

Response Surface Optimisation and Curing Kinetic Study of NR/SBR based Tyre Tread Formulation in the Presence of Expanded Clay

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A zinc stearate intercalated montmorillonite, ZnSt-MMT, was synthesised and partly replaced with carbon black in an NR/SBR based truck tyre tread formulation. The XRD results revealed that the basal spacing of the organoclay has been successfully expanded in the rubber network. A central composite design was employed to study the cis BR substitution (with NR), change of oil and sulphur content on the physical properties of carbon black/ZnSt-MMT-filled NR/SBR compounds. The response surface models for tensile strength, modulus, elongation, heat buildup (HBU), DeMattia cut growth (DCG), abrasion, hardness and delta torque of vulcanisates were developed and employed for optimisation through nonlinear programming algorithm framework. It was observed that the formulations with better balance of properties than reference may derive from response surface methodology (RSM) optimisation framework in the presence of ZnSt organoclay. A kinetic study was conducted on the basis of the rheometry data. It was observed that the Isayev and Deng kinetic model were able to fit all experimental design points with very high accuracy.

Keywords: Intercalated clay; statistical modeling; optimisation; abrasion; crack growth; kinetic study

Layered silicates such as montmorillonite (MMT) clay with sheet-like platelets that are about 1 nm in thickness and 100–1000 nm in width and length are proven to have the potential to reinforce polymer and rubber composites^{1–4}. To render layered silicates miscible with polymer matrices which are organophilic and to obtain good interfacial adhesion and mechanical properties, one

must convert the normally hydrophilic silicate surface to an organophilic one^{4–9}.

Several routes can be employed to modify clays and clay minerals^{5–10}. Ion exchange with alkylammonium ions is well-known preferred method to prepare organoclays^{1–2,5,9}. The principal building elements of the MMT are two-dimensional arrays of silicon-oxygen

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tetrahedral and two-dimensional arrays of aluminium or magnesium-oxygen/hydroxyl octahedral units which are superimposed in a 2:1 ratio. Partial replacement of trivalent Al by divalent Mg in the octahedral sheet of MMT results in a high negative surface charge of the layer. This fact renders the space between the layer surfaces capable of accommodating cations. Furthermore, the charge compensating cations on the layer surfaces may be easily exchanged by other cations when available in aqueous solution. Hence, they are called exchangeable cations. By exchanging interlayer cations for organic cations, the surface energy of MMT decreases and the interlayer spacing expands. The resulting material is called organoclay.

Organically modified montmorillonites have been widely studied fundamentally and in practical applications in the area of polymer and rubber composites and nano-scale composites. In the past ten years, several rubbers served as matrices in organoclay-filled systems^{11–13}. Mohamed and Simon¹¹ and Utracki¹² recently reported the most significant advances happened in the preparation, characterisation and properties of organoclay/rubber nanocomposites based on several rubber matrices. However, the benefits of organoclay and nanocomposites for some applications such as tyre tread compounds have been limited. Ammonium salts are widely used for preparation of commercially organoclays. Galimberti^{15,16} investigated the filler networking phenomena in the presence of ammonium salt modified clays and confirmed that organoclay is able to form a hybrid filler network with carbon black (CB), revealing affinity for carbonaceous filler, bringing about a decrease of filler networking phenomena. The networking phenomena is reflected through the increase of Payne effect and higher Young's modulus, dynamic modulus, tan delta, heat buildup and hence, higher rolling resistance. Galimberti's

results demonstrated¹⁵ that organophilic ammonium cation effectively interacts with polar oxygenated groups present on the CB surface. The decrease of the filler networking phenomenon appears, due to the presence of a finely diffused CB network with the ammonium salt acting as network building block.

Indeed, type of surfactant plays a vital role in organoclay properties^{4–8,11–14}. Singla¹⁴ recently reported the montmorillonite modification with different water soluble and water insoluble organic cationic surfactants. Increase in basal spacing was successfully achieved by using zinc stearate as surfactant. Zinc stearate is a fatty acid which has hydrophobic effect. They are cheap and easily available. So, they have potential for commercial production. The application of zinc stearate modified clay in rubbery materials has not been addressed in the literature. The present study aims to investigate the benefits of this substitution in a typical blend of elastomers. Blending of elastomers has often been used to obtain an optimum number of desirable combinations, physical properties, processability and cost. The philosophy of mixing materials involves combining good properties of the individual materials, while mitigating their respective detrimental characteristics. The blend of natural rubber with styrene butadiene and butadiene rubber is typical in tyre applications. However, very limited studies were aimed to investigate the effect of expanded clays in these blends¹⁷.

In this study, we present a systematic study on the basis of response surface methodology to investigate the potential of zinc stearate expanded clay in a typical NR/SBR(/BR) tyre tread formulation to give better balances between the physical and the mechanical properties. A kinetic study was also conducted to investigate the curing behaviour of the

compounds in the presence of zinc stearate modified clay.

antiozonants and accelerators were supplied by Henan Chemicals, China.

EXPERIMENTS

Material

Natural rubber, (SMR20–MR9, Mooney viscosity ML (1+4) 100°C = 88, density = 0.910 gr/cm³, plasticity retention index, PRI = 59.9) was supplied by Marub Co., Malaysia. *Cis* butadiene rubber (PBR-1220, Mooney viscosity ML(1+4)100°C = 45, density = 0.908) and emulsion styrene butadiene rubber (SBR1502-5553, % styrene = 22.5, Mooney viscosity ML (1+4)100°C = 48, density = 0.954) were obtained from Arak Petrochemical, Iran and Bandare Imam Petrochemical, Iran, respectively. Carbon black N375 (density = 1.78, pH = 8.68, iodine number = 90, dibutyl-phtalate specific surface area, DBP = 115 ml/g) were obtained from Doodeh Sanati Pars Co., Iran. Zinc stearate (density = 1.09, melting point = 120°C) was purchased from Ideh Gostarane Farayand Co., Iran. Aromatic oil (flash point = 232°C, aniline point = 33, density = 0.99, viscosity = 26cst, acid number = 0.47mgKOH/g) used as a processing aid was obtained from Behran Oil Co. Zinc oxide (density = 5.5) and stearic acid (iodine value = 3.2, acid value = 206) were supplied by Pars Oxide Co., Iran and Palm Oleo Co., Malaysia, respectively. Sulphur was supplied from Tesdak Co., Iran.

The minerals including bentonite (Ca–Montmorillonite, pH = 9.7 density = 2.6), kaolin (density = 2.5, pH = 8.2), calcium carbonate (pH = 9.4, density = 2.52, BET = 7 m²/g) and talc powder (pH = 8.9, density = 2.56) were obtained from Toos Co., Kaolin Khorasan Co., Iran, Chemie Madani Hamadan Co., and Omya Pars Co., Iran, respectively. Other chemicals including antioxidants,

Organoclay Preparation

Ca-MMT (Ca-montmorillonite) was provided by Toos Co. Aqueous slurry of Ca-MMT was prepared by adding 20 g of Ca-MMT to 1000 cc of water at 80°C and agitation for 90 minutes. By adding hydrochloride acid solution (0.1 N) and zinc stearate (0.03 M) to above slurry and heating at 80°C, filtering, washing with a hot water/ethanol mixture and drying, a solid precipitate organoclay was obtained. The product has been named as ZnSt-MMT in this study. The pH of ZnSt-MMT was 6.8 and it was very hydrophobic when dispersed in water.

Organoclay Characterisation

XRD analysis on MMT and ZnSt-MMT samples was performed on a Rigaku RINT2200/PC diffractometer with Cu-K α radiation at 40 kV and 30 mA. The X-ray diffraction of the clay/rubber nanocomposites was determined using a XPert MPD Philips X-ray diffractometer using monochromatic Co radiation at 40 kV and 40 mA with 2 θ scan range of 1 up to 12 and step size of 0.02°/s. The spacing between the intercalated layers of the clay was calculated from Braggs law:

$$n\lambda = 2d \sin \theta \quad \dots 1$$

where, d is lattice spacing, λ is the wavelength of incident wave, θ is diffraction angle and n is a positive integer.

