Influence of Carbon Black, Calcium Carbonate and Dioctyl Phthalate Compositions on the NBR Vulcanized Rubber Properties Through Experiments Design

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Summary: In industrial practice involving mixtures of raw materials, it is desirable to be able to predict how a change in their proportions will affect the product's properties. In this work the effect of three major vulcanized rubber raw materials was investigated. All other raw materials, as well as processing conditions, were kept constant. Ten formulations were vulcanized by compression moulding (175 °C, ~17 MPa, during 5 minutes) and characterized. The statistically valid property equations calculated from the characterization results show that a range of compositions exists within which the final product has the desired properties and can still be comfortably manufactured.

Keywords: composites; experiments with mixtures; mechanical properties; modelling; NBR rubber

Introduction

The rubber industry includes a variety of products manufactured from complex mixtures of different kinds of raw materials using several processes (*e.g.* mixing, extruding, cutting, moulding, vulcanising).[1–3] With the introduction and generalised usage of the ISO 9000 series of standards, the performance and manufacture of rubber products has been receiving more and more attention. Sharp market competition demands shorter product development cycles and reduced costs, which include raw materials and processing but also research and development costs. All of that makes it difficult to define an adequate new formulation by simple adjustment of older ones, based on rule of thumb or virtue of experience. Thus, the application of experimental techniques which can contribute to improve research and development of rubber compound will be welcome either to scientific research or industry.

Because of its oil-and-fuel-resistant characteristics, nitrile rubber (NBR) finds its greatest market in applications where these characteristics are necessary. NBR can be compounded to obtain a broad range of properties. Reinforcing fillers are necessary in order to achieve optimum properties with NBR. Vulcanisation can be achieved with sulphur, sulphur-donor, or peroxide systems. Organic peroxides are used to vulcanise rubbers that are saturated or do not contain any reactive groups capable of forming crosslinks. This type of vulcanization agent does not enter into the polymer chains but produces radicals which form carbon-to-carbon linkages with adjacent polymer chains.[1–3]

The effect of raw materials on the physical properties of rubber compounds has been the objective of interesting research studies[4–6] but the results cannot

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be easily extrapolated to different compositions. The application of the statistical design of experiments (DoE) to the industrial formulation of rubber mixtures can become a convenient and accurate means of obtaining reliable quantitative estimates of properties as the result of any change of raw materials contents. The modelling of a given property using the design of mixture experiments is becoming a common practice[7,8] and has proven, in most of cases reported, to lead to greater efficiency and confidence in the results obtained, resulting in more reliable conclusions, demanding less time, material and human resources.

The design of mixture experiments configures a special case in response surface methodologies using mathematical and statistical techniques.[9] The basic assumption is that the selected mixture property depends solely on the fractions ($\sum x_i = 1$) of specific components, or ingredients, of the mixture, and not on the amount of the mixture (*i.e.* the property is not extensive). This means that the change in (or the response of) the property is assumed to be entirely determined by the proportions of those components in the mixture and an equation describing the response surface as a function of composition can be used to predict the property value for any mixture.

In this work DoE technique was used to study NBR formulations aiming to find optimum compositions which can be used as automobile rubber components. Thus, regression models were calculated from the results of variance analysis, relating hardness, tensile strength and elongation at break of rubber compounds with the proportions of fillers (carbon black and calcium carbonate) and processing oil (dioctyl phthalate) in the raw materials mixture, under constant processing conditions and other raw materials contents (NBR elastomers, ageing inhibitor, activator and vulcanizing agent).

Methodology

The rubber components and the original formulation used in this study were based on the oil resistant compounds manufactured by CARIBOR—Tecnologia da Borracha Ltda, Joinville, SC, Brazil (Table 1). Two nitrile-butadiene rubber (NBR) elastomers, A and B, were used: NBR A, with 45 wt. % acrylonitrile, and NBR B, with 33 wt. % acrylonitrile, 50 phr (per hundred of rubber by weight) oil filled. Other ingredients included carbon black (Spheron 5000), dioctyl phthalate and calcium carbonate. Besides these ingredients, the mixtures include special additives, namely, aging inhibitor (Naugard 495), ZnO activator and vulcanizing agent dicumyl peroxide.

As shown in Table 1, the proportions of carbon black (CB), calcium carbonate (CC) and dioctyl phthalate (DOP) were varied in the compositions, but the other raw materials and additives contents, as well as processing conditions, were kept constant. The chosen processing conditions closely followed the conventional laboratory rubber compound procedure used in industrial practice[1–6] and require that lower bound composition limits are used, which were 35 wt. % CB, 35 wt. % CC and 10 wt. % DOP.

