Modeling NBR- Layered Silicate Nanocomposites: A DoE Approach

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ABSTRACT: The mechanical behavior of acrylonitrile butadiene rubber (NBR) – organo modified layered silicate was modeled using Design of Experiments (DoE). Response surface methodology (RSM), a DoE tool was used to optimize the formulations for optimal performance of the nanocomposites. A Box-Behnken design with three factors and three levels was used to model the relationship between mechanical properties and levels of ingredients. The factors studied for the design are silica content, nanoclay loading and vulcanization system. The nanocomposites were evaluated for tensile strength, modulus, elongation at break and hardness. The effect of heat aging on mechanical properties was also studied. The predicted properties of the nanocomposites are in good agreement with the experimental results, which confirmed the prognostic ability of response surface methodology. The model equations were used to generate response surfaces and contour plots to study the interaction between the variables. The contour plots were overlaid within the applied constraints to identify the required combination of variables that gives the optimum performance for the nanocomposites. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 3300–3310, 2010

Key words: nanocomposite; optimization; contour plot; response surface; Box-Behnken design; nitrile rubber; nanoclay

INTRODUCTION

Reinforcing polymers with nanosized clay particles yields materials with enhanced performance without recourse to expensive synthesis procedures.[1-3] Among the various clays used, organoclays (layered silicate) of montmorillonite family have been widely used in both thermoplastic and elastomeric systems.[2,4,5] These composites have comparatively much better mechanical properties, barrier properties and fire and ignition resistance than conventional microcomposites. The size of the nanoclay particles, the modifications of the nanofiller and the amount of filler used play a major role in the development of the properties of the rubber.[6-10]

Several techniques based on computational chemistry (Monte Carlo, molecular dynamics etc.) and computational mechanics (micromechanical models, finite element methods) have been reported in literature for modeling mechanical properties of polymer nanocomposites.[11-14] Conventional micromechanical models like rule of mixtures, Hui-Shia and Halpin-Tsai models[14] are based on a number of simplifying assumptions like uniform size, shape and alignment of nanoparticles, excellent bonding between the nanoparticles and the polymer matrix and uniform exfoliated distribution of nanoparticles. Though many attempts have been made to use these models for real polymer systems, they rarely hold well due to these assumptions. This is especially true in the case of elastomer based nanocomposites in which apart from the nanofiller, many other ingredients like cross-linking agents, accelerators, activators and other particulate fillers are incorporated into the matrix during nanocomposite preparation.

Use of Design of Experiments (DoE) allows simultaneous evaluation of a number of factors and eliminates the need for large number of independent runs that is required in a conventional step by step approach. DoE is a structured statistical technique, which increases the productivity of the experiments by minimizing the number of experiments involving multiple parameters and maximizing the accuracy of results. Use of DoE not only allows identifying significant factors affecting the responses but also accounts for the interactions between the parameters. DoE techniques have been widely used in

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various fields like optimizing process parameters in polymer processing,[15-18] component design,[19-21] and biomedical studies.[22,23] DoE has been successfully used in optimizing polymer formulations[24-26] and modeling the mechanical properties.[27,28] The steps in DoE involve identifying the objective functions, choosing the influencing factors and determining the main and interaction effects of the factors on the responses. Response surface methodology (RSM) is a collection of mathematical and statistical techniques used in DoE. RSM is very useful for modeling, analysis and optimization of responses that are influenced by several variables.[29] RSM also provides surface and contour plots that aid in visualizing the interactions.

Acrylonitrile-butadiene rubber (NBR) is a special purpose, oil resistant rubber and hence can be used in applications where oil resistance is required. Our earlier work on NBR nanocomposites showed that incorporation of nanoclay into the matrix resulted in remarkable improvement in mechanical properties.[30] In this work, we used response surface methodology to model the cure characteristics and mechanical properties of NBR nanocomposites. The formulations were optimized for mechanical and heat aging properties. A Box-Behnken design for three factors was used for analysis.

EXPERIMENTAL

Materials

Nitrile rubber used in the study was JSR N230SL form Japan Synthetic Rubber with 35% Acrylonitrile content and Mooney viscosity of ML (1 + 4) at 100°C = 42. The organo modified layered silicate Cloisite 20A, a natural montmorillonite modified with quaternary ammonium salt (organic modifier - dimethyl dehydrogenated tallow, quaternary ammonium, modifier concentration 95 meq/100 g clay and d_{001} = 24.2Å) was procured from Southern Clay Products, USA. Silica [Ultrasil], sulfur, dicumyl peroxide, and other compounding ingredients, were obtained from standard suppliers. The recipe used for the study included NBR, sulfur (varied), zinc oxide (5 phr), stearic acid (1 phr), nanoclay (varied), diethylene glycol (DEG, varied maintaining silica: DEG ratio at 20 : 1), dioctyl phthalate (DOP, varied maintaining silica: DOP ratio at 4 : 1), MBTS (varied), and TMTD (varied).

Preparation of nanocomposites

Cloisite 20A was mixed into NBR in the ratio 1 : 3 using an internal mixer type Fissions Haake Rheocord 90 at 60 rpm and at 50°C for 10 min. The internal mixer has an eight-shaped chamber, in which two sigmoid, counter-rotating blades turn. The NBR-layered silicate masterbatch was then compounded with NBR and other compounding ingredients in laboratory size two roll mill (15 cm x 33 cm) with friction ratio 1 : 1.25 at room temperature using standard procedures. The rubber formulations were evaluated for cure characteristics on TechPro Rheotech ODR. (ASTM D-2084)). Curing was done at 150°C and 200 kg/cm^2 for the optimum cure time in a hydraulic press to make ~ 2 mm thick rubber sheets.