Design of the Experiments

The NR/SBR reference (control) model truck tyre tread formulation is presented

in *Table 1*. Initial simple experiments were conducted to highlight the important factors and overall behaviours as well as determination of some aspects of the levels of factors in the presence of ZnSt-MMT. *Table 2* demonstrates the initial experiments including the formulations and the results. Substitution of carbon black with some minerals such as unexpanded MMT, precipitated calcium carbonate (CaCO_3) and talc powder was also investigated in similar hardness of compounds. In the next step, based on results of the first study, a central composite design (CCD) was employed to model the dependency of physical and mechanical behaviours according to the ingredients levels in the presence of ZnSt-MMT.

Preparation of the Compounds

A laboratory-sized internal mixer (POMINI MIX32) was used to prepare the master rubber compounds. The mixing conditions were set as follows; fill factor: 0.75, rotor speed: 60 rpm, initial chamber temperature: 70°C, ram pressure: 6 bar, mixing producers: 1-mastication of rubbers, chemicals and organoclay/minerals (40s), 2 additions of

carbon black (30s), 3 additions of oil (30s), 4 dumpings (when the temperature reaches 170°C or the time to reach 100s in dumping step). The efficient mixing times of about 200–220s with mixing energies in the range of 0.13–0.16 kWh/kg of compound was recorded according to the above mixing conditions for the compounds in the present study. After mixing, the compounds were sheeted out using the two-roll mill (MCCIN 152 X 305 R - E). Vulcanisation ingredients were added 24 h later on a two-roll mill.

Curing and Test

Cure characteristics were determined using an oscillating disk rheometer (ODR) and moving die rheometer (MDR), produced by Alpha Technology. Delta torque (DH) is the maximum torque minus the minimum torque. Sheets and test specimens were vulcanised by compression moulding in a curing press at 151°C for the definite period as determined according to the ODR optimum curing time. Tensile stress-strain properties were determined according to *ASTM D 412*. Dumbbell shaped tensile strength samples were punched out from the vulcanised sheets.

TABLE 1. CONTROL AND MODEL TRUCK TREAD FORMULATIONS

	Reference Formula	CCD Formulations
NR	60	44–56
SBR	40	40
cis BR	0	4–16
N375	50	42
Minerals/Organoclay	0	5
OIL	10	4–11
S.A	2	2
ZnO	4	4
ANOX	1	1
6PPD	1.5	1.5
RIOWAX	2	2
Accelerator	0.9	0.9
Sulphur	1.49	1.6–2.1

TABLE 2. THE FORMULATION AND RESULTS OF PARTLY SUBSTITUTION OF CARBON BLACK WITH NC (ZNST-MMT) BEFORE DOE STUDY

Compound Code	Factors and their levels				Responses (Physical/mechanical properties of vulcanisates)							
	BR	Oil	S	N370/minerals	DH (N.m)	Tensile strength (MPa)	Elongation	M300 (MPa)	Hardness (shore A)	HBV (°C)	DCG (mm in 20kc)	Abrasion (mm3)
a ₁ *	0	10.02	1.49	50/0	2.37	23	532	9.2	59	28	8	150
a ₂	0	10.02	1.49	40/0	1.93	20	637	5.8	54	32	5	150
a ₃	0	10.02	1.49	45/ 5 ZnSt MMT	1.98	21	584	7.5	58	33	6	144
a ₄	0	10.02	1.49	40/ 5 ZnSt MMT	1.90	21	641	6.3	54	30	5	141
a ₅	0	7.02	1.49	40/ 5 ZnSt MMT	1.93	22	622	6.8	54	30	6	136
a ₆	10	7.02	1.49	40/ 5 ZnSt MMT	1.95	22	638	6.5	52	32	7	129
a ₇	10	7.02	1.80	40/ 5 ZnSt MMT	2.24	22	580	7.9	57	29	8	127
a ₈ **	16.4	7.29	1.88	42/ 5 ZnSt MMT	2.32	20	523	8.8	61	28	10	133
a ₉	16.4	7.29	1.88	42/ 5 MMT	2.11	19	522	8.5	59	27	11	147
a ₁₀	16.4	7.29	1.88	42/ 5 Talc	2.50	22	492	11.03	60	29	16	132
a ₁₁	16.4	7.29	1.88	42/ 5 prc. CaCO3	2.49	20	476	10.3	62	27	14	134

*Reference Compound, see also *Table 1*

** Optimised formulation, see section response surface modeling and response surface optimisation

DH: Delta Torque

At least five tests were carried out for each sample. In all cases, good reproducibility was obtained indicating absence of large-scale in homogeneity.

DIN abrasion was performed as per *ISO 4649* and hardness test was determined according to *ASTM D 2240*. The crack growth of vulcanisates was measured using a DeMattia crack growth tester. The average crack growth (mm) of six samples in 20 k-cycles was reported. Heat build up was determined using a Goodrich Flexometer (load: 11 kg; stork: 0.445 cm; frequency: 30 Hz).

Development of Response Surface Models

Response surface methodology (RSM) requires initially a proper design of experiments to estimate the model parameters effectively. Based on the special criteria and the selection of experimental points, different experimental designs may be performed. The next step of RSM is to approximate a suitable model to fit the experimental data¹⁸⁻¹⁹. The most common polynomial models which are used for RSM analysis are first-order and the quadratic or second-order model. For the responses that have curvature, a second-order model is recommended:

$$Y = b_0 + \sum_{i=1}^k b_i x_i + \sum_{i=1}^k b_{ii} x_i^2 + \sum_i \sum_j b_{ij} x_i x_j + \varepsilon r \quad \dots 2$$

Parameters of the polynomial models (b) are estimated by the least squares method. Y is (n × 1) vector of responses. X defined as (n × p) matrix of independent variables; b, as an (p × 1) vector of parameters to be estimated and ε , as (n × 1) vector of errors. Thus, *Equation 2* can be written in matrix form as: $Y = Xb + \varepsilon$. The least squares estimator of b that minimises sum of the squares of the errors is $\hat{b}$ given by:

$\hat{b} = (X^T X)^{-1} X^T Y$ where X^T is the transpose of the matrix X and $(X^T X)^{-1}$ is the inverse of the matrix $(X^T X)$. The regression coefficient, R^2 value is a useful test for goodness of fit. Values of R^2 range from 0 to 100. It is important that R^2 is not the only test of fit for a model as large values of R^2 could also result from overfitting the data.

The principal model analysis is based on analysis of variance, which provides numerical information for the F-value and the P-value. The last two tests imply significance of a model degree and particular linear, quadratic or interaction terms. Usually, P-values smaller than 0.05 signify that the particular term of a model has a significant effect on the response. F-value of regression and F-value of lack of fit are used to check the adequacy of the response surface models. F-regression is defined according to *Equation 3*.

$$F_{\text{regression}} = MSR/MSE \quad \dots 3$$

where MSR is mean sum of regression and MSE is mean square error. This value is compared with a standard F distribution value obtained at the appropriate degrees of freedom and significance level (95%). If the value of the F-statistic is less than the associated F distribution value, the test suggests that the model fits the data and the polynomial has adequacy according to the statistical judgment. A nonlinear optimisation programming according to the desirability concept was conducted for multi-optimisation purposes.

Kinetic Study

Typical cure curves can be obtained with an MDR which is technically a curemeter. This equipment is used to measure the torque required to oscillate the die. As vulcanisation proceeds at a specific temperature, the torque required to shear the rubber compound

increases and a curve of torque versus curing time can be generated. The state of cure or degree of cure, α , which represents the extent of reaction, has been obtained from MDR data according to the following equation:

$$\frac{M(t) - ML}{MH - ML} \dots 4$$

where ML , MH and $M(t)$ are minimum, maximum and torque in time t , respectively. To model the kinetics it is necessary for deriving an equation expressing $\frac{d(\alpha)}{dt}$. Several phenomenological and mechanistic kinetic models have been presented to demonstrate the sulphur curing behaviour of rubbery materials²⁰⁻²¹. In this study, cftool GUI in MATLAB 2009 was used to conduct curve fitting of different kinetic models according to the experimental α values in each experiment. The nonlinear curve fitting was done with the method of nonlinear least squares and trust-region algorithm.

