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Optimization of properties in a rubber compound containing a ternary polymer blend using response surface methodology

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ABSTRACT: In order to find the best combination of three synthetic rubbers, that is, styrene-butadiene rubber (SBR) grade 1712, SBR grade 1721 and high-1,4-cis polybutadiene, that produce a compound with specific end-use properties, a statistical experimental design is proposed in this work. The design consists of ten mixtures containing specific amounts of total styrene and BR content. A number of properties are tested in each mixture, selecting those related to requirements for the tread of a high performance tire: glass transition temperature (T_g), the ratio between the viscous modulus and the elastic modulus (tanδ@60 °C), Mooney viscosity, and the tensile properties. The values obtained for each property are fit to statistically significant models, obtaining the respective response surfaces. These are next used to define a desirable formulation with the optimal ratio of each rubber, and finally the optimized formulation is validated by comparing the experimental and predicted values for each modeled property. © 2018 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2018**, *135*, 46548.

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INTRODUCTION

Elastomeric blends are one class of composite materials used in polymer-based industrial products. The need for making a polymer blend in the development of a compound may be given by several reasons, for example, to improve some mechanical property of the original rubber, to increase the processability of the resulting blend, or to decrease compound costs. All elastomeric materials have some deficiency in one or more of its mechanical properties, and blending is a way to obtain a compound with an improved overall performance. However, the mixture, in addition to having beneficial mechanical properties, must be capable of being processed in a production scale without excessive energy consumption and providing a homogeneous material in terms of performance.[1]

The development of a polymer blend to make a compound with a specific end use is a complicated task in the field of rubber technology. Obtaining the proper rubber formulation is not simple and involves a careful selection of the ingredients, since each one will have a certain impact on the final material. In particular, the selection of the rubbers to be used in a formulation presents the main effect on the properties of the compound, since there are different types of rubbers, each affecting differently a given property. In addition to this, many formulations are based on mixing two or more rubbers of different composition, since it is an effective way to achieve certain properties in a compound.

One additional difficulty in the development of a particular compound is the relationship between the ingredients within a formulation and the properties of the material obtained. In this field it is known that “you can never change just one thing”, implying that the change in any ingredient of a formulation will simultaneously affect various properties of the material. Then, by implementing any kind of change in the compound formulation trying to improve a property, this change will affect other properties, either for better or worse, and therefore this is complex when more than one change is desired within the formulation. To solve this problem, a compounder can rely on their

Additional Supporting Information may be found in the online version of this article.

experience and intuition, and usually undertakes a series of trial and error experiments, of the type "one change at a time", until reaching the correct balance in all the desired properties of the compound.

A different approach to solve the previously stated problem is to use a statistical Design of Experiments (DoE), in order to achieve the optimal set of properties in a compound. By means of a DoE, multiple changes can be studied simultaneously and many responses can be analyzed, generating a mathematical solution. Usually the DoE requires some preliminary experiments in order to define the base formulation, select the variables to be changed and set the limits for such variables, and finally establish the right design. However, this technique is more effective in terms of finding the best combination among the changes made, and achieving the desired requirements in all the whole properties of the compound, with a lower consumption of materials and with saving of time, which eventually results better than changing one variable at a time.[2]

When a process is studied using DoE, the design allows choosing which are the experiments that will provide the greatest amount of information, avoiding investing experimental effort in irrelevant trials. In addition, the design provides a systematic approach to analyze the way in which the variables affect the process, with the ability to discriminate the actually significant ones and the least important factors, and to detect possible interactions between them as well.

A properly implemented design will always provide useful information about such process, and may even reveal non-trivial aspects, if any. While the optimization of the process is the most important result expected from the DoE, the design can also indicate if the equipment used is appropriate, if the process will be able to provide a certain response, and so on. It can thus be said that applying DoE for the study of a process is worth the effort.[3]

It is important to mention that not only the materials in the compound can affect its properties, but also the operations of processing, and the variability of the performance tests, and therefore this has to be considered when carrying out a DoE in a rubber compound development.