Characterization of NBR Nanocomposites

Dumbbell specimens were punched out from the molded sheets and stress–strain characteristics were evaluated as per ASTM D412 method on a UTM with a crosshead speed of 500 mm/min. To study the effect of heat aging on mechanical properties, the dumbbell specimens were subjected to heat aging at 100°C for 48 h followed by evaluation of mechanical properties.

X-ray diffraction and transmission electron microscopy were used to characterize the state of dispersion and exfoliation in the nanocomposites. X-Ray diffraction studies were done at 3°/min on a Bruker D8 ADVANCE X-ray diffractometer with Cu X-ray beam of wavelength 1.5406 A°. The *d*-spacing of the nanoclay was determined from the 2Θ position of the diffraction peak based on Bragg's law.

Transmission electron microscopy (TEM) images were taken with JEOL-2010 electron microscope with an accelerator voltage of 200 kV. The nanocomposite samples for TEM analysis were prepared by ultra cryomicrotomy at −80°C using Leica Ultracut UCT. Freshly sharpened glass knives with cutting edge of 45° were used to get the cryosections of 100 nm thickness.

Statistical analysis

The objective function of this study is to model the cure time, mechanical properties, and heat aging behavior of NBR nanocomposites. An optimum formulation to maximize the tensile strength, elongation at break, and modulus of the nanocomposites while minimizing the effect of heat aging on these properties was also determined.

Considering its efficiency in the number of required runs, a Box-Behnken design was chosen to optimize the nanocomposite formulation and model the main, quadratic, and interactive effects on the properties under study. The Box-Behnken design is a rotatable design characterized by a set of points lying at the midpoint of each edge of a multidimensional cube and center point replicates (Fig. 1). This design does not contain any points at the vertices. Hence it is very useful in situations where physical constraints in upper and lower limits of the variables

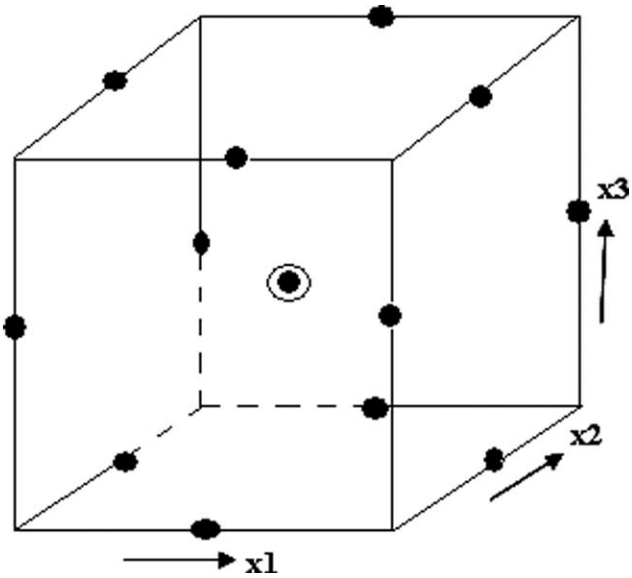

Figure 1 Geometry of Box Behnken design for three variables.[35]

make it impossible to test these points. Central Composite Circumscribed (CCC) and Central Composite Inscribed (CCI) require five levels, with some of the factor settings outside the range of the factors in the factorial part. Face-Centered central composite (CCF) designs provide relatively high quality predictions over the entire design space and do not require using points outside the original factor range. However, they give poor precision for estimating pure quadratic coefficients. For three factors, the Box-Behnken design offers some advantage compared to central composite designs in requiring a fewer number of runs. Box-Behnken design allows us to vary each design parameter at three levels, giving the ability to capture second-order behavior.[25-29,31-34]

The three level three factor Box-Benken design employed in this study required 15 experiments. With silica content (X_1), nanoclay loading (X_2), and sulfur/Accelerator ratio (X_3) as the independent variables. Coded values are generally used to represent the factor levels, −1, 0, and +1 corresponding to the minimum, central point, and maximum levels of the factors, respectively. Use of coded values enables easy interpretation of the coefficients. Table I shows the independent variables along with their low, medium, and high levels, which were selected based on results of previous experiments. The compositions were optimized for mechanical and heat aging properties.

TABLE I
Variables in Box-Benken Design

	Levels used, actual (coded)		
Factor	Low (−1)	Medium (0)	High (+1)
X_1 = silica content (phr)	0	10	20
X_2 = nanoclay loading (phr)	0	5	10
X_3 = sulfur/accelerator ratio	0.3	2.0	3.7

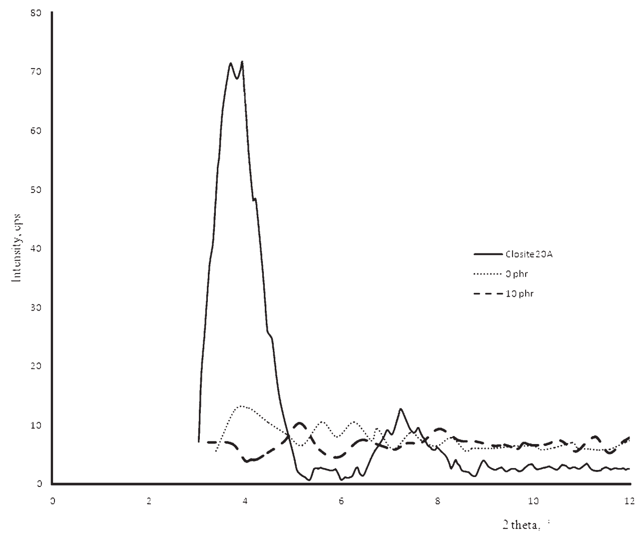

Figure 2 XRD pattern for NBR nanocomposite and nanoclay.