RESULTS AND DISCUSSION

XRD

The enhancement of properties in rubber nanocomposites is directly related to the extent and quality of dispersion and to the degree of clay mineral exfoliation and/or rubber intercalation in the nanocomposite as well as quality of adhesion at the rubber–clay interface¹⁻¹⁴. XRD of different samples of modified MMT clay give the values of basal spacing. The XRD patterns of the MMT and ZnSt modified MMT are shown in *Figures 1* and *2*, respectively. The neat MMT showed the (001) reflection at $2\theta = 7.08^\circ$ corresponding to the basal spacing of 1.25 nm (*Figure 1*). The exchange of the interlayer cations of the neat MMT with Zn ions enlarges the interlayer spacing from 1.25 nm to 1.34 and 1.99 nm

($2\theta = 6.6^\circ$ and $2\theta = 4.4^\circ$) as shown in *Figure 2*. The XRD result in *Figure 2* consequently confirms the successful intercalation of Zn cations into MMT plates. *Figure 3*, a peak at approximately $2\theta = 2.13$ represents the (001) diffraction of clay in rubber matrix and the corresponding basal spacing is ca 4.8 nm.

One Variable at a Time Study Results

Table 2 presents the formulation and the results of vulcanisates. The compound a_1 is the reference formulation. 10 phr decrease of N375, without introducing of ZnSt-MMT (compound a_2) shows significant decrease of M300, tensile strength and hardness as presented in *Table 2*. The higher elongation at break and also lower modulus and hardness resulted from the lower crosslink density (DH values, *Table 2*) and the lower total filler loading. Five phr replacing of N375 with 5 phr ZnSt-MMT (compound a_3) shows the increase of HBU and some improvement of abrasion, compared to a_1 compound.

However, 10 phr replacing of N375 by 5 phr ZnSt-MMT (compare a_4 and a_1 compounds) shows improving effect on abrasion and DeMattia cut growth (DCG) while only the M300 has been decreased. The N375/ ZnSt-MMT = 40/5 was selected and in the next steps the effect of oil content, *cis* butadiene rubber (BR) replacing and sulphur (S) was studied. Compound a_5 presents the effect of oil decreasing in N375/ ZnSt-MMT (40/5) vulcanisates. The results reveal that M300, tensile strength and abrasion improved to some extent, while an increase in DCG and also heat built up (HBU) were observed compared to the compound a_4 . Partly substitution of natural rubber with *cis* butadiene rubber (BR) has improved abrasion resistance (a_6 compound). However, a decrease in hardness, M300 and an increase in HBU were observed. Finally, the high level of sulphur has improved M300,

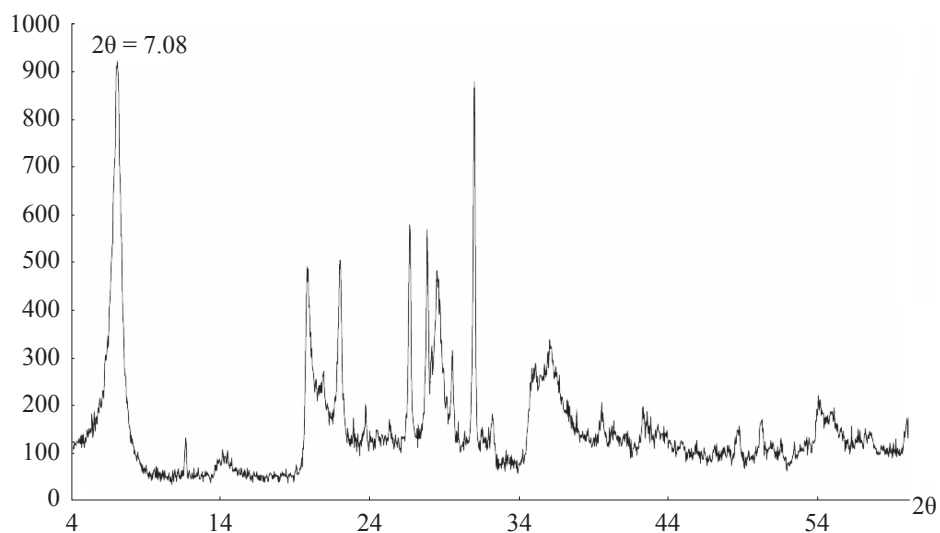


Figure 1. XRD pattern of MMT, $2\theta = 7.08^\circ$ corresponding to the basal spacing of 1.25 nm.

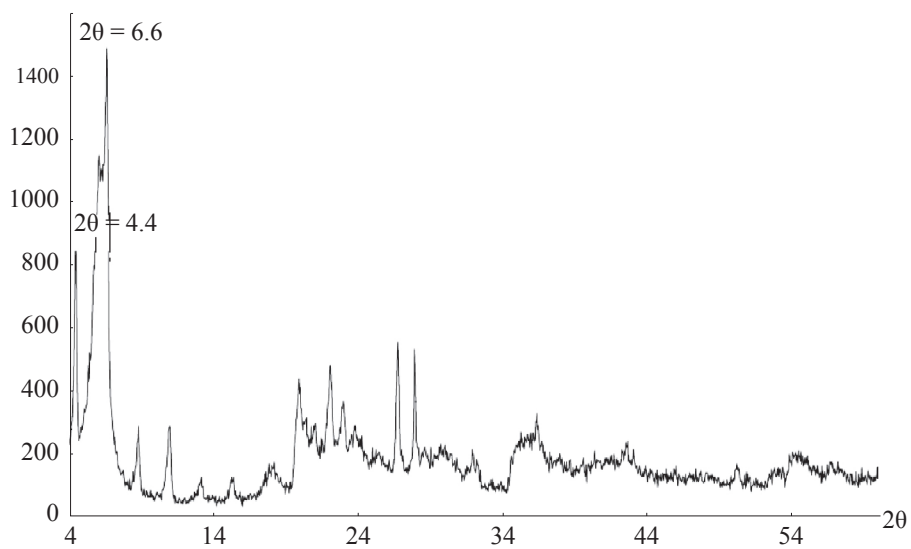


Figure 2. XRD pattern of ZnSt-MMT, $2\theta = 6.6^\circ$ and $2\theta = 4.4^\circ$ corresponding to the basal spacing of 1.34 and 1.99 nm, respectively.

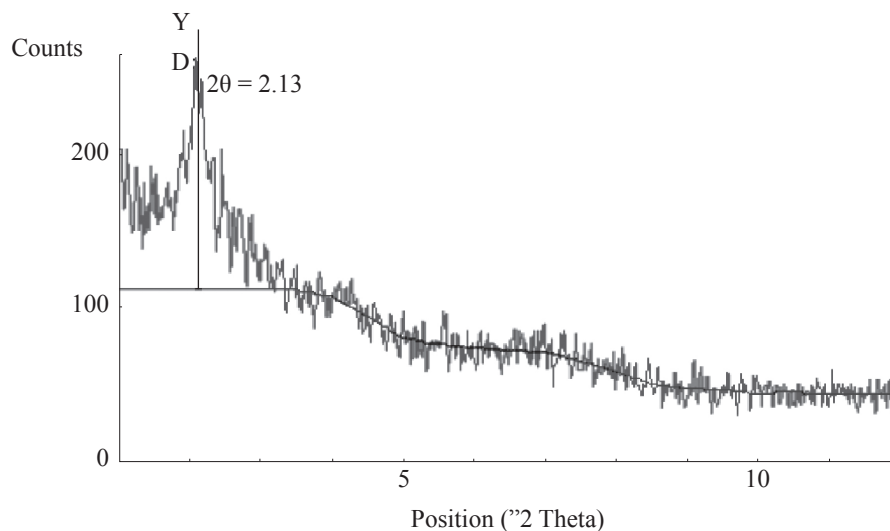


Figure 3. XRD patterns of clay/rubber nanocomposites based on NR/SBR blends. The peak at approximately $2\theta = 2.13$ represents the (001) diffraction of clay in rubber matrix and the corresponding basal spacing is ca. 4.8 nm.

hardness and HBU without significant effect on the abrasion as observed in compound a_7 . The results reveal that comparing with the reference compound (a_1), blend of N375/ZnSt-MMT (40/5) after some modification of other formulation ingredients (a_7) gave better balance of properties especially in DIN abrasion. Compound a_8 shows the results of optimised compound according to response surface methodology. Details are presented in the next section.

In addition some substituted compounds with other minerals such as unmodified MMT (compound a_9), talc (compound a_{10}) and precipitated CaCO_3 (compound a_{11}) in similar hardness have been investigated. In general, the results in Table 2 clearly show better performance of ZnSt-MMT according to the balances between tensile strength, DCG and DIN abrasion. The results also present that the ZnSt-MMT (5 phr) has the same reinforcing efficiency as that of the 4–10 phr of N375 in NR/SBR and NR/SBR/BR compounds.

