	3	2.6858	2.6858	0.8953	3.18	0.122
Interaction	3	3.1425	3.1425	1.0475	3.73	0.095
Residual Error	5	1.4058	1.4058	0.2812		
Lack-of-Fit	3	1.0925	1.0925	0.3642	2.32	0.315
Pure Error	2	0.3133	0.3133	0.1566		
Total	14	16.4166				

Analysis of Variance for M300						
Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	9	13.9809	13.9809	1.55344	6.93	0.023
Linear	3	13.3662	13.3662	4.45541	19.89	0.003
Square	3	0.1945	0.1945	0.06483	0.29	0.832
Interaction	3	0.4202	0.4202	0.14008	0.63	0.629
Residual Error	5	1.1200	1.1200	0.22400		
Lack-of-Fit	3	0.8162	0.8162	0.27207	1.79	0.378
Pure Error	2	0.3038	0.3038	0.15190		
Total	14	15.1010				

Analysis of Variance for C.G.R						
Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	9	0.170883	0.170883	0.018987	7.01	0.023
Linear	3	0.125283	0.125283	0.041761	15.42	0.006
Square	3	0.029351	0.029351	0.009784	3.61	0.100
Interaction	3	0.016249	0.016249	0.005416	2.00	0.233
Residual Error	5	0.013545	0.013545	0.002709		
Lack-of-Fit	3	0.006932	0.006932	0.002311	0.70	0.634
Pure Error	2	0.006613	0.006613	0.003306		
Total	14	0.184428				

Analysis of Variance for Tear						
Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	9	1391.45	1391.453	154.606	16.36	0.003
Linear	3	971.90	971.898	323.966	34.29	0.001
Square	3	126.10	126.103	42.034	4.45	0.071
Interaction	3	293.45	293.453	97.818	10.35	0.014
Residual Error	5	47.24	47.244	9.449		
Lack-of-Fit	3	42.44	42.438	14.146	5.89	0.149
Pure Error	2	4.81	4.807	2.403		
Total	14	1438.70				

Analysis of Variance for Abrasion						
Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	9	2921.67	2921.67	324.630	12.01	0.007
Linear	3	2243.06	2243.06	747.688	27.65	0.002
Square	3	412.63	412.63	137.544	5.09	0.056

TABLE-4  
OPTIMIZING AND PREDICTION OF OPTIMIZED FORMULATION PROPERTIES

<b>Response optimization</b>						
Parameters	Goal	Lower	Target	Upper	Wight	Import
Tear	Target	35.0	45.0	55.0	1	1
Tensile	Target	20.0	21.0	24.0	1	1
C.G.R	Target	0.2	0.5	0.6	1	1
Abrasion	Target	55.0	70.0	80.0	1	1
Hardness	Target	51.0	53.0	56.0	1	1
Resilience	Target	23.0	24.0	25.0	1	1
M300	Target	5.0	7.0	9.0	1	1

**Global solution:** BR = 40.0586; Silica = 18.9537; S = 1.3400.

**Predicted responses:**

Tear = 48.9676; desirability = 0.60324;      Tensile = 21.9226; desirability = 0.69247  
 C.G.R = 0.5217; desirability = 0.78335;      Abrasion = 67.1521; desirability = 0.81014  
 Hardness = 51.2416; desirability = 0.12082;      Resilience = 24.3205; desirability = 0.67952  
 M300 = 6.7908; desirability = 0.89539

