Title

Optimization of the NBR Blends for Achiving of Optimized Hardness by Mixture Design

Authors

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Abstract

The extreme vertices mixture design was applied for optimization of the NBR blend for hardness response. The 15 treatment combinations out of 29 candidate points investigated (as proposed by Minitab 14 software) Contained varying proportions of carbon black, sulfur, MBTS (Dibenzothiazyl disulfide), and Antioxidant as four variable factors while other factors were kept constant. The significant model coefficients are interpreted in term of interacting linear and quadratic effects of the NBR variable blend constituents. Based on the three dimensional surface, contour, and response trace plot, MBTS exhibits an adverse negative effect, while sulfur exhibits a strong positive effect on the hardness. Carbon black and antioxidant have, respectively, weak and moderate negative effect on the response. The model was used to predict the treatment combination of the NBR blend in the optimum hardness response. (Hardness response was 54.07, A: 3.52, B: 1.5467, C: 91.9733, D: 2.96). There is no significant difference between the result of the model and which obtained in the laboratory.

Key words

NBR; Extream vertices mixture design; Optimization.

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Introduction

The nitrile butadiene rubber (NBR) is an oil resistant rubber that its mechanical properties are dependent to type and amount of constituents. The NBR used for the friction covering, transmission belts, shoe soling, roll covering and so forth.

One of the most effective property of the NBR is hardness. In general, the hardness range of NBR is from 20 shoreA to ebonite [1, 2].

The NBR blend consists of NBR, sulfur, Carbon black, stearic acid, ZnO, plasticizer The Antioxidant, and accelerator.

It is possible to improve the hardness of the rubber blend by adjusting its composition by adding or subtracting certain amount of carbon black, sulfur, accelerator, and antioxidant. This can be investigated by a systematic study of the rheological and physical behavior of blendes while varying the proportions of carbon black, antioxidant, accelerator and sulfur.

Mixture Designs are among the most widely used tools for product formulation [3]. They provide polynomial equations and convenient graphical representation that enable the chemist to easily predict responses for a wide range of mixtures. It should be noted that factorial designs cannot be used to study such mixtures since the variables are not independent [4].

The aim of this paper is to determine the conditions allowing to increase the hardness by varying the composition of the variables (carbon black, sulfur, accelerator and antioxidant) according to a four constituents mixture design and to propose an optimized quantity model.

Methodology

The section [5] is devoted to briefly review some principles governing the construction and analysis of the mixture designs characterized by a lower and upper bound restrictions on their component proportions.

A mixture experiment is a special type of response surface experiment in which the factors are the constituent of a mixture and the response is a function of the proportions of each ingredient. The coordinate system for mixture proportion is a simplex coordinate system. With four constituent, the experimental region is a tetragon. Each of the four vertices corresponds to a mixture that is made up of a pure component.

In many mixtures, there are restrictions on the component proportions X that prevent the experimenter from exploring the entire simplex region. These restrictions take the form lower (L) and upper (U) constraints on the component proportions. The general form of the constrained mixture problem is:

$$\Sigma X=1 \qquad (1)$$
$$L \leq X \geq U$$

The effect of the upper and lower bound restriction is to limit the feasible space for the mixture experiment to a sub-region of the original simplex, which becomes in general, an irregular convex polygonal. In mixture problems, the purpose of the experimental program is to model the blending surface with some form of mathematical equation so that predictions can be made empirically. In general, we choose a polynomial model, which takes a canonical form because of a second-order mixture (quadratic model) for four constituents takes the form of the following "interaction model". Where b

and e are, respectively, the coefficient and the error of the model.

$$y = b_1x_1 + b_2x_2 + b_3x_3 + b_4x_4 + b_{12}x_1x_2 + b_{13}x_1x_{23} + b_{14}x_1x_4 + b_{23}x_2x_3 + b_{24}x_2x_4 + b_{34}x_3x_4 \quad (2)$$

In order to study the shape of the constrained sub-region, it is useful to start by enumerating the vertices of the sub-region and determining their coordinates. This is important because the vertices and convex combinations of some of the vertices are primary candidates for the design pointes to be used in collecting data to fit the polynomial model. To this end, a computer software package, based on an algorithm that computes the coordinates of the extreme vertices and convex combination of vertices and selects a subset of the pointes to be used as design pointes, is required.

The D-optimal criterion can be used to select the subset pointes for a mixture design in a constrained region. This particular criterion selects design pointes from a list of candidate pointes so that the variances of the model regression coefficients are minimized.