Response Surface Modeling

Table 3 shows the design matrix and experimental results for those factors in the modeling trials. The level of BR substitution, oil and sulphur was changed according to the experimental design. The level of carbon black and ZnSt-MMT were kept constant at 42 and 5 phr, respectively for all formulations. The experimental results (Table 3) obtained from RSM were fitted to a second-order polynomial equation (Equation 2), giving the second-order response surface model. The regression coefficient and ANOVA results revealed that the obtained model was significant (Tables 4 and 5). The correlation coefficient (R^2), adjusted R^2 and predicted R^2 for all models are high. Therefore, the models are good fits for the design space. The analysis of variance (ANOVA) was conducted at 95% confidence interval and the results are presented in Tables 4 and 5. The $P\text{-value} < 0.05$ states that the model is statistically significant. It is evident that all models were highly significant, as suggested

TABLE 3. CENTRAL COMPOSITE ROTATABLE DESIGN (CCRD) MATRIX OF INDEPENDENT VARIABLES AND EXPERIMENTAL RESULTS

Compound Code	Factors and their levels			Responses (Physical/mechanical properties of vulcanisates)							
	BR	Oil	S	DH (N.m)	Tensile strength (MPa)	Elongation (MPa)	M300 (shore A)	Hardness (°C)	HBU (mm in 20kc)	DCG (mm ³)	Abrasion
C. 1	10.50	8.00	1.85	2.15	22	575	8.3	57	29	7	186
C. 2	10.50	4.64	1.85	2.37	22	512	10.1	60	30	7	166
C. 3	4.61	8.00	1.85	2.15	22	520	9.4	57	29	6	154
C. 4	14.00	6.00	1.70	2.26	23	572	8.8	59	31	5	157
C. 5	10.50	8.00	1.85	2.15	23	558	8.9	58	28	7	164
C. 6	16.39	8.00	1.85	2.26	21	546	8.7	59	28	6	143
C. 7	10.50	8.00	2.10	2.37	22	528	9.7	58	28	10	136
C. 8	10.50	11.36	1.85	2.03	20	576	7.7	56	29	4	178
C. 9	14.00	6.00	2.00	2.49	22	540	9.6	59	29	10	128
C. 10	7.00	10.00	2.00	2.26	22	557	8.8	58	29	6	135
C. 11	7.00	6.00	2.00	2.37	21	488	10.2	61	29	10	140
C. 12	10.50	8.00	1.60	1.81	21	590	7.5	56	28	8	209
C. 13	14.00	10.00	2.00	2.15	21	536	8.8	57	28	6	167
C. 14	10.50	8.00	1.85	2.03	21	553	8.5	58	28	7	179
C. 15	7.00	10.00	1.70	1.92	22	579	7.9	56	28	5	194
C. 16	7.00	6.00	1.70	2.03	22	522	9.4	56	27	5	198
C. 17	14.00	10.00	1.70	1.92	20	549	7.9	57	27	6	194

TABLE 4. COEFFICIENTS OF FITTED EQUATIONS AND THEIR SIGNIFICANCE

	DH		M300		Elongation		Tensile strength	
	Coefficient	P	Coefficient	P	Coefficient	P	Coefficient	P
Constant	2.11	0.00	8.57	0.00	561.97	0.00	22.10	0.00
BR	0.05	0.03	-0.31	0.03	11.77	0.02	-0.20	0.33
Oil	-0.18	0.00	-1.07	0.00	25.30	0.00	-0.71	0.01
S	0.25	0.00	0.87	0.00	-25.25	0.00	0.22	0.29
BR*BR	0.1	0.026	0.51	0.04	-29.62	0.01	-0.51	0.20
Oil*Oil	0.09	0.03	0.39	0.10	-18.83	0.04	-0.81	0.06
S*S	-0.02	0.67	0.05	0.83	-3.71	0.64	-0.21	0.57
BR*Oil	-0.16	0.01	0.45	0.11	-54.24	0.00	-1.64	0.01
BR*S	-0.08	0.11	-0.04	0.88	4.20	0.65	0.12	0.79
Oil*S	0.00	1.00	0.03	0.90	11.00	0.26	0.93	0.07
Statistics/ANOVA								
R2	97.8		96.17		95.30		85.51	
R2adj	94.97		91.24		89.26		66.89	
R2Pre	92.50		80.16		76.52		39.61	
F_Regression	34.56		19.52		15.78		4.59	
P_Value	0.00		0.00		0.00		0.03	

TABLE 5. COEFFICIENTS OF FITTED EQUATIONS AND THEIR SIGNIFICANCE

	DCG		Abrasion		HBU		Hardness	
	Coefficient	P	Coefficient	P	Coefficient	P	Coefficient	P
Constant	4.94	0.00	176.13	0.00	27.21	0.00	57.66	0.00
BR	-0.14	0.27	-4.78	0.17	-0.60	0.05	0.29	0.23
Oil	-0.58	0.00	10.78	0.01	-1.63	0.00	-1.94	0.00
S	0.93	0.00	-36.48	0.00	-0.02	0.94	1.52	0.00
BR*BR	-0.91	0.00	-27.43	0.00	0.66	0.19	0.46	0.30
Oil*Oil	-0.75	0.01	-3.89	0.53	2.16	0.00	0.46	0.30
S*S	1.69	0.00	-3.12	0.61	0.16	0.73	-0.54	0.23
BR*Oil	0.34	0.24	30.39	0.00	-3.89	0.00	-0.35	0.49
BR*S	0.24	0.38	21.51	0.02	-0.35	0.54	-2.47	0.00
Oil*S	-1.89	0.00	0.61	0.93	1.41	0.04	-1.06	0.07
Statistics/ANOVA								
R2	97.43		96.60		94.95		95.89	
R2adj	94.12		92.24		88.46		90.61	
R2Pre	81.62		88.12		61.15		67.94	
F_Regression	29.45		22.13		14.62		18.15	
P_Value	0.00		0.00		0.00		0.00	

by the model F-value and a low probability value ($P_{\text{model}} > F$). The analysis of variance (F-test) shows that the second models were well adjusted to the experimental data. The student's *t*-distribution and the corresponding *p*-value, along with the parameter estimate, are given in *Tables 4* and *5*. The *P*-values are used as a tool to check the significance of each of the coefficients. The smaller the *P*-values, the bigger the significance of the corresponding coefficient.

Delta Torque

From *Table 4*, it was observed that the linear effects of all variables on delta torque (DH) were significant ($P < 0.05$). Among the squared terms, coefficient of BR^2 and oil^2 was significant. The plots of the quadratic model with one variable kept at constant level and the other two varying with the experimental ranges are shown in *Figure 4*. In this plot, delta torque increased with an increase in BR and sulphur content. However, the results obtained from *Table 4* and *Figure 4* revealed that the interaction between BR and oil ($P = 0.01$), is statistically significant.

Tensile Strength Properties

The estimated regression coefficients as well as statistical analysis of tensile strength, modulus and elongation are presented in *Table 4*. The modulus of vulcanisates decreases with increase of oil and BR and it increases as sulphur increases as presented in *Table 4* and response surface plot in *Figure 5*. Among the squared terms, coefficient of BR^2 was statistically significant and the interactions between the factors were not significant. The results of *Table 4* reveal that the increase of BR content as well as oil would increase the elongation at break. However, sulphur would decrease the elongation. The interaction between BR and

oil was statistically significant. Among the squared terms, coefficient of BR^2 and oil^2 were significant. *Figure 6* shows the effect of BR and oil content on elongation of vulcanisates at low and high level of sulphur. The dependency of tensile strength on the understudy variables is shown in *Table 4* and response surface plot in *Figure 7*. The variations of tensile strength are shown to be very limited. However, the response surface model has been successfully developed.

Hardness

Figure 8 exhibits the relative effects of any two variables when the other variables are kept constant. Hardness increases with the increase of sulphur and it decreases with the increase of oil. However, the results obtained from *Table 5* and *Figure 8* revealed that the interaction between BR and S was significant ($P = 0.000$).