**Composite desirability = 0.56974**

**Tensile and modulus:** The variation in tensile strength and modulus with content of BR, silica and sulfur are shown as surface plots in Figs. 2 and 3, respectively. Tensile strength is the force needed to rupture a dumbbell specimen. Modulus is an expression of the force per cross sectional unit area required to stretch a test specimen to a given elongation. It may also be considered as resistance to elongation or as stiffness in the vulcanizates. From Fig. 2a it is clear that the tensile strength decreases in high BR and silica levels. The statistical analysis presented in table 3 shows that the negative effect of silica and BR on the tensile behaviour is significant while it is not like that for sulfur. However the interaction term BR\*S is significant (P = 0.047). As shown in Fig. 2b, the increasing of the sulfur contents increase the tensile strength in particular in high BR domains. The same behaviour is observed in high silica domains (the results has not been demonstrated). There is a significant dependency between modulus and the silica and sulfur variables as shown in Fig. 3. The modulus 300 % decreases with increase of silica levels and decreases after increase of sulfur content, while no significant change is observed in BR substituted compounds. No significant square and interaction terms are observed. The negative effect of silica on the modulus shows that the silica (even beside silanes) diminishes the filler-rubber interactions. This is due to lower compatibility of modified silica with rubber domains compared to the carbon black. On the other hand the decrease of crosslink density has a negative effect on modulus in silica domains. Increase of sulfur levels increases the crosslink density and modulus.

**Dematia crack growth rate:** The statistical analysis of crack growth rate (CGR) clearly show the significant effect of BR, silica and sulfur. The square term for S is significant (the P-valule of S\*S is 0.029). The variation in crack growth rate with content of silica, BR and sulfur are shown as surface plots in Figs. 4a and 4b. The



silica substituting has a positive effect on crack growth behaviour while increase of BR level has a negative effect. However the negative effect of BR substituting diminishes in high silica domains.

Effect of sulfur on crack growth rate is presented in Fig. 4b. The crack growth rate increases up to the maximum beyond which it becomes nearly constant. Again the negative effect of sulfur on crack growth rate is more obvious in absence of silica and less obvious in high silica domains (Fig. 4b).

Comparing surface plots 1 and 4 show that there is similarity between the curves. In order to study governing mechanisms on tearing and crack growth behaviour, it is important to know that in order that a failure occurs, 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. The first is called catastrophic energy dissipation and the second noncatastrophic energy dissipation<sup>17,18</sup>.

Increasing modulus, will increase the stored elastic energy and as the result the available energy in crack tips will increase. So the crack growth rate will increase. The very significant and positive effect of silica on dimatia crack growth behaviour could be plausible from it's negative effect on crosslink density and modulus. In low modulus domain the BR substitution has a little negative effect on crack growth rate.

However as shown in Figs. 3 and 4 although the increase of sulfur amount would increase the modulus, the crack growth rate approaches to a maximum and remain constant with further increase of sulfur levels. So the other mechanisms could be considered. It is widely thought that the polysulfidic links results in higher 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<sup>27-29</sup>. The increase of sulfur contents would increase the percentage of polysulfidic bonds.

**Tear strength:** According to the statistical analysis as presented in Table-3, the calculated regression coefficient of BR (-4.788), silica (6.875) and sulfur (-7.143) are significant statistically (the calculated P-value is 0.007, 0.001, 0.001, respectively), that means these factors have a significant role on tear strength. The silica has a positive effect, but the BR and sulfur have a negative one. Dependency of tear to BR is linear, however the square term for sulfur and silica is significant. (The P-value for S × S is 0.05 and for silica × silica is 0.043). The regression coefficient of silica × BR and silica × S interaction terms are also significant (the calculate P-value is 0.048 and 0.008, respectively).

Change in tear strength with content of silica and butadiene rubber in fix amount of sulfur plotted as surface is shown in Fig. 5a.

The overall behaviour of the tear strength is that it increases significantly with increase in silica and decreases with increase of BR. However, the improving effect of silica on tear resistance is enhanced in high amount of BR substituting. In addition, the negative effect of the increase of BR diminishes in high silica domain as presented in Fig. 5a. No significant change is observed on tear resistance when BR amount increases in 20 phr silica substitution.

The effect of sulfur on tear resistant has been shown in surface plot (Fig. 5b). The tear resistant decreases with increase of sulfur amount. However this negative behaviour diminishes in high silica domains. On the other hand the improving effect of silica diminishes in low content sulfur domains.