A {3, 2} centroid simplex-lattice design augmented with interior points was used to define the ten mixtures (Table 2 and Figure 1) of those raw materials that should be investigated.[9] The CB, CC and DOP contents were changed from the phr base values to weight fractions. For each of the ten different formulations, the selected amounts of raw materials were mixed in a two-roll laboratory mill (200 mm diameter, 500 mm length, 1.2 gear ratio),

Table 1.
Base composition of industrial NBR rubber vulcanized.

Ingredients	Content [phr][a]
NBR A	50.00
NBR B[b]	75.00
Carbon black (CB)	various
Calcium carbonate (CC)	various
Dioctyl phthalate (DOP)	various
Naugard 495	2.50
ZnO	5.00
Di-cumyl peroxide	3.00

[a]Per hundred of rubber by weight.[b]Rubber containing 25 phr DOP oil.

Table 2.
Mixture compositions and measured values of hardness (HD), tensile strength (TS) and elongation at break (EB) for the ten simplex mixtures.

Mixture	Weight fraction			HD	TS	EB
	CB	CC	DOP	[Shore A]	[MPa]	[%]
1	0.383	0.483	0.134	64 ± 1	12.8 ± 0.1	175.7 ± 2.1
2	0.483	0.383	0.134	66 ± 1	15.5 ± 0.2	167.3 ± 2.2
3	0.550	0.350	0.100	71 ± 1	18.3 ± 0.2	165.7 ± 1.8
4	0.450	0.350	0.200	62 ± 1	13.2 ± 0.2	164.4 ± 1.9
5	0.417	0.417	0.166	63 ± 1	12.5 ± 0.1	165.7 ± 2.1
6	0.350	0.350	0.300	54 ± 1	9.5 ± 0.1	181.2 ± 2.6
7	0.350	0.550	0.100	65 ± 1	13.4 ± 0.2	180.1 ± 2.3
8	0.350	0.450	0.200	60 ± 1	10.9 ± 0.1	178.3 ± 2.0
9	0.383	0.383	0.233	59 ± 1	11.9 ± 0.1	180.9 ± 2.4
10	0.450	0.450	0.100	67 ± 1	14.9 ± 0.1	164.3 ± 1.9

as recommended by the ASTM D 15 Standard.[10] The mixtures were vulcanized by compression moulding at 175 °C during 5 minutes under ~17 MPa in an electrical resistance heating press, and characterized.

The hardness (HD) test was carried out according to ASTM D 676 Standard[11] using a Zwick durometer. The tensile strength (TS) and elongation at break (EB) tests were carried out according to ASTM D 412 Standard[12] using an EMIC DL 2000 test machine. For each mixture, the property final value was taken as the average of the test results obtained for five different test pieces.

Those experimental results were then used to iteratively calculate the coefficients of a regression equation, until a statistically relevant model and response surface was obtained, relating the hardness, tensile strength and elongation at break of the rubber compound with the weight fractions of carbon black, calcium carbonate and DOP present in the corresponding mixture of raw materials (the calculations were carried out with *STATISTICA* — StatSoft Inc., 2007).

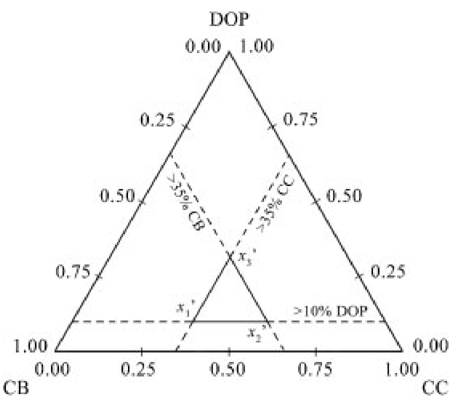

Figure 1.
The ternary system CB-CC-DOP (independent components), showing: the raw materials triangle, the restricted pseudo-components triangle and simplex points restrictions.

Results and Discussion

Table 2 presents the mixture compositions and measured values for hardness (HD), tensile strength (TS) and elongation at break (EB) obtained for the ten mixtures.