DCG

From statistical analysis (*Table 5*), it is evident that sensitivity of DCG to BR content reduces in the presence of carbon black/ZnSt-MMT. The regression coefficient of butadiene term is statistically insignificant from *t*-student test ($P = 0.27$). This is very critical in the design of the compound and shows that the negative effect of BR on DCG has not been statistically significant.

The statistically significant regression term of $oil * S$ suggests the complicated dependency of DCG on oil and S levels. *Figure 9* shows response surfaces established from the quadratic model (*Equation 2*) summarised in *Table 5* and reveals that DCG decreases according to the oil content in high sulphur levels but it increases in low sulphur levels. The estimated regression coefficients and

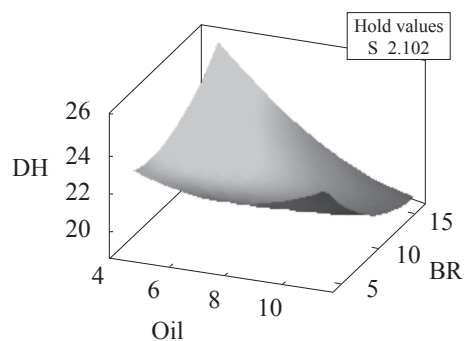
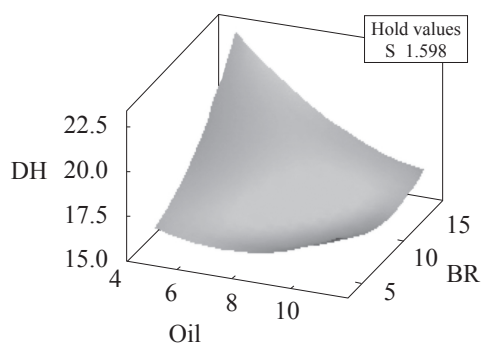


Figure 4. Response surface plots showing the effect of oil and BR on delta torque of vulcanisates. Sulphur content is held at high and low levels.

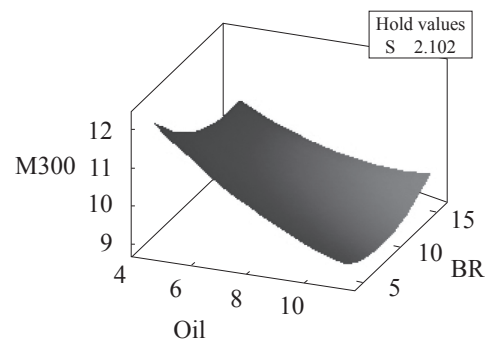
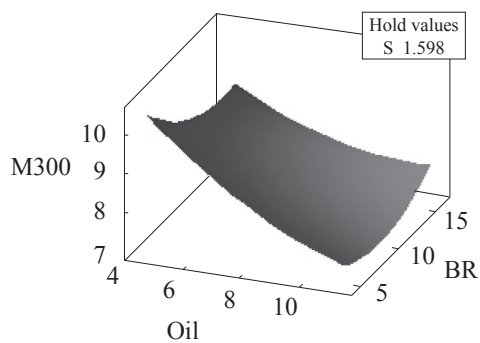


Figure 5. Response surface plots showing the effect of oil and BR on modulus of vulcanisates. Sulphur content is held at high and low levels.

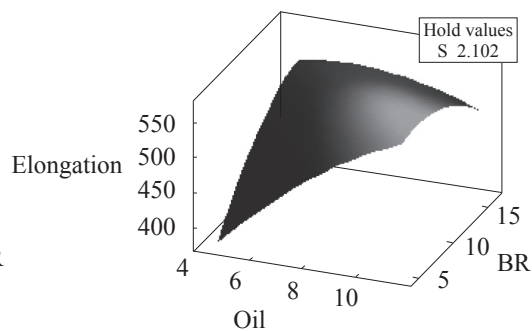
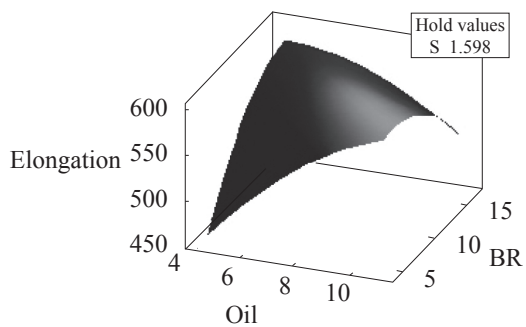


Figure 6. Response surface plots showing the effect of oil and BR on elongation of vulcanisates. Sulphur content is held at high and low levels.

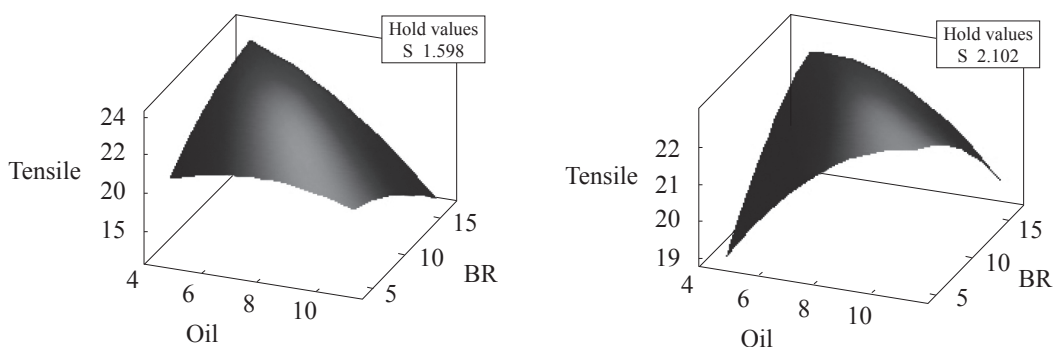


Figure 7. Response surface plots showing the effect of oil and BR on tensile strength of vulcanisates. Sulphur content is held at high and low levels.

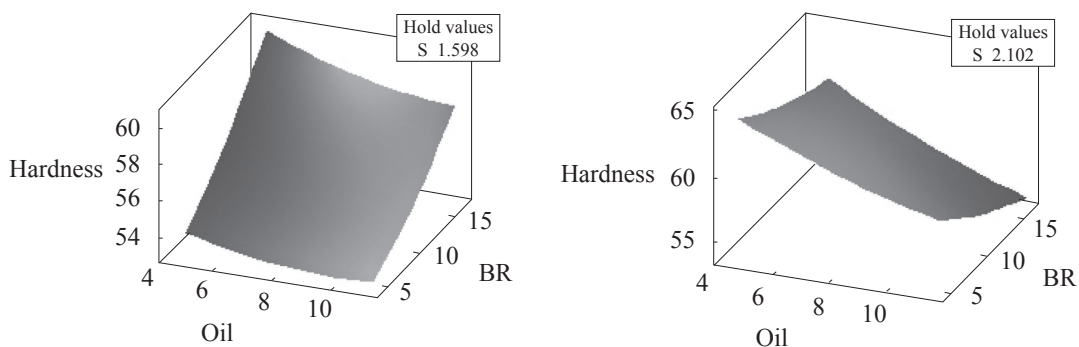


Figure 8. Response surface plots showing the effect of oil and BR on hardness of vulcanisates. Sulphur content is held at high and low levels.

statistical analysis of Table 5 and the response surface plot (Figure 9) show that sulphur has a statistically significant increasing effect on DCG property of CB/ZnSt-MMT-filled NR/SR/BR compound.

Abrasion

Statistical analysis demonstrates that DIN abrasion loss of vulcanisates decreases with the increase of sulphur and it increases with the increase of oil. However, the interaction terms

between BR and S and also BR and oil were statistically significant that show the complex dependency of abrasion according to the BR content. The response surface plots of Figure 10 depicts that the improving effect of BR is completely dependent on the oil and sulphur content. At high oil levels, the BR substitution shows a negative effect on the abrasion in all sulphur levels. However, at high sulphur levels and low oil levels, the abrasion resistance is improved by BR. So, the improving effect of BR may be obtained in optimum levels of oil and sulphur.