The desirable effect of silica on tears and crack growth behaviour of understudy formulations could be explained according to the governing mechanisms. The lower interaction of silica/rubber results in higher rubber chain deformation capability. However due to silanization reaction, 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. It seems that presence of silica could optimize the rubber/filler interaction. This leads to more consumption of input elastic energy through noncatastrophic energy dissipation process rather catastrophic energy dissipation.

The same explanation exists for the negative effect of sulfur on tear strength; the increase of crosslinks would restrict the rubber movement.

So it is predictable and it has been shown in Fig. 5b that in high silica domains where the movement of the rubber chains is considerable, the increase of sulfur has no negative effect on tear strength.

**Abrasion behaviour:** From Fig. 6a it is evident that abrasion loss ( $\text{mm}^3$ ) decreases with increase of BR and decreases with increase of silica. The P-values are significant in view of statistical analysis. This behaviour shows that lower filler-rubber interaction is harmful for abrasion behaviour.

It is important to note that in high amount of BR (45 phr), the increase of silica content has a little negative effect on abrasion loss (the P-value for silica  $\times$  BR is 0.034).

The effect of sulfur on abrasion behaviour is nearly insignificant (P-value = 0.376). However a little increase up to a maximum is observed when sulfur content increases (Fig. 6b).

The negative effect of silica on abrasion behaviour is also diminishes in high sulfur domains that support the importance of filler-rubber and rubber-rubber interactions in abrasion behaviours.

**Hardness:** Hardness in rubber is defined as the ability to resist indentation. It can be seen from Fig. 7 that, silica gives lower hardness values compared to N330. However, as the loading of sulfur increases, the hardness increases. The change of BR level has no effect on hardness.

The hardness behaviour is dependent on the crosslink density and filler-rubber interactions. The lower crosslink density and filler-rubber interaction is the main reasons for lower hardness in silica substituted compounds.

**Impact resilience:** Impact resilience (rebound) represents the per cent of returned energy when a pendulum is dropped against a sample. No significant change is observed in resilience in different BR levels (Fig. 8a). However, the effect of sulfur on resilience is significant (Fig. 8b). The resilience of compound would increase with increase of crosslink density. Resilience decreases with increase of silica level to some extent. The negative effect of silica on resilience is not as high as its effect on the hardness because the lower filler-rubber interaction is favour of resilience.

**Optimization:** The procedure of optimizing is presented in Table-4. First, the target and lower and upper limits for each property has been specified as shown in upper section of the table. Then, the best amount for BR, silica/silane and sulfur have been calculated by the software (the middle part of Table-4) and the values for this condition have been predicted as shown in lower section of Table-4. The calculations have been made with the help of the mathematic equation derived for each property.

According to the calculations it is possible to decrease the amount of NR/BR from 75/25 to 60/40 in presence of 19 phr silica while the amount of sulfur keeps high. The predicted values are: tear strength; 49, tensile; 21.9, CGR; 0.52, hardness; 52, modulus; 6.8 resilience; 24.3, abrasion; 67.

Compared to the reference compound, tear strength; 41.6, tensile; 23.1, CGR; 0.59 hardness; 55, modulus; 8.9, resilience; 24.2, abrasion; 76.7, the optimized formulation with lower NR/BR ratio (rather than reference one) has a better failure behaviour (tear, crack growth and abrasion), the same resilience but the lower modulus, hardness and tensile.

## Conclusion

According to the results which are obtained from response surface methodology, the silica would improve the tear and crack growth behaviour while the drop in abrasion, hardness, resilience and tensile is observed in silica substituted compounds. However, when levels of BR increase the negative effect of silica on abrasion decreases. On the other hand in high silica domains increase of sulfur content has no significant negative effect on tear and crack growth. So it is possible to decrease the ratio of NR/BR in high silica domains and sulfur.

However the optimized formulation has a lower hardness compared to the reference one and may be a critical negative factor. It seems that increase of sulfur levels up to 1.34 would improve the hardness without significant effect on the failure properties. The increase of filler contents, optimization of silane amounts, use of novel fillers such as sulfron 3000 could help to achieve the better balances between the properties. Theses subjects are under study now.