DoE

In the implementation of the experimental design, factors or variables should be selected for the system under investigation, differentiating the observed or measured variables (i.e., the system responses, in this case the properties of the compound) and the independent variables or factors that describe the state of the system (i.e., the ingredients and its amounts in the formulation). The purpose of the experimental design is to specify the value of the independent variables, as well as to select the appropriate response.[4] The response model is a mathematical formulation capable of describing the response of the system corresponding to the selected independent variables; there are four important steps in building the most appropriate model:

1. Select levels for the independent variables.
2. Develop an appropriate mathematical representation for these variables.
3. Identify any potential interactions between the independent variables, as well as any nonlinear responses in the dependent variables.
4. Validate the model, for example evaluating its ability for predicting a final property.

The use of an experimental design has already been shown on rubber materials, either to study the properties of the rubber or its compounds, as well as in the polymer production stage. It has been reported by Balachandran *et al.*[5] in the application of DoE to evaluate and predict the final mechanical properties of an NBR rubber by varying the fillers and the vulcanization system within the formulation. DoE has been used also in some works Kundu and coworkers[6,7] with the goal of establishing a functional relationship between the amount of carbon black and vegetable oil with different properties of the rubber, as well as to find the optimum amount of vegetable oil that works as a coupling agent. In a similar way, Sridhar *et al.*[8] used DoE to find the best combination of carbon black and nanoclays filler loading a chlorobutyl rubber using a minimum number of experiments. The effects of processing parameters on the properties and the production of polymer blends and vulcanizates using DoE and response surface methodology were reported.[9,10] It has been also reported the use of DoE to find the appropriate parameters in the polymerization of a high cis BR by Maiti *et al.*[11] In such work, the statistical tool is applied to find an efficient catalytic system and the appropriate polymerization conditions of butadiene.

Use of Rubber in High Performance Tires

In this work, we present the application of DoE for the optimization of compounds containing styrene-butadiene rubber (SBR), which is one of the most important synthetic polymers in terms of production volume and variety of applications. About 40% of the world consumption of synthetic elastomers is based on SBR, its most important application being the manufacture of tires for all kind of vehicles. We have previously applied a similar optimization approach in the case of SBR polymerization, modeling the response for some reaction parameters and measuring important structural properties as polymer molecular weights and polydispersity.[12,13]

In the present study, we apply DoE for the optimization of SBR compounds, and, in addition, we use polybutadiene rubber (BR), which is in second place among the synthetic rubbers produced and used worldwide. BR represents approximately 23–25% of the total synthetic rubber consumed. About 70% of the BR produced is used in different stages of tire manufacturing. Another important use of BR is as impact modifier in the production of high impact polystyrene.

Globally, the trend towards "high performance" tires, designed to respond to environmental concerns, is evident. Environmental consciousness gives rise to new regulations in multiple areas, and the manufacture of tires does not escape this generalization; the regulations in this case involve the tires as final product, as well as the rubber used as raw material and even other components such as plasticizing oils. For example, the requirements of a modern high-performance tire include fuel economy, use of low aromatic oils, minimization of the release of rubber

Table I. Properties of the Rubbers Used in Blends

	Rubber		
Property	E-SBR1712	E-SBR1721	BR
Styrene (%)	23.5	40	—
1,4-cis units (%)	12	12	98
Extender oil (%)	27.5	27.5	—
Mooney Viscosity (MV)[a]	53.7	52.4	38.7
Tensile (MPa)[b]	18.6	18.6	n.d.

n.d., not determined.
[a] Measured on the rubber polymer.
[b] Measured on the vulcanized compound.

particles into the environment, noise minimization, together with issues related to safety such as tire grip on a wet pavement and safe handling of tire waste.

All these technical requirements call for some changes and new development in the materials used in the design of a rubber compound with which the tire is manufactured. The challenge of new rubber materials can be approached from two different points of view: developing polymers with new molecular structure, or generating new blends of known polymers, which provide different properties. Examples of the first strategy are the development of BR rubber with high cis-chain content in its microstructure (which is obtained by solution polymerization with metallocene catalysts using Nd), or the development of SBR polymerized in solution (S-SBR) with controlled microstructure. Regarding the second strategy, the replacement of the carbon black used in the rubber formulation by silica has been recently proposed for tire compounds, as well as the use of different mixtures of SBR and BR.[14]