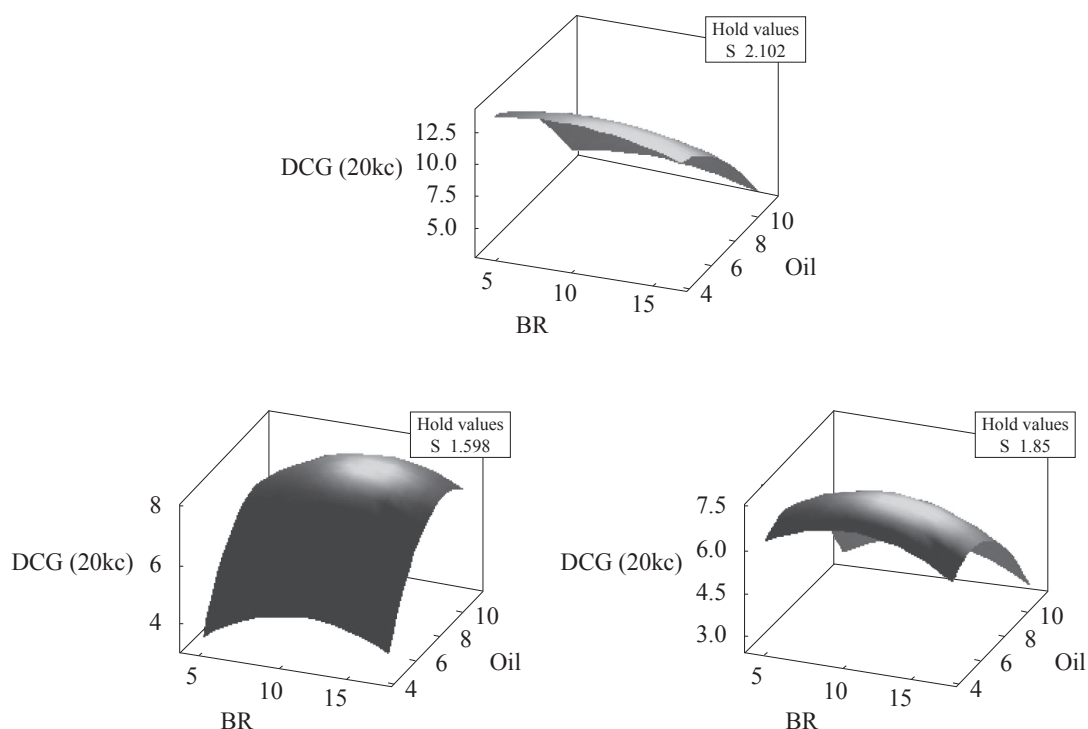


Figure 9. Response surface plots showing the effect of oil and BR on DeMattia crack growth of vulcanisates. Sulphur content is held at low moderate and high levels.

Heat Build Up

Generation of heat *via* viscous dissipation of cured filled rubber compounds can lead to significant temperature increment that affects the performance of rubber goods. This phenomenon is called heat build up (HBU) and it has been the subject of several experimental and theoretical studies^{22–25}. HBU may be influenced by the type and the amount of rubber, filler, oil and curative levels. Usually, lower levels of reinforcing fillers, larger particle sizes and higher structures are favourable for HBU²³.

Figure 11 exhibits the response arising from the interaction between sulphur, oil and butadiene. The results obtained from Table

5 and Figure 11 revealed that the interaction between BR and oil was significant ($P=0.000$), as well as the interaction between oil and S ($P=0.040$). The interaction between BR and S was not significant ($P=0.54$). In Figure 11, HBU was decreased by enhancing oil in high BR levels. HBU was also decreased by increasing BR in higher oil levels.

Response Surface Optimisation

Nonlinear programming multi objective optimisation approach was conducted with the aid of MINITAB 15 statistical software. The response surface models of DCG, abrasion, tensile strength, elongation, M300, HBU and hardness were used and lower and upper levels

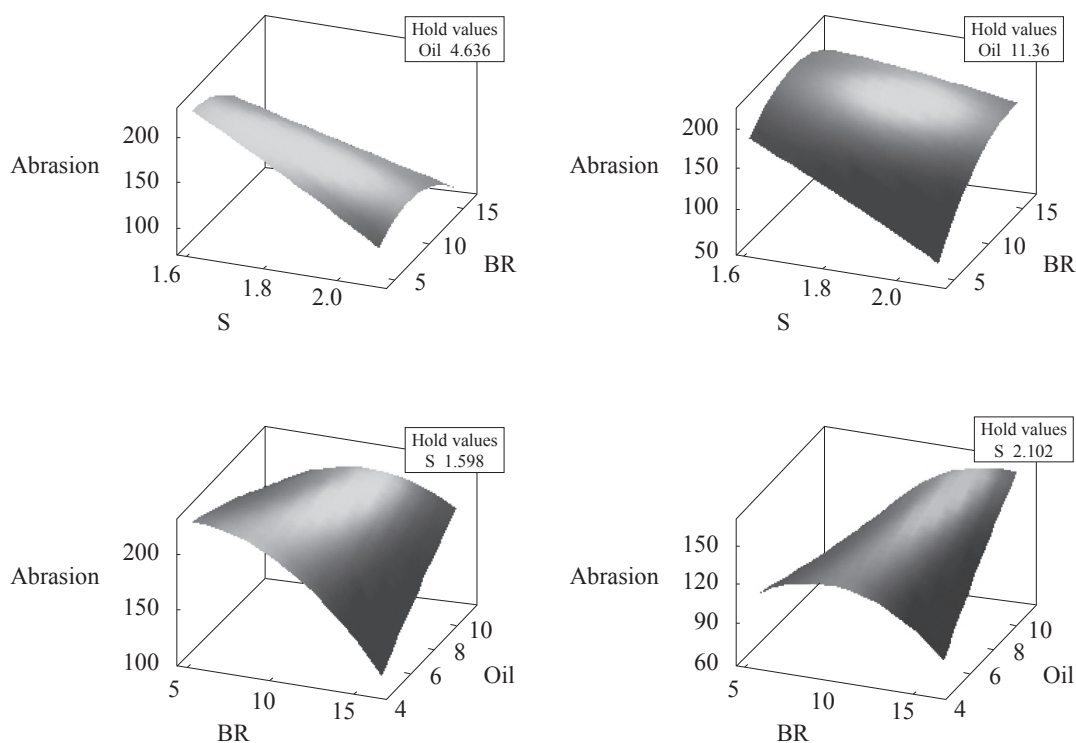


Figure 10. Response surface plots showing the effect of oil, BR and S on abrasion of vulcanisates.

as well as the target for each property were specified. The solution of BR=16.4, S=1.88 and oil = 7.29 gave the following results after running the software: DCG: 6.3, abrasion: 133.3, tensile strength: 21.9, elongation: 546.8, M300: 9.0, HBU: 28.5 and hardness: 59 with composite desirability of 0.50. The a_8 formulation was prepared according to the results of software optimisation (BR = 16.4, S = 1.88 and oil = 7.29) and the experimental results (Table 2) are very close to the software predictions. In addition, the solution of BR = 7.6, S = 2.1 and oil = 10.6 gave the following results after running the software: DCG: 6.3, abrasion: 115.9, tensile strength: 22.3, elongation: 555.6, M300: 9.0, HBU: 30.7 and

hardness: 58 with composite desirability of 0.45.

Comparing the results of above optimisations (output of software and also compound in Table 2) with reference formulation (formula a_1 in Table 2) reveals that in both optimisation cases, a simultaneous improvement in abrasion and DCG has been achieved in the similar hardness and M300 level. This means that incorporation of ZnSt-MMT with combination of response surface optimisation framework develop a better formulation with better balances between physical and mechanical properties of the vulcanisates.