Having a measured value for the property response at specific coordinates (Table 2), a regression equation can be sought for each property. Both linear and quadratic regression models were evaluated, subjected to a significance level of 5%. Table 3 shows some results of the variance analysis (ANOVA) of the regression equations obtained for HD, TS and EB, using the nomenclature commonly found in the literature. The major statistical properties *p*-value and coefficient of multiple determination (R^2) were selected to present the results of the variance analysis.[9]

Using the p-value approach to hypothesis testing (*i.e.* p-value ≤ significance level), Table 3 shows that the quadratic model does not reach the stipulated

Table 3.
Major statistical properties, relevant for variance analysis[9].

Property	Regression model	Variance analysis results	
		p-value	R^2
Hardness (HD)	Linear	0.0000	0.9911
	Quadratic	0.1008	0.9951
Tensile strength (TS)	Linear	0.0000	0.9662
	Quadratic	0.2576	0.9864
Elongation at break (EB)	Linear	0.0187	0.6794
	Quadratic	0.3431	0.8491

significance value (it is not statistically significant) for the three properties studied. Due to high p-value obtained for the three properties (0.1008, 0.2576 and 0.3431 for HD, TS and EB, respectively) to use quadratic model to model the properties will undermine the viability of the equation. According to results there are not interactions among the factors. If it admits interaction and the quadratic model is used to modelling the properties as function of composition, it could there be high probability of the models do not predict accurately the properties, due to high p-value obtained through variance analysis. Otherwise, the linear model is statistically significant at that level in all cases (Table 3) and the corresponding coefficients of multiple determinations show that the linear model explains most of variability in the data.

The final equations, relating the HD, TS and EB with the proportions of the independent components are shown by Eq. (1) to (3). These equations are all referred to the weight fractions of components CB, CC and DOP, so that mixing of raw materials can easily be carried out.

$$\text{HD [Shore A]} = 87.54\,(\text{CB}) + 60.88\,(\text{CC}) + 7.54\,(\text{DOP}) \tag{1}$$

$$\text{TS [MPa]} = 30.63\,(\text{CB}) + 5.85\,(\text{CC}) - 11.42\,(\text{DOP}) \tag{2}$$

$$\text{EB [\%]} = 120.49\,(\text{CB}) + 205.83\,(\text{CC}) + 218.33\,(\text{DOP}) \tag{3}$$

The effect of each raw material on the studied properties can be best visualised in terms of constant property contour plots of the Eq. (1) to (3). Figure 1 shows the location of the pseudo-components triangle defined by the lower bound composition limits, within the full composition triangle.

Rubber hardness usually increases with the fillers content (both CB and CC) due to higher crosslinking density (*i.e.* filled vulcanized rubber is harder than gum vulcanised rubber),[1–6] which is confirmed by the constant hardness contour plot presented in Figure 2. Figure 2 also shows very clearly the strong hardening effect of carbon black and the comparatively innocuous effect of calcium carbonate, which is commonly used as cost reducing filler. Hardness values of 60–68 Shore A are reached for high contents of carbon black and low contents of DOP, namely, in the raw materials

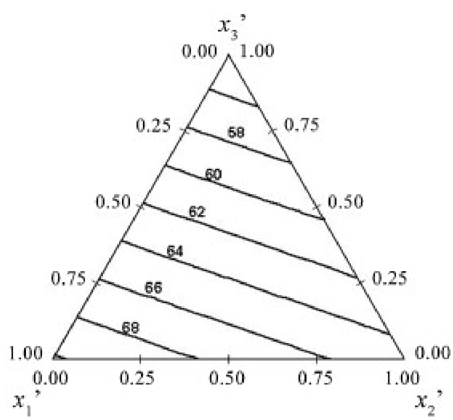

Figure 2.
Predicted constant property contour plots as a function of composition (pseudo-components x_1', x_2', and x_3' correspond to carbon black, calcium carbonate and DOP fractions, respectively) for the hardness (Shore A).

composition range of 42–53 wt. % carbon black, 35–55 wt. % calcium carbonate and below 17 wt. % DOP.

Carbon black reinforcement and vulcanization generates a unique three-dimensional visco-elastic network that transforms a soft elastomer into a strong, elastic product. This reinforcement effect can be explained by the partial immobilization of the polymer chain segments due to the presence of carbon black.[1–6] This can be confirmed in the constant tensile strength contour plot shown in Figure 3. As expected, compounds containing high carbon black amounts show high tensile strength whereas increasing calcium carbonate contents tend to reduce the compound's tensile strength. Tensile strength values above 12 MPa are reached for high contents of carbon black and low contents of DOP, namely, in the raw materials composition range above 41 wt. % carbon black, 35–55 wt. % calcium carbonate and below 16 wt. % DOP.