RESULTS AND DISCUSSION

Morphology of NBR- layered silicate nanocomposites

The morphology of the NBR nanocomposites were studied using XRD and TEM. XRD patterns indicate the state of dispersion of the filler in nanocomposites.[12,36,37] In exfoliated composites, the silicate layers are delaminated in the polymer matrix and this is indicated by disappearance of XRD peaks. A shift in the basal reflection to 2Θ corresponding to a larger d value indicates intercalation.[6,38] XRD patterns for the NBR nanocomposites are shown in Figure 2. For the Cloisite 20A, the peak occurs at 3.775° corresponding to a d-spacing of 2.3387 nm. As seen from the figure no peaks are observed for NBR composite without nanoclay as well as composite containing 10 phr nanoclay. This indicates that exfoliation of nanoclay in the composites has occurred.

The transmission electron microscopy images of NBR nanocompoaites are shown in Figure 3. Figure 3(a) shows the typical TEM image of nanocomposite containing 5 phr nanoclay (coded value of $X_2 = 0$) and 20 phr silica (coded value of $X_1 = 1$). The TEM image of NBR nanocomposite containing 10 phr nanoclay (coded value of $X_2 = 1$) and 20 phr nanoclay (coded value of $X_1 = 1$) is shown in Figure 3(b). Both figures indicate that TEM observations are in agreement with XRD pattern and that nanoclay is exfoliated in the NBR matrix.

The mechanical properties of NBR nanocomposites prepared as per the design are shown in Table

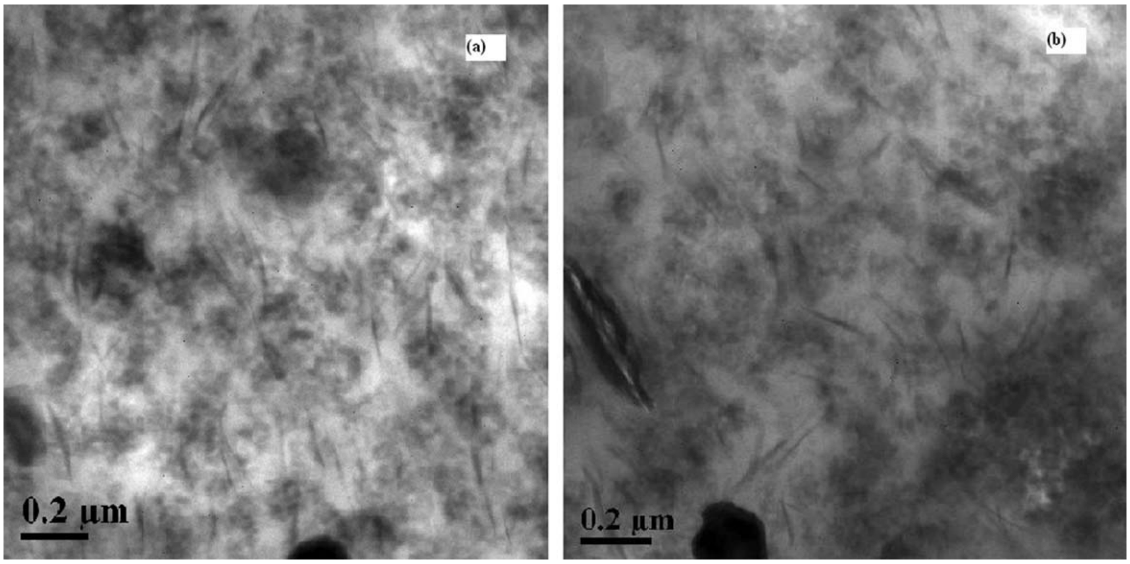

Figure 3 TEM micrograph of NBR nanocomposite containing (a) 5 phr nanoclay (b) 10 phr nanoclay.

II. A wide range of values were observed for the different NBR compounds.

Statistical analysis

The experimental data were analyzed by the response surface regression procedure using the following second-order polynomial equation:

$$y = \beta_0 + \sum_{i=1}^{3} \beta_i x_i + \sum_{i=1}^{3} \beta_{ii} x_i^2 + \sum \sum_{i<j=1}^{3} = \beta_{ij} x_i x_j \quad (1)$$

where y is the response, x_i and x_j are the coded independent variables and β_0, β_i, β_{ii}, and β_{ij} are intercept, linear, quadratic, and interaction constant coefficients, respectively. Each coefficient estimates the change in the mean response per unit increase in x when all other predictors are held constant. For example the equation for tensile strength in terms of the coded variable is given by

$$\begin{aligned} TS = 7.89 + 3.13X_1 + 1.70X_2 + 1.20X_3 \\ + 0.13X_1^2 - 0.08X_2^2 - 0.43X_3^2 \\ - 0.85X_1X_2 - 0.98X_1X_3 - 0.80X_2X_3 \end{aligned} \quad (2)$$

where X_1, X_2, and X_3 are the silica content, nanoclay content, and sulfur to accelerator ratio in terms of coded variables. In terms of the actual

TABLE II
Three Variable Box – Behnken Design and Mechanical Properties of NBR – Layered Silicate Nanocomposites