For mixture experiment, the D-optimal design algorithm requires:

1. a set of reasonable candidate pointes from which the design pointes are selected;
2. a convenient method for actually identifying the coordinates of these pointes in the constrained design space;
3. a systematic procedure or set of rules for selecting the pointes.

Following the program of experimentation, the data are analyzed as in the response surface methodology (RSM). The results are used to:

-Fit the empirical model;

-test the adequacy of the fitted model;

-visualize the shape of the three-dimensional response surface;

-plot the contours of the predicted responses;

-determine the optimal settings of the component proportions or understand the roles played by separate mixture constituent.

Experimental

Materials

NBR (33% acrylonitril) and plasticizer (DOP) were obtained from Korea. Stearic acid (95%) was obtained from Palma Leo Sdn.Bhd company of Malaysia. Sulfur (99.7%) was purchased from Tesdak Company of Iran. Carbon black (N375), antioxidant (IPPD), and accelerator (MBTS) purchased from Pars Company of Iran, China and Germany, respectively.

Apparatues

The blend of the NBR with other constituents was carried out by a laboratory size two-roll mixing mill (SYM-6, WELL SHYANG Company of Taiwan). Optimum curing time is obtained by Rheometer (Hiwa 900). Hardness test have been taken by HARDNESSMETER (49038, SHORE A, BAREISS Company).

Software

In this work, the experimental design was carried out by Minirab14 for all calculations and the treatments of data.

Design of blendes

The different blends of the NBR were prepared by mixing the fixed and variable constituents. Carbon black, sulfur, accelerator, and plasticizer defined as variable constituent and others constituent were kept constant. Since the variables (sulfur, carbon black, accelerator, and antioxidant) were not independent, mixture design was used for design the prepared

blendes.

Preparation of the blendes

The compounding of NBR with vulcanization ingredients and other constituents was carried out by a two-roll mixing mill. The amounts of constituents are in terms of parts per hundred of rubber and the composition of the NBR blend with variable and fixed factors are given in Table 1.

At first step the required amounts of stearic acid and ZnO were mixed with masticated NBR at 55 °C after which the carbon black was mixed and finally accelerator, antioxidant, sulfur, and plasticizer were added sequentially after cooling down the mixing mill.

After mixing the rubber as described above, the obtained compounded sample, was subjected to curing study to get the optimum curing time. This study was carried out with the help of a rheometer at 160 °C. The stocks were cured under pressure at 160 °C to the optimum cure (t_{90}).

Determination of the Hardness test

After 48 h from curing, the Hardness test was carried out according to ASTM 2240.

Resultes and Discussion

The variable constituents are A: MBTS, B: Sulfur, C: Carbon black (N-373), D: Antioxidant (IPPD).

The constraints have been imposed on the constituent as shown in Table 1. The extreme vertices-mixture design has employed for the analysis of the data. These results in a design with 29 runs at least 10 must be selected in order to fit the quadratic model. Additional experiments must be run so that an estimate of error can be obtained and the model adequacy can be checked. The D-optimal design selected 15 pointes out of 29 Condidated pointes, as shown in Table 2.

Table 1- The levels of variable factors

Component	Minimum	Maximum
A(MBTS)	0.024	0.048
B	0.008	0.0024
C (N-373)	0.888	0.952
D (IppD)	0.016	0.040

Table 2- Mixture design for variable factors.

RUN	MBTS	Sulfur	Carbon (N-375)	Anti oxidant (IPPD)
1	2.4	0.8	95.2	1.6
2	4.8	2.4	88.8	4
3	4.8	1.6	92	1.6
4	2.4	2.4	91.2	4
5	2.4	2.4	93.6	1.6
6	2.4	0.8	92.8	4
7	4.8	0.8	90.4	4
8	4.8	2.4	90	2.8
9	3.6	1.6	92	2.8
10	3.6	2.4	90	4
11	3.6	0.8	94	1.6
12	2.4	0.8	94	2.8
13	4.8	0.8	91.6	2.8
14	3.6	0.8	91.6	4
15	2.4	2.4	92.4	2.8

The fixed and variable amounts are listed in Table 3. Measurement of hardness (H) is carried out as indicated above and listed in Table 3.