It is known that in a high-performance tire an S-SBR is used, which has a modified microstructure with high content of 1,2-vinyl units, blended with a BR of high content of 1,4-cis units, therefore improving the processability and lowering the rolling resistance. In this work, we propose to use a blend of E-SBR grade 1712, E-SBR grade 1721, and high cis BR, to obtain a formulation with properties comparable to those found in high performance tires. With the implementation of an experimental design, it is intended to establish a functional relationship between the factors, that is, the amount of each rubber in the ternary blend, and the measured variables, that is, the compound properties, representing such relationship as a response surface. In each surface, it is possible to find a maximum, corresponding to a specific combination of the factors. Nevertheless, when dealing with more than one measured variable, a compromise value is required among every surface maximum. This can be accomplished with the aid of the desirability function, which can define the optimal value for each factor (i.e., the three polymers in the formulation) that will give rise to the material with the desired properties.

EXPERIMENTAL

Materials

The polymers used in this work were two grades of SBR, E-SBR 1712, and E-SBR 1721, which were provided by Pampa Energía (Argentina). A commercial BR, high-cis CB 728T (Arlanxeo, Brazil) was also used. Table I summarizes the properties of the rubbers used in the experimental design.

The extender oil used in the raw SBR rubbers and in compounds was low aromatic oil provided by YPF (Argentina). For compound preparation, some other ingredients were used, all of them provided by Pampa Energía (Argentina): secondary accelerants (stearic acid, zinc oxide), antioxidants, antiozonants (TMQ, DPPD), and vulcanizing system (sulfur, CBS, DPG), see Table II.

Setup of DoE

A central composite design (CCD) was chosen because it is efficient for a study in which two factors are involved. The two factors to be considered are: total styrene (%Sty.) and amount of BR rubber (pHR BR). In this design, the number of experiments is determined by eq. (1).

$$N=2^k+2k+m \tag{1}$$

where N is the number of experiments, k is the number of factors and m is the replicates of the central point. In this work, two factors make $k=2$, and therefore nine blends were prepared, having a different amount of each rubber. In addition, a compound corresponding to the central point was prepared in duplicate ($m=1$). It was first necessary to fix the limits for the two factors, that is, %Sty. (16–26%) and pHR BR (30–50 pHR). These ranges encompass the values usually employed in the production of a high performance tire. The %Sty. and pHR BR required in each experiment of the design is accomplished by blending a defined amount of every polymer. Table III shows the combinations of the two factors in the prepared compounds.

Before the preparation of the 10 blends of the design, two compounds were prepared, using the extreme values of the factor range. In this screening step, it was verified that the differences between the values of the properties were significant, so that

Table II. Compound Formulation

Ingredient	pHR	Mass (g)
E-SBR 1712	[a]	[a]
E-SBR 1721	[a]	[a]
high cis BR	[a]	[a]
Zinc oxide	6.5	1.50
Stearic Acid	2.7	0.62
TMQ	2.7	0.62
DPPD	2.7	0.62
Total oil	38	8.74
N330 carbon black	91	20.93
CBS	1.6	0.37
DPG	0.4	0.09
Sulfur	2.4	0.55
Total	278	63.94

[a] The amount to be used in each compound is determined by the pHR BR and %Sty. established in the CCD.
TMQ, 2,2,4-trimethyl-1,2-dihydroquinoline polymer; DPPD, *N*,*N'*-diphenil-*p*-phenylenediamine; CBS, *N*-cyclohexyl-2-benzothiazole sulfenamide; DPG, diphenyl guanidine.

Table III. Values for the Two Factors in Each Compound of the Experimental Design

Compound	Factors	
	% Sty.	pHR BR
1	21.30	30.00
2	25.05	33.00
3	17.55	33.00
4	26.60	40.00
5	21.30	40.00
6	21.30	40.00
7	16.30	40.00
8	25.05	47.00
9	17.55	47.00
10	21.30	50.00

these factors would be appropriate in order to obtain response surfaces, once the properties of the 10 compounds were measured.

Selection of Measured Properties

The properties tested as the design responses were those related to characteristics required for the tread of a high performance tire. They include: (a) the glass transition temperature (T_g), related to the elasticity of the material at