	Coded variable				Before heat aging				After Heat Ageing			
RO	Silica	Nano-clay	S/A ratio	Cure time (min)	TS (N/mm^2)	Eb (%)	M100 (N/mm^2)	M300 (N/mm^2)	TS (N/mm^2)	Eb (%)	M100 ($N/mm^{2)}$)	M300 (N/mm^2)
1	−1	1	0	7.59	6.44	757	1.36	2.39	4.96	486	1.58	2.97
2	0	0	0	6.02	7.89	1063	1.20	1.91	6.87	736	1.43	2.40
3	0	1	−1	9.49	7.99	1279	1.13	1.62	6.81	919	1.21	1.81
4	0	0	0	6.01	7.28	1013	1.06	1.81	7.76	797	1.53	2.55
5	−1	0	1	4.48	5.07	556	1.35	2.57	4.49	400	1.55	3.23
6	1	−1	0	9.07	11.14	1378	1.01	1.54	8.70	917	1.27	2.09
7	0	−1	1	8.20	5.16	762	1.00	1.61	5.49	601	1.26	2.27
8	0	−1	−1	14.13	4.76	1392	0.74	0.95	4.03	958	0.83	1.11
9	1	0	−1	10.18	8.15	1488	0.90	1.36	7.81	1116	1.04	1.36
10	−1	−1	0	10.45	2.77	720	0.78	1.18	2.43	536	0.92	1.37
11	1	1	0	5.07	11.41	1129	1.37	2.46	11.46	870	1.72	3.21
12	−1	0	−1	9.27	4.23	958	0.79	1.31	4.01	748	1.01	1.59
13	1	0	1	7.30	12.90	944	1.54	2.98	11.37	644	2.05	4.30
14	0	0	0	5.58	8.49	1079	1.09	1.93	7.94	771	1.47	2.56
15	0	1	1	5.34	11.60	766	1.80	3.74	9.16	515	2.34	4.90

TABLE III
Regression Coefficients for Properties of of NBR – Layered Silicate Nanocomposites

Term		Cure time	Before heat aging: Tensile Strength	Before heat aging: Eb	Before heat aging: M100	After heat aging: Tensile strength	After heat aging: Eb	After heat aging: M100
Constant	β_0	5.87	7.89	1051.51	1.12	7.52	768.18	1.48
Silica	β_1	−0.02	3.13	243.30	0.07	2.93	172.23	0.13
Nanoclay	β_2	−1.80	1.70	−40.21	0.27	1.47	−27.68	0.32
S/A Ratio	β_3	−2.22	1.20	−261.21	0.27	0.98	−197.72	0.39
Silica × Silica	β_{11}	0.35	0.13	−59.37	0.00	−0.05	−43.48	−0.05
Nanoclay × Nanoclay	β_{22}	1.83	−0.08	3.84	0.02	−0.59	−22.19	−0.05
S/A Ratio × S/A Ratio	β_{33}	1.59	−0.43	−5.62	0.03	−0.56	2.35	−0.02
Silica × Nanoclay	β_{12}	−0.29	−0.85	−71.57	−0.05	0.06	0.66	−0.05
Silica × S/A Ratio	β_{13}	0.48	0.98	−35.55	0.02	0.77	−30.99	0.12
Nanoclay × S/A Ratio	β_{23}	0.45	0.80	29.22	0.10	0.22	−11.78	0.18

values for the variables, the equation for tensile strength is

$$TS = 2.346 + 0.257X_1 + 0.351X_2 + 0.254X_3 + 0.001X_1^2 - 0.003X_2^2 - 0.149X_3^2 - 0.017X_1X_2 - 0.0.57X_1X_3 - 0.094X_2X_3 \quad (3)$$

Similar regression equations for elongation at break and M100 were generated. Equations for these properties after heat aging were also obtained. The regression coefficients for the various parameters are tabulated in Table III. MINITAB software package was used for regression analysis.

The factors with positive coefficients have a positive effect on the property and vice versa. The analysis of data from a designed experiment is done using analysis of variance (ANOVA). Table IV illustrates the analysis of tensile strength of the nanocompoistes. For example, it can be seen from eq. (2), the regression coefficient for silica (in terms of coded variables) is 3.13. This positive value of the coefficient implies that increase in silica content increases the tensile strength. Numerically, a unit increase (i.e., addition of 10 phr) in silica content increases the tensile strength by 3.13 MPa. The increase in tensile strength on addition of silica can be attributed to the fact that the filled polymer allows the load to be distributed among the chains, which have been reinforced with particulate filler. This increases the resistance of the rubber to failure. Addition of nanoclay also increases the tensile strength of the nanocomposite. Addition of 5 phr nanoclay increases the tensile strength by 1.70 MPa. The tensile

TABLE IV
Analysis of Variance for Tensile Strength of NBR–Layered Silicate Nanocomposites

Term	Coef	SE Coef	*t*	*p*
Constant	7.88670	0.6027	13.087	0.000
Silica	3.13473	0.3690	8.494	0.000
Nanoclay	1.70090	0.3690	4.609	0.006
S/Accl Ratio	1.20055	0.3690	3.253	0.023
Silica × Silica	0.13175	0.5432	0.243	0.818
Nanoclay × Nanoclay	−0.07664	0.5432	−0.141	0.893
S/Accl Ratio × S/Accl Ratio	−0.43048	0.5432	−0.792	0.464
Silica × Nanoclay	−0.84729	0.5219	−1.623	0.165
Silica × S/Accl Ratio	0.97875	0.5219	1.875	0.120
Nanoclay × S/Accl Ratio	0.80271	0.5219	1.538	0.185

S = 1.04383 PRESS = 77.1615
R-Sq = 95.77% R-Sq(pred) = 40.10% R-Sq(adj) = 88.16%

Analysis of Variance for Tensile strength N/mm^2

Source	DF	Seq SS	Adj SS	Adj MS	*F*	*P*
Regression	9	123.365	123.365	13.7072	12.58	0.006
Linear	3	113.287	113.287	37.7625	34.66	0.001
Square	3	0.797	0.797	0.2655	0.24	0.863
Interaction	3	9.281	9.281	3.0936	2.84	0.145
Residual Error	5	5.448	5.448	1.0896		
Lack-of-Fit	3	4.720	4.720	1.5734	4.32	0.193
Pure Error	2	0.728	0.728	0.3638		
Total	14	128.813				