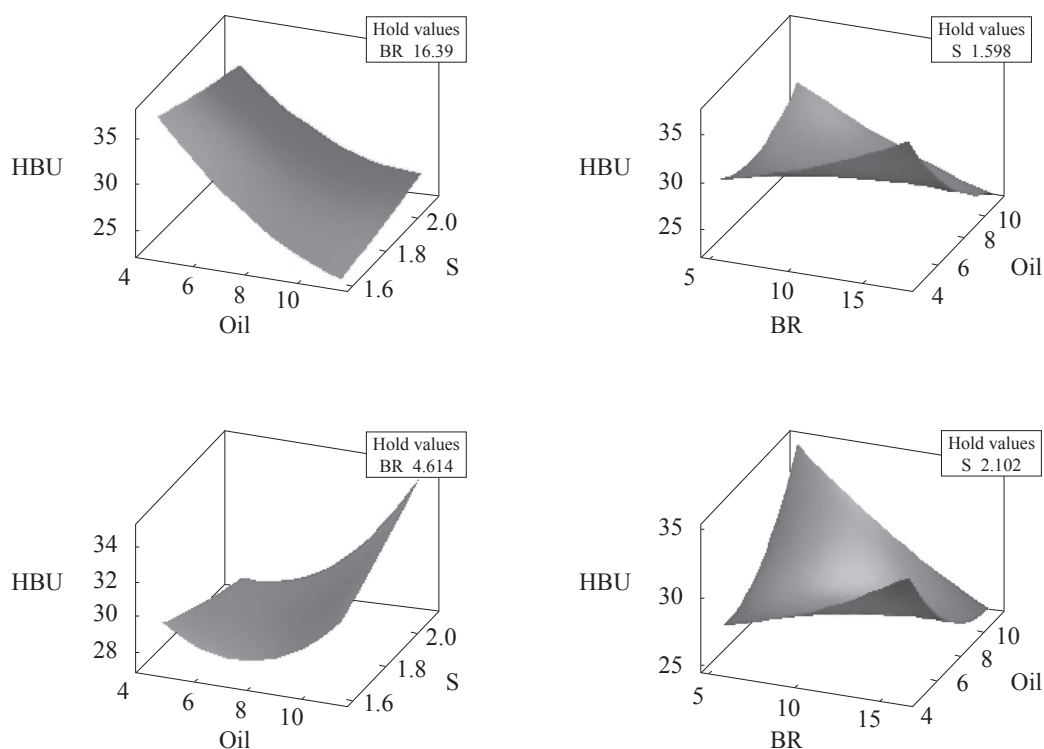


Figure 11. Response surface plots showing the effect of oil and BR and sulphur on HBU of vulcanisates.

Mechanistic Discussion of the Results

In order to fundamentally understand the reinforcing mechanism of polymer-layered silicate composites, there are several reports dealing with the micromechanics of polymer-clay composites and nanocomposites²⁶⁻³⁰. From view point of filler reinforcement, improved mechanical properties such as tensile strength and elastic modulus of reinforced polymers depend on several factors: filler particle size and concentration, aspect ratio, dispersion and morphology.

As conventional inorganic fillers such as unmodified MMt, talc powder and calcium carbonate, the interfacial interaction between the fillers and the rubber chains is weaker

than that between the CB particles and the rubber chains. During the stretching process, the rubber chains are stretched *via* slippage and orientation under the influence of filler particles. In general, a stronger filler-rubber interaction leads to less sliding deformation and more stress is needed to break the chain. The modulus of partial mineral substituted compounds of present study has been decreased according to the above fact. However, in partial substitutions, the modulus of the mineral substituted compounds may adjust with increase of crosslink density (through increase of sulphur) and decrease of oil (Table 2). In this situation the better performance of DCG of ZnSt-MMT filled composites may be observed.

Nah³² proposed a model to explain the reinforcement of clays on polymer nanocomposites that the increase of the crack path around these silicate layers is capable of dissipating input energy to withstand greater stress than those with carbon black. The better DeMattia cut growth behaviour of ZnSt-MMT-filled composites may be attributed to the above fact. According to Griffith theory, crack growth proceeds as a result of competition between strain energy release and surface energy required to create new fracture surfaces. Fracture energy per unit area of fracture plane, also termed tearing energy, consists of two parts: (1) The energy expended to break bonds across the fracture plane and (2) That due to hysteretic losses^{33,34}. Hence, in relatively similar modulus (similar input strain energy) the DCG behaviour of ZnSt-MMT has been better than other partially substituted minerals probably due to an increase of the crack path around these silicate layers and increase of dissipating input energy³². Partly substitution of very high crack growth resistance natural rubber with very high elastic and low crack growth resistance *cis* polybutadiene (BR) has not shown a statistically significant effect on the DCG behaviour of compounds in the presence of ZnSt-MMT as evidenced through response surface plots, where other minerals fail to impart this effect.

In addition, considerable differences are observed between abrasion behaviour of ZnSt-MMT compounds and unmodified MMT-filled compounds as well as reference (black-filled) compound. The governing mechanisms on the abrasion behaviour of rubbery materials are complex^{35,36}. The response surface plots of the present study clearly show the complex dependency of abrasion to the formulation agents. The negative effects of oil content and the favourable effects of sulphur reveal that higher filler-rubber and rubber-rubber interactions are necessary for abrasion. The

improving effect of BR substitution was only achieved at optimum levels of oil and sulphur as may be deduced from the response plots. The better performance of ZnSt-MMT rather than unmodified MMT may be attributed to the better filler-rubber interactions^{15-16,29-31}.

A comprehensive concept to understand the mechanism of rubber abrasion was provided by Fukahori³⁷⁻³⁹. Friction and fracture in abrasive wear of rubber was linked through the formation of periodic surface pattern, abrasion pattern, generated by two kinds of periodic motions, stick-slip oscillation and micro-vibration. By defining the mean strain amplitude in the stress field ϵ^* and considering the wear abrasion behaviour of rubbery materials as a fatigue crack growth process according to the ϵ^* , an efficient theoretical model for abrasion behaviour of rubbery materials has been provided by Fukahori³⁷⁻³⁹.

In the present study, we have employed the qualitative aspect of the above model to explain at least qualitatively the abrasion behaviours of vulcanisates according to the formulation variants. The mean strain amplitude ϵ^* of Fukahori model is governed by the friction constant μ , Young's modulus, E of the material and the normal load P , as $\epsilon^* = \mu P/ES$ where S is the cross-sectional area. The rate of abrasion loss $\dot{D}$ has been expressed as follows $\dot{D} \propto \frac{d}{dt}(c(\epsilon^*))$, where c is cut growth.

So the role of formulation ingredient on abrasion behaviour of rubbery materials may be investigated through two separate sections; first, its effect on ϵ^* and second it's effect of crack growth behaviour of rubber. All abrasion behaviours of present study were described. For example, the carbon level would decrease the friction coefficient to some extent, μ ³⁷⁻³⁹ and significantly decrease the modulus, leading to an increase in the ϵ^* . On the other hand, the crack growth characteristic of the vulcanisates improved according to the DCG

results in *Table 2* (compound a_2). It may be concluded that the abrasion behaviour of the compounds becomes unchanged as shown in *Table 2* (compound a_2 vs a_1). Compared to a_2 compound, the presence of expanded clay (compound a_3 and a_4) has increased the modulus and probably a slight increase of μ (= decrease) without significant change of DCG, so the abrasion behaviour has been improved (a_3 and a_4 vs a_2). This is a very critical aspect of present expanded clay to impart better balances between properties. Reducing oil content was reflected in the modulus of a_5 compound without significant change of DCG. Hence, compared to the compound a_4 the abrasion loss has slightly decreased for compound a_5 .

According to literature, incorporation of BR has significant decreasing effect on the friction coefficient. So, the ϵ^* may decrease (compound a_6) in the presence of BR. On the other hand, the DCG behaviour of the compounds remains unchanged in the presence of expanded clay. Thus, the improving effect of BR substitution on abrasion behaviour may be described successfully (compound a_5 vs a_6). The increase of sulphur has an increasing effect on the modulus of compound a_6 , while a slight increase in DCG behaviour was observed. From the conclusion of two opposite effects, no significant change of abrasion was observed (compound a_6 vs a_7). Compound a_8 presents optimum compound from response surface optimisation. Compared to the reference (compound a_1), better abrasion behaviour of compound a_8 , (in the similar modulus and slightly higher DCG) may be attributed to the presence of BR. The effects of unmodified MMT (compound a_9), talc powder (compound a_{10}) and precipitated CaCO_3 (compound a_{11}) are also interesting. Compared to the expanded clay, ZnSt-MMT, all these fillers fail to impart an efficient DCG in the presence of BR. MMT also has decreasing effect on the

modulus where the abrasion has dropped to the range of reference compound even in the presence of significant amount of BR (a_9 vs a_1). However, in the case of CaCO_3 and talc powder (compound a_{10} and a_{11}), the abrasion behaviour has improved due to significant increase of modulus even though the DCG of the compounds has dropped.