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### REFERENCES

1. G. Kraus, Reinforcement of Elastomers, John S. Wiley & Son, New York (1965).
2. W.C. Fultz and L.R. Evans, J.M. Hubber Corp., Tire Tread Compound With Silica/CB Blends, *Rubber World*, pp. 39-42 (1998).
3. B. Schwaiger and A. Blume, Degussa-Huls AG, Silica/Silane a Winning Reinforcement Formula, *Rubber World*, pp. 32-33 (2000).
4. C. Hartshorn, *Tire Technol. Int.*, 94 (2007).
5. M.A. Ansarifar, *Tire Technol. Int.*, 63 (2001).
6. M.P. Wangner, *Rubber Chem. Technol.*, **49**, 703 (1976).
7. P. Sae-oui, C. Sirisinha, U. Thepsuwan and K. Hatthapanit, *Eur. Polym. J.*, **42**, 479 (2006).
8. M.A. Ansarifar and R. Nijhawan, *Tire Technol. Int.*, 47 (2000).
9. M.-J. Wang and S. Wolf, Filler Elastomer Interactions. Part 1: Silica Surfaces Energies and Interactions with Model Compounds, Presented at Meeting of Rubber Division, American Chemical Society, Loss Vegas, Nevada, May 29 to June 1 (1990); *Rubber Chem. Technol.*, **64**, 559 (1991).
10. M.J. Wang, S. Wolff and J.B. Donnet, *Rubber Chem. Technol.*, **64**, 714 (1991).
11. E. Tan, S. Wolf, M. Haddman, H. Grewatta and M.J. Wang, *Rubber Chem. Technol.*, **66**, 594 (1993).
12. M.-J. Wang and S. Wolf, *Rubber Chem. Technol.*, **65**, 715 (1992).
13. A.S. Hashim, B. Azahari, Y. Ikeda and S. Kohjiya, *Rubber Chem. Technol.*, **71**, 289 (1997).
14. G.R. Hamed, H.J. Kim and A.N. Gent, *Rubber Chem. Technol.*, **69**, 807 (1996).
15. R.G. Stacer, L.G. Yanoyo and F.N. Kelley, *Rubber Chem. Technol.*, **58**, 421 (1985).
16. H.Y. Kim and J. Kim, *J. Fatigue*, **27**, 263 (2005).
17. G. Hamed, *Rubber Chem. Technol.*, **67**, 529 (1994).
18. G.R. Hamed, *Rubber Chem. Technol.*, **64**, 493 (1991).
19. G. Derringer, *Rubber Chem. Technol.*, **61**, 377 (1987).
20. D.C. Montgomery, Design and Analysis of Experiments, JohnWiley and Sons, NewYork, USA, edn. 4, pp. 575-651 (1996).
21. F.C. Weissert and R.R. Cundiff, *Rubber Age*, **92**, 881 (1963).
22. D.V. Sarbach, R.W. Hallman, J.A. Paeoff and J.L. Stiness, *Rubber World*, **16-29**, 10, 61 (1970).
23. G.C. Derringer, *Rubber Age*, **101**, 66 (1969).
24. T.R. Kukreja, D. Kumar, K. Prasad, R.C. Chauhan, S. Choe and P.P. Kundu, *Eur. Polym. J.*, **38**, 1417 (2002).
25. J. Linda, Improved Black Sidewall Compound Performance Using Precipitated Silica, *Rubber World*, June 1 (1993).
26. G.C. Derringer, *Rubber Chem. Technol.*, **43**, 1526 (1970).
27. R.H. Gary, Materials and Compounds, USA, Ch. 2, pp. 12-34.
28. B. Chung, H.R. Tomlinson and T. Miller, Cure System and Carbon Black Effects on NR Compound Performance in Truck Tires, *Rubber World*, November (2002).
29. W.V. Mars, *Rubber Chem. Technol.*, **77**, 391 (2004).