TABLE V
Summary of Analysis of Responses for Response Variables

Model term	Cure time	*p*-value					
		Before heat aging			After heat aging		
		Tensile strength	Eb	M_{100}	Tensile strength	Eb	M_{100}
X_1	0.001	0	0	0.057	0	0	0.003
X_2	0.964	0.006	0.006	0	0.001	0.062	0
X_3	0.011	0.023	0.023	0	0.003	0	0
X_{11}	0.004	0.818	0.818	0.926	0.875	0.051	0.187
X_{22}	0.625	0.893	0.893	0.669	0.083	0.250	0.181
X_{33}	0.04	0.464	0.464	0.460	0.097	0.896	0.654
X_{12}	0.062	0.165	0.165	0.210	0.831	0.969	0.171
X_{13}	0.675	0.120	0.120	0.574	0.033	0.117	0.015
X_{23}	0.489	0.185	0.185	0.042	0.432	0.504	0.003
R^2	91.44%	95.77%	95.77%	97.72%	98.61%	99.07%	99.13%
Predicted R^2	0.00%	40.10%	40.10%	75.27%	86.91%	89.56%	89.04%
Adjusted R^2	76.03%	88.16%	88.16	93.61%	96.12%	97.39%	97.56%

properties are influenced by the dispersion of nanoclay in the matrix and the interfacial interaction between the matrix and the nanoclay.[14,39,35] As seen from the XRD and TEM images, the nanoclay is exfoliated in the rubber matrix. The improvement in tensile strength can be attributed to the dispersion of nanoclay in the rubber matrix, rigidity of the nanoclay, and affinity between nitrile rubber and the organo-modified nanoclay. A similar increase in tensile strength can be seen on increasing the sulfur to accelerator ratio. This is due to the increase in cross-link density and the increase in polysulphide linkages[40] The effect of these factors on the properties can be visualized in the main effect plots. The

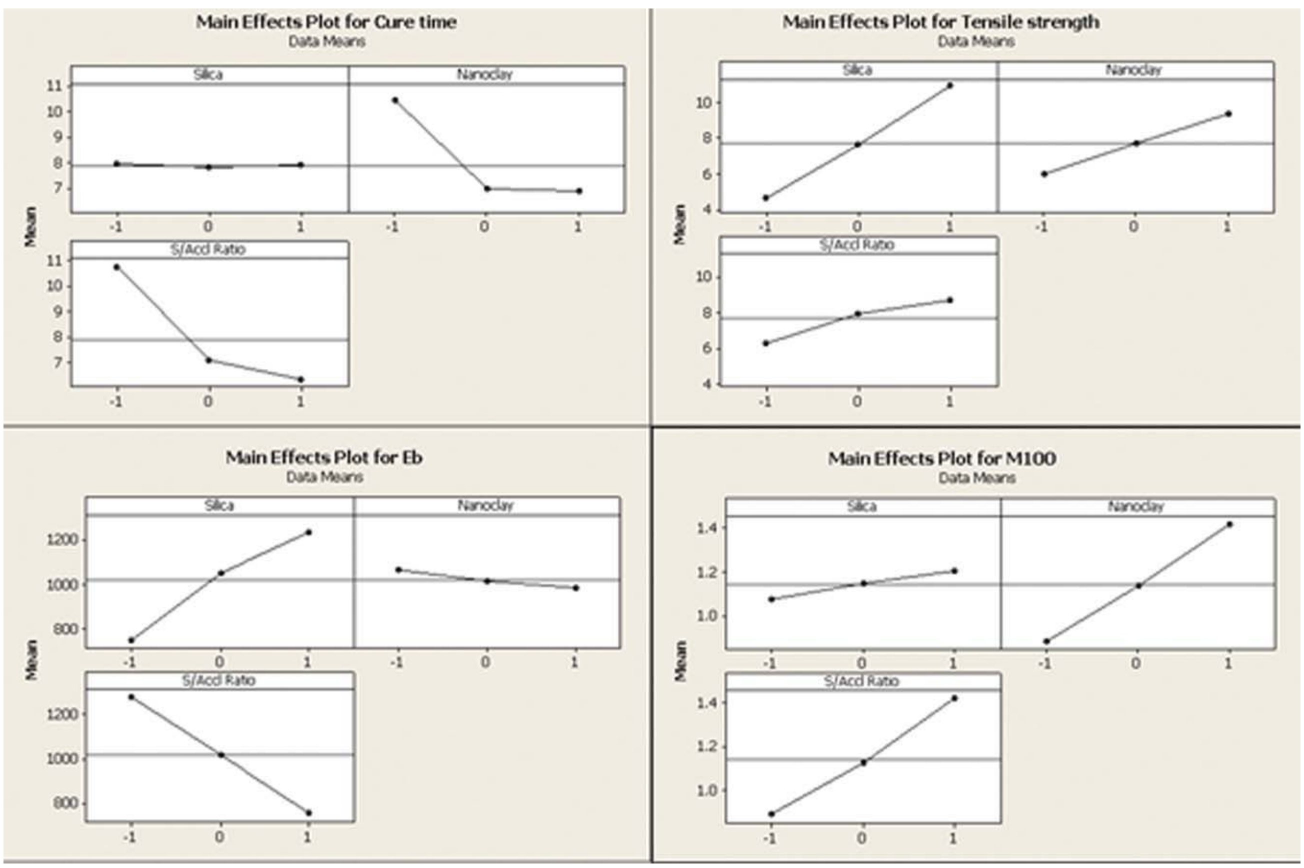

Figure 4 Main effects plot for cure time and mechanical properties of NBR – layered silicate nanocomposites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