Fitted to the 15 pointes in Table 3, the second-order models for hardness are represented by Equation (3):

$$H= -2341X_1+ 10542X_2- 4X_3- 7169X_4+25539\ X_1X_3+ 30746\ X_2X_3 \quad (3)$$

The analysis of variance for this model is shown in Table 4 .The regression of sum of squares is statistically significant (their p value is less than 0.05) [6,7,8]. In this case ,the correlation coefficient is equal to 92.94%.

Table -3 The constant and variable amount of factors and measured response.

RUN	NBR	ZNO	Stearic acid	(DOP)	MBTS	Sulfur	carbon (N-375)	Anti oxidant (IPPD)	Hardness
1	160	8	1.6	35	2.4	.8	95.2	1.6	42.4
2	160	8	1.6	35	4.8	2.4	88.8	4	54.4
3	160	8	1.6	35	4.8	1.6	92	1.6	52.6
4	160	8	1.6	35	2.4	2.4	91.2	4	53.4
5	160	8	1.6	35	2.4	2.4	93.6	1.6	46.2
6	160	8	1.6	35	2.4	.8	92.8	4	43.6
7	160	8	1.6	35	4.8	.8	90.4	4	58
8	160	8	1.6	35	4.8	2.4	90	2.8	56.8
9	160	8	1.6	35	3.6	1.6	92	2.8	55.2
10	160	8	1.6	35	3.6	2.4	90	4	55.4
11	160	8	1.6	35	3.6	.8	94	1.6	45.4
12	160	8	1.6	35	2.4	.8	94	2.8	50.8
13	160	8	1.6	35	4.8	.8	91.6	2.8	48.6
14	160	8	1.6	35	3.6	.8	91.6	4	48.4
15	160	8	1.6	35	2.4	2.4	92.4	2.8	55.4

Figure 1 presents a plot of the residuals versus the fitted values .[9] This plot is satisfactory.

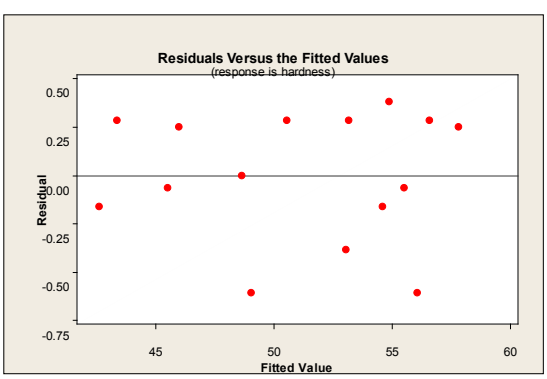

Figure 1- Study of the residuals of the hardness response

By taking a look at the coefficient estimated for the model, it is very difficult to describe the hardness behavior of NBR blendes, while varying the proportions of variable factors either together or separately over the constrained region. Equation (3) is used for generating response surface plot as a contour or a three-dimensional surface plot over the constrained region as shown in Figure 2. In this study, it is important to obtain a high hardness response. The contour plot in Figure 2 indicates that there are several formulations that will meet that requirement.

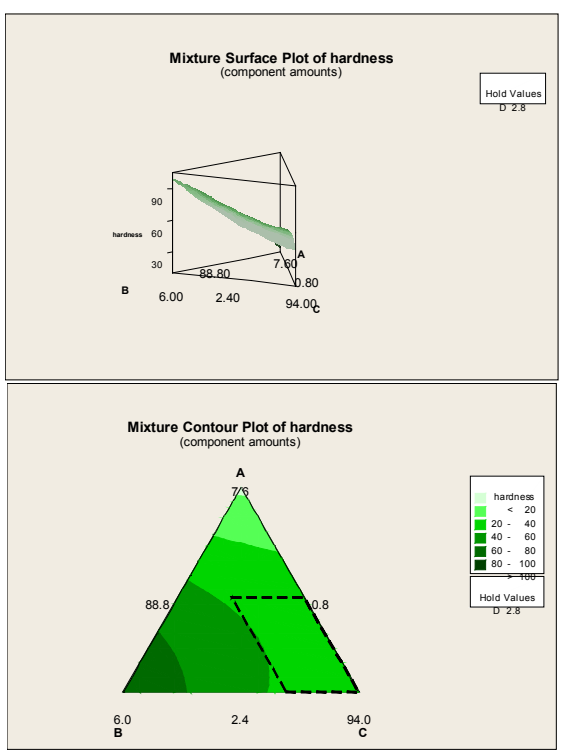

Figure 2- Contour plots and three-dimensional surface plot of the hardness response at a constant level of D equal to 2.8

The area of the highest hardness is located on the left edge of the plots. Both the contour and the surface plot show that the hardness of NBR blend is highest when the mixture contains much sulfur, little or no MBTS and little carbon black.