Figure 4 presents the constant elongation at break contour plot. As expected, Figure 4 shows the inverse trend, that is, increasing carbon black contents favour a decrease in EB, while increasing DOP or calcium carbonate contents contribute to raise EB. Elongation at break values above 168% are reached for high contents of DOP and low contents of carbon black, namely, in the raw materials composition range below 47 wt.% carbon black, of 35–55 wt.% calcium carbonate and above 18 wt.% DOP.

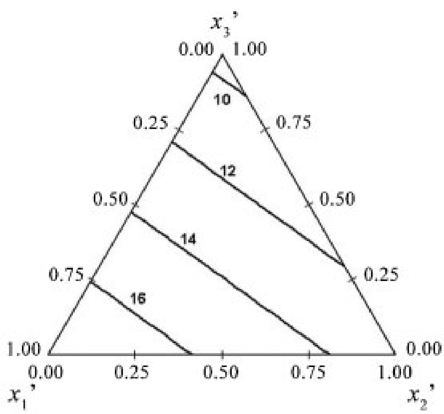

Figure 3.
Predicted constant property contour plots as a function of composition (pseudo-components x_1', x_2', and x_3' correspond to carbon black, calcium carbonate and DOP fractions, respectively) for the tensile strength (MPa).

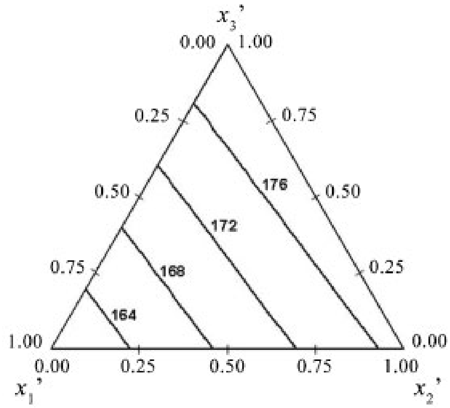

Figure 4.
Predicted constant property contour plots as a function of composition (pseudo-components x_1', x_2', and x_3' correspond to carbon black, calcium carbonate and DOP fractions, respectively) for the elongation at break (%).

Two extra mixtures, 11 and 12, were used to validate the calculated statistical models (check-point mixtures). Table 4 presents the compositions of those two mixtures, in terms of independent components (the mixtures and their test pieces were prepared following the same procedure used before), and the corresponding measured and predicted values for HD, TS and EB. It can be seen that the error of the estimate calculated using Eq. (1) to (3) is low when compared with the corresponding experimental value, which validates the calculated models.

Conclusion

The design of mixture experiments and the use of response surface methodologies enabled the calculation of valid regression models relating the hardness, tensile strength and elongation at break of vulcanized rubber

Table 4.
Composition of check-point mixtures and corresponding measured and calculated values of hardness (HD), tensile strength (TS) and elongation at break (EB).

Design	Weight fractions			HD	TS	EB
mixture	CB	CC	DOP	[Shore A]	[MPa]	[%]
11	0.410	0.390	0.200	62 ± 1	12.75 ± 0.10	163 ± 2.11
12	0.470	0.410	0.120	68 ± 1	15.79 ± 0.17	158 ± 1.87
Predicted value, check-point mixture 11				61	12.55	173
Predicted value, check-point mixture 12				67	15.42	167

compounds with composition, after the same processing. Those models can be used to select the best combination of carbon black, calcium carbonate and dioctyl phthalate contents to produce a rubber compound with specified properties.

Furthermore, the calculated models readily show that, for the particular raw materials and processing conditions under consideration, there is an optimum composition range within which it is possible to simultaneously specify the values of hardness, tensile strength and elongation at break, kept same conditions and processing procedures.

The use of intersecting surfaces showed that, for the particular raw materials and fabrication process under consideration, there is an optimum composition range of 42–53 wt. % carbon black, 35–55 wt. % calcium carbonate and below 17 wt. % dioctyl phthalate within which the studied NBR rubber compounds are expected to present hardness values between 60 and 68 Shore A, tensile strength above 12 MPa and elongation at break above 168%.

In this way, the specified characteristics of the desired product can be subjected to restrictions typical of the manufacture process and a range of compositions can still be selected so that the final product has the desired properties and can be comfortably manufactured.

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