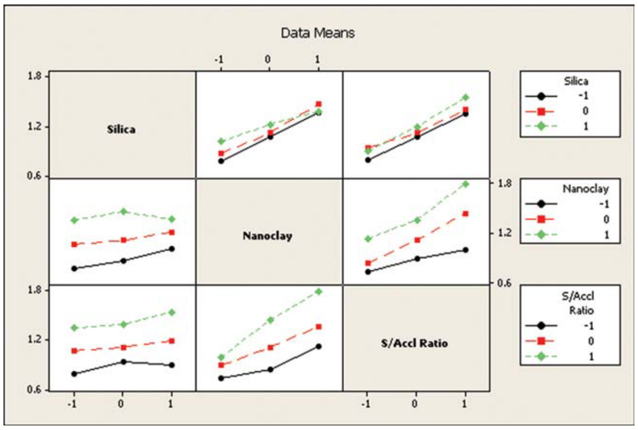

Figure 5 Interaction plot for M100 of NBR-layered silicate nanocomposites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

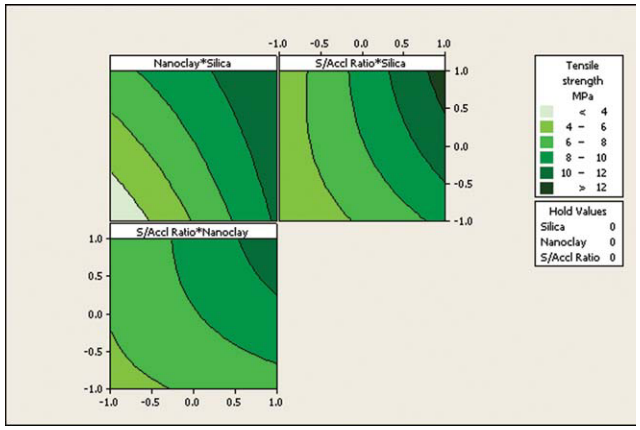

Figure 6 Contour plots for tensile strength of NBR – layered silicate nanocomposites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

coefficients of the interactive terms in eq. (2) are negative but of smaller magnitude and implies that the interactive effect of the factors slightly diminishes the tensile strength. These effects are visualized in the interaction plots described later.

Table V shows a summary of all the responses, the terms that were significant in their models, and summary statistics for each model. The standard error of coefficient (SE Coef) is useful in determining whether the predictor has a significant effect on the response. Small values of SE coefficients indicate a more precise estimate. The p-value that quantifies the significance of terms in the polynomial model should ideally be less than the chosen α-level, such as 0.05, for the term to be significant. In the case of tensile strength for example, the p-values of the regression and linear term are lower than 0.05 and hence are significant terms in the prediction equation. The quadratic and interaction terms have p-value considerably higher than 0.05, hence can be removed from the model. R-square is the percentage of response variable variation that is explained by its relationship with one or more predictor variables. The higher the R-squared values are, the better the polynomial is at either describing the system or making predictions about the system. For the responses under study, the R-squared values of >95% indicate that the polynomials represent very good description of the relationship between the

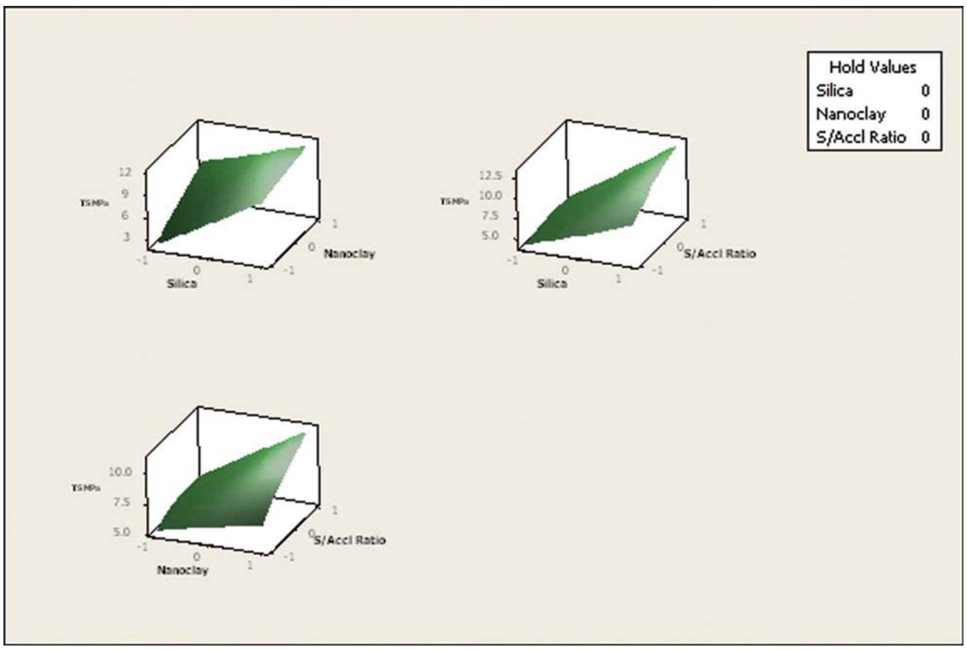

Figure 7 Response surface plots for tensile strength of NBR – layered silicate nanocomposites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

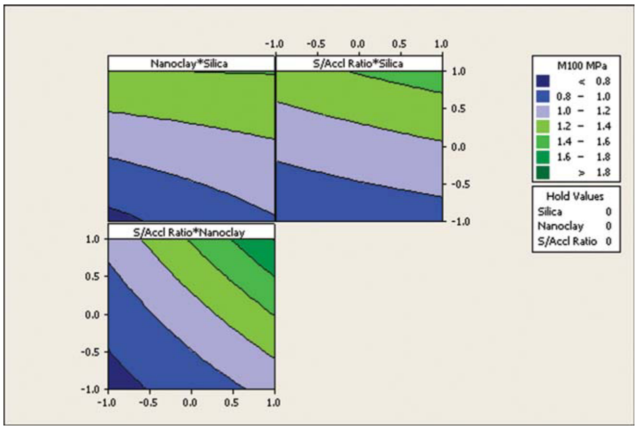

Figure 8 Contour plots for M100 of NBR-layered silicate nanocomposites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

three factors and the responses. Typically, some of the responses will fit to polynomials better than others.