In order to evaluate the contribution of each of the four constituents, the response trace technique can be utilized. This technique measures changes in the estimated response that are brought about by changing the proportion of a single component while keeping the relative proportions of the other constituents fixed [9].

In practice, the response trace is a plot of the estimated response values as we move away in general, (the centroid of the experimental region) and along the constituent axes. Figure 3 shows the response trace of hardness responses using the centroid of the constrained domain (A=3.6, B=1.6, C=92, D=2.8) as reference mixture S. In this figure, the vertical axis is the predicted response and the horizontal axis is the incremental change in each component. The reference mixture is shown as the point 0.000 on the horizontal axis. This graph is readily interpreted: it clearly shows that B (sulfur) really exhibits a positive strong effect, while C (carbon black) and A (MBTS) exhibit a weak and strong negative effect on the hardness, respectively. As expected, D (antioxidant) has an adverse effect on the hardness but the magnitude of this effect is less than A (MBTS).

According to Equation (3), interactions of A*C and A*D, indicate that the two constituents act either synergistically or are complementary. It means that, the mean hardness response for the blend is greater than the simple mean of the two hardness responses for each pure mixture.

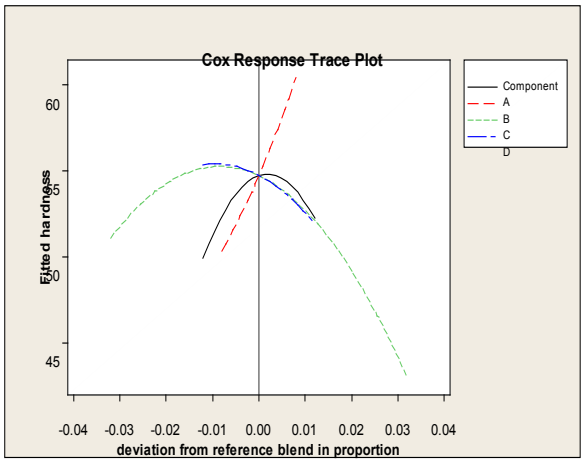

Figure 3- Response trace of hardness.

Optimization

Response optimization helps to identify the combination of input variable settings that jointly optimize a single response or a set of responses. Joint optimization must satisfy the requirements for all the responses in the set, which is measured by the composite desirability

Optimization was carried out on the variable factors and the optimum point for hardness response was determined.

The amounts of variables in the optimum point presented in Table 5 (predicted response: 54.0792 composite Desirability =1.0000). Composite desirability has a range of zero to one. One represents the ideal case and zero indicates that one or more responses are outside their acceptable limits. Composite desirability is the weighted geometric mean of the individual desirabilities for the responses.

Table 4- Analysis of variance of the response hardness

Sourse	Df	Seq ss	Adj ss	Adj Ms	F	P
regression	9	345.454	345.4538	38.3838	21.48	0.002
linear	3	295.654	35.5020	11.8340	6.62	0.034
Quadratic	6	49.799	49.7993	8.2999	4.64	0.057
Residual error	5	8.936	8.9355	1.7871		
total	14	354.389				

Table 5- The amounts of constituents in the optimum point.

constituent	amount
A	3.5200
B	1.5467
C	91.9733
D	2.9600

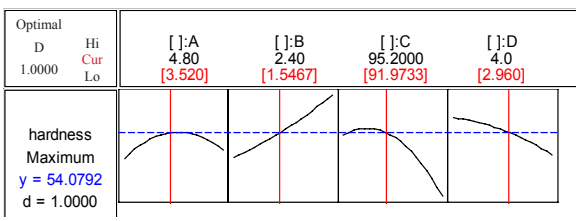

Figure-4 Response optimization plot for hardness.

The proposed blend was made in laboratory and hardness test was carried out on the blend. The amount of hardness (53.9) was similar to the result that obtained by the model.

Conclusion

The mixture design, performed in this study in order to determine the effect of each of four variable constituents on the hardness of NBR blendes. It clearly shows that:

- Sulfur has a strong benefit on the increasing hardness.
- MBTS, antioxidant, and carbon black have strong, moderate, and weak negative effects on the increasing hardness, respectively.

The proposed optimized model was examined in the laboratory and the same results were obtained, thereby, the optimized model is confirmed.

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