Response surface plots of the present study may demonstrate the abrasion behaviours in higher ranges and confirm the results at a time study approach. Statistical analysis and response surface plotting of abrasion according to the oil level clearly shows the detrimental effect of oil on the abrasion. Oil has an increasing effect on μ and also a decreasing effect on modulus both in direction of ϵ^* increase. Overall increase of abrasion is observed especially in high BR levels when oil increases. Increase of sulphur has an increasing effect on DCG of vulcanisates, but its improving effect on modulus is so that the abrasion behaviour has improved with the increase of sulphur level. On the other hand, as Gent and Pulford indicated³⁵, abrasion wear of rubber is not accounted for solely by crack growth properties of material but involves other failure processes, for example reaction with oxygen, *etc.*^{35,36}. Hence, abrasion of rubber involves both tearing and general decomposition of molecular network. Improving effect of BR substitution may be attributed to this phenomenon. Radicals formed in BR by main chain rupture are known to react with polymer itself, leading to further crosslinking rather than decomposition. However, it is important to note that in the case of higher oil levels, the increase of BR has no improving effect (and even a deteriorating effect) on the abrasion as evidenced in response surface plots. Hence, the mechanisms of crack growth as presented by Fukahori still play an important role in the abrasion behaviour of vulcanisates in the present study.

Kinetic Study

An attempt has been made here to develop a kinetic model for curing of vulcanisates according to the MDR data (*Figure 12*). The following kinetic model was found to be able to fit MDR data with very high accuracy as presented in *Table 6*.

$$\frac{kt^n}{1 + kt^n} \quad \dots 5$$

This model has been presented by Isayev and Deng²¹. The calculated R^2 value is very high for all experimental points. An attempt was made to develop a response surface model for n and k in accordance to the sulphur, BR and oil. It was found that response surface model of n according to the BR, S and oil level is statistically significant (P-value of F regression (4.4) was found to be $0.0302 < 0.05$

and $R^2 = 0.8495$). However, the response surface model could not be developed for k in accordance to the statistical results. The response surface plot of n is presented in *Figure 13*. Surface plots in *Figure 13* show that the interactions term between sulphur and oil ($S*Oil$) and BR and oil ($BR*Oil$) are significant.

Therefore, a complex dependency of n on ingredients has been evidenced. Compared to the mechanistic kinetic models, the main defect of experimental kinetic models such as Isayev and Deng is that they are not able to model the sulphur curing behaviour of rubbery materials according to the curing ingredients amount. This study presents a simple way to enhance the performance of experimental kinetics models from coupling of kinetic coefficients with formulation ingredient through statistical models.

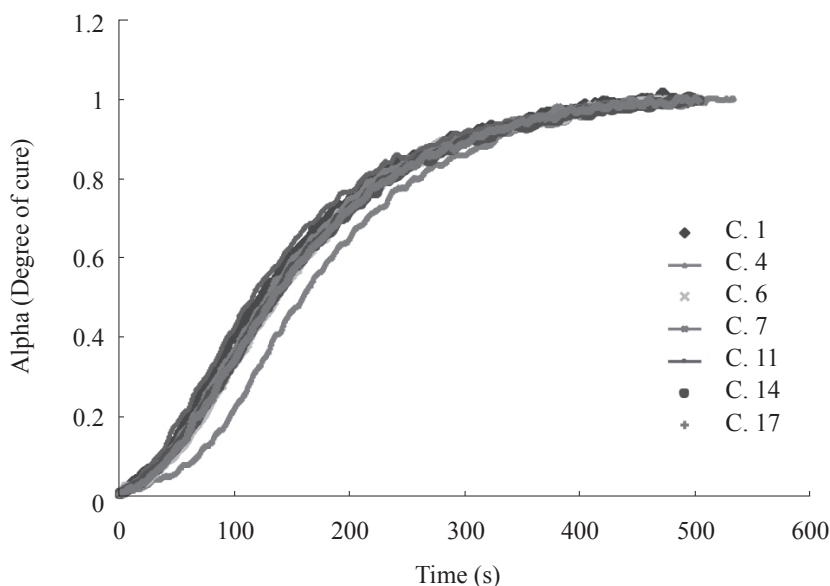


Figure 12. MDR curves of some experimental points at 170°C.

TABLE 6. KINETIC PARAMETERS ACCORDING TO ISAYEV AND DENG KINETIC MODEL (TEMPERATURE 170°C)

Points	Factors			Kinetic Parameters according to the Isayev and Deng kinetic model		Statistical criteria			
	BR	Oil	S	n	k	R ²	R ² _{adj}	RMSE	SSE
C. 1	10.5	8	1.85	2.365	1.20E-05	0.9937	0.9937	0.02478	0.5022
C. 2	10.5	4.64	1.85	2.489	5.22E-06	0.9969	0.9969	0.01791	0.2679
C. 3	4.61	8	1.85	2.3	5.02E-06	0.9968	0.9968	0.0178	0.266
C. 4	14	6	1.7	2.935	3.55E-07	0.9972	0.9972	0.01809	0.2869
C. 5	10.5	8	1.85	2.35	1.20E-05	0.993	0.993	0.02219	0.3223
C. 6	16.39	8	1.85	2.532	4.24E-06	0.9958	0.9958	0.02087	0.359
C. 7	10.5	8	2.1	2.446	6.60E-06	0.995	0.995	0.02247	0.423
C. 8	10.5	11.36	1.85	2.717	1.42E-06	0.9965	0.9965	0.01977	0.3294
C. 9	14	6	2	2.589	2.80E-06	0.9985	0.9985	0.0128	0.1411
C. 10	7	10	2	2.608	3.28E-06	0.9941	0.9941	0.02534	0.425
C. 11	7	6	2	2.272	2.13E-05	0.9953	0.9953	0.02083	0.3576
C. 12	10.5	8	1.6	2.471	5.31E-06	0.9949	0.9949	0.022285	0.4345
C. 13	14	10	2	2.531	4.22E-06	0.996	0.996	0.02038	0.3511
C. 14	10.5	8	1.85	2.454	6.16E-06	0.9961	0.9961	0.01994	0.3305
C. 15	7	10	1.7	2.302	1.69E-05	0.9948	0.9947	0.02235	0.4079
C. 16	7	6	1.7	2.54	4.31E-06	0.9951	0.9951	0.02249	0.4239
C. 17	14	10	1.7	2.491	5.25E-06	0.9952	0.9952	0.02218	0.4088

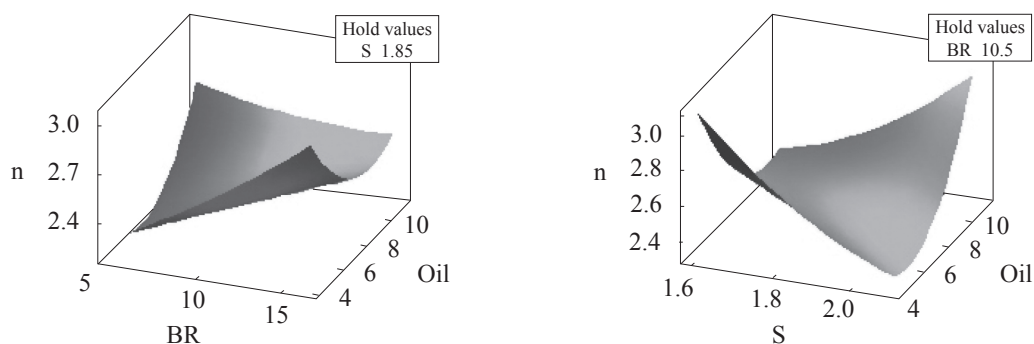


Figure 13. Response surface plots showing the effect of oil and BR and sulphur on kinetic parameter "n" (cure kinetic model).

CONCLUSIONS

Montmorillonite as cationic clay of the smectite family was successfully modified using zinc stearate, a cheap and easily available fatty acid. The XRD results showed intercalation of the organic cations between the clay mineral layers. A central composite design and response surface methodology were employed to optimise formulation in the presence of organoclay. The response surface models (RSM) of the physical and mechanical properties were found to adequately describe the experimental range. Response surface models have several advantages compared to the classical experimental or optimisation methods in which one variable at a time technique is used. A kinetic study according to the multifactor dimensionality reduction (MDR) data revealed that the MDR curves of zinc stearate organoclay compounds fit well with Isayev and Deng kinetic model in the range of experimental points. In addition, the kinetic parameters can be described well through RSM.

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