Main effect plots

Main effect plots are used to visualize the effect of the factors on the responses and to compare the relative strength of the effects. When the change in the mean response across the levels of a factor is significant a main effect is present. The slope of the line indicates the strength of the effect. A horizontal line (slope = 0) indicates absence of main effect. The greater the slope of the main effect plot stronger is the effect. Figure 4 gives the main effect plots for the responses. The overall mean of the responses is also plotted across the graph. It can be seen that the silica content has no effect on the cure time of the nanocomposites. Increasing silica content appreciably increases the tensile strength and elongation at break while its effect on M100 is small.

The main effect plot of nanoclay shows that increasing nanoclay content increases the tensile strength and modulus appreciably. The increase in these properties with increasing filler content, both silica, and nanoclay, can be attributed to the reinforcement of the rubber matrix by the fillers. It can be seen that addition of nanoclay decreases the cure time appreciably (indicated by the negative slope in the region −1 to 0) but the amount of nanoclay in the composite has no effect on cure time (a near horizontal line in the region 0 to +1). This is caused by the amine functionalities in the nanoclay. It has been reported that amine containing compounds will facilitate the curing reaction of NBR stocks.[30,41,42] It can also be seen from the main effect plot of nanoclay on elongation at break (near horizontal line) that the increase in strength is brought about without much change in the extensibility of the material. As the ratio of sulfur to accelerator increases, the

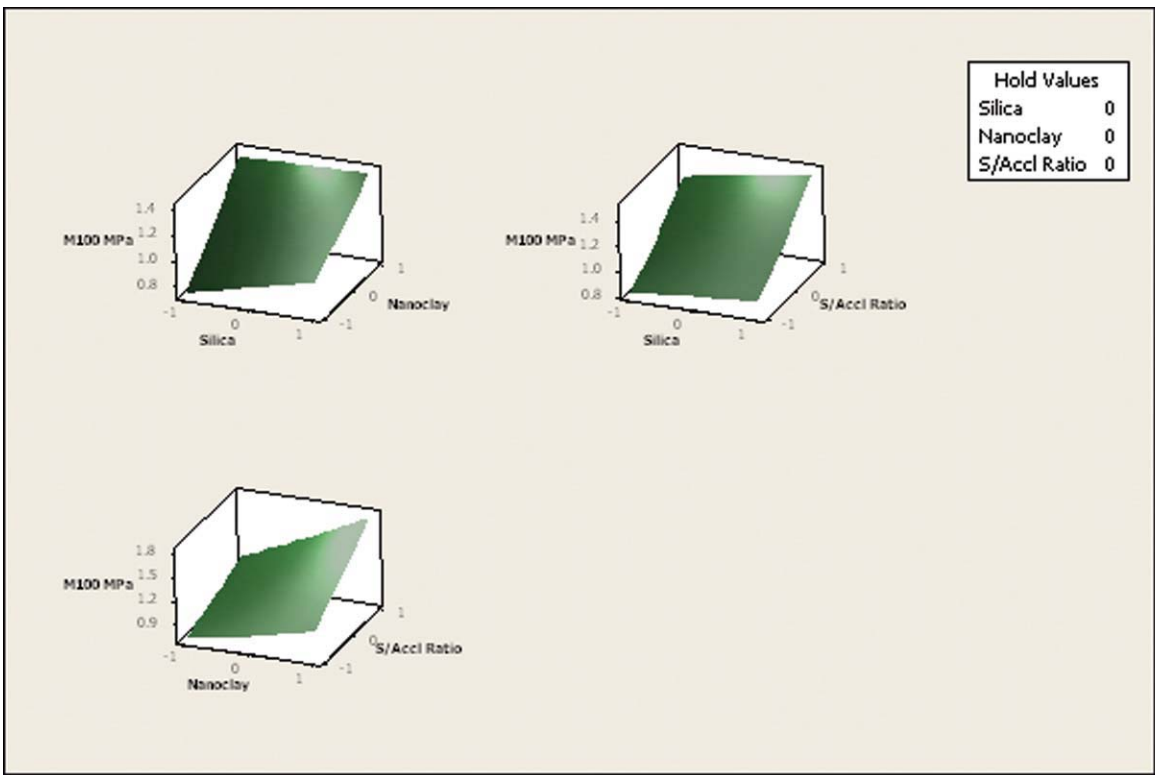

Figure 9 Response surface plots for M100 of NBR – layered silicate nanocomposites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE VI
Comparison of Predicted and Observed Values for Verification Experiment

Properties		Predicted	Observed	% change from actual
Before heat Ageing	Tensile strength (MPa)	7.40	7.68	3.7
	Elongation at Break (%)	914	811	−12.6
	M100 (MPa)	1.24	1.27	2.6
After heat Ageing	Tensile strength (MPa)	6.62	7.53	12.1
	Elongation at break (%)	652	602	−8.2
	M100 (MPa)	1.56	1.64	5.0

tensile strength and modulus increase while reducing the elongation at break indicating formation of more cross links in the matrix. These effects are clearly shown in the main effect plots.

Interaction plots

Interaction plots are used to visualize the interaction effect of factors on the responses and to compare the relative strength of effects. If the change in the mean of the response from a one level of a factor to another depends on the level of another factor, the two factors are said to have interaction effects. Parallel lines represent absence of interaction between the factors. The greater the deviation from parallel, greater is the interaction between the factors. As observed in Figure 5 for M100 data, the interactions between the factors are not significant. Similar tends were observed for other properties.

Response surface plots and contour plots

Response surface plots and contour plots are based on the model equations obtained in the regression analysis. The response surface plot is a three dimensional graph that represents the functional relationship between the response and two variables, while the other variables are held at constant levels. The plot is used to visualize how a response reacts to changes in variables. The two dimensional contour plot is a series of curves that identify different combinations of variables for which the response is constant. Such diagrams illustrate the change in properties when two or more variables vary together and allow predictions to be made for combinations not actually evaluated. Figures 6–9 gives the response surface and contour plots for tensile strength and M100.

Verification experiments

Confirmatory experiments were carried out to validate the equations, using combinations of independent variables, which were not part of the original experimental design but were within the experimental region. The coded values of the variables used in the confirmatory experiments are silica −0.5, nanoclay +0.5 and sulfur/accelerator ratio 0. In terms of the actual values, they are 5 phr, 7.5 phr and 2.0 for silica, nanoclay and sulfur/accelerator ratio, respectively. The predicted and experimental values for mechanical properties before and after aging listed in Table VI were in good agreement. These

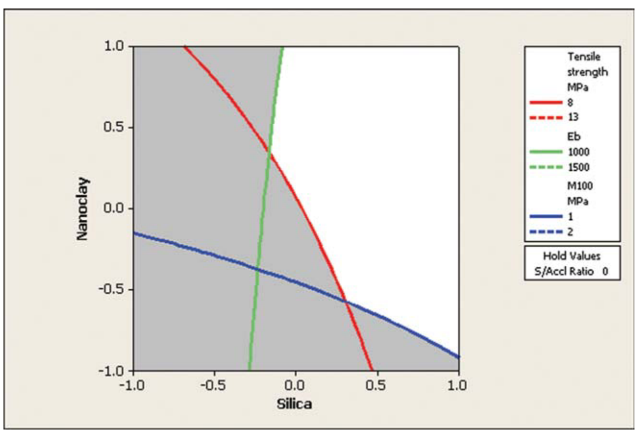

Figure 10 Overlaid contour plots for mechanical properties of NBR-layered silicate nanocomposites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

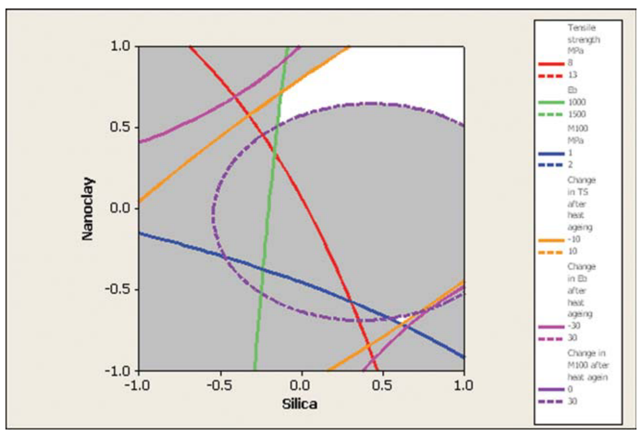

Figure 11 Overlaid contour plots for mechanical properties and heat aging effects of NBR-layered silicate nanocomposites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE VII
Constraints on Responses for Overlaying Contour Plots

Dependent variables (Responses)	Constraints
Y_1 = Tensile strength	8–13 MPa
Y_2 = Elongation at Break	1000–1500%
Y_3 = M100	1–2 MPa
Y_4 = Change in tensile strength after heat aging	±10%
Y_5 = Change in Elongation at break after heat aging	±30%
Y_6 = Change in M100 after heat aging	±30%

validations confirmed the suitability of the design chosen, method of sample preparation, and property evaluation.

Optimization of nanocomposite formulation

The contour plots for tensile strength, elongation at break, modulus at 100% elongation and changes in tensile strength and modulus after heat aging were overlaid to find the feasible region (shown as white region) having desired properties (Figs. 10 and 11). The desired values of all these properties can be obtained at any given combination within the optimized region. For the purpose of overlaying, nanoclay and silica contents were chosen as variables keeping the value of sulfur/accelerator ratio constant at mid point. The constraints on the responses are shown in Table VII. A typical optimized formulation is silica 20 phr ($X_1 = +1$), Nanoclay 10 phr ($X_2 = +1$) and sulfur/accelerator ratio 0.956 ($X_3 = -0.614$). The predicted properties for this formulation are as given below.

Before aging

Tensile strength: 9.94 MPa, Elongation at break: 1289%, M100: 1.18 MPa.

After aging

Tensile strength: 9.92 MPa, Elongation at break: 996%, M100: 1.64 MPa.

CONCLUSION

Silica loading, nanoclay content, and sulfur/accelerator ratio of NBR compounds were optimized using Design of Experiments approach. The nanocomposites were characterized for Tensile Strength, Modulus, and Elongation at break, both before and after heat aging. The data obtained were used to generate models by linear regression analysis using MINITAB package. Contour plots (a series of curves that identified different combinations of variables for which the response was constant) for tensile strength, elongation, modulus and change in tensile strength, and modulus after heat aging were overlaid to provide an optimum region for a desired set of specifications. Results from verification experiments were found to be within reasonable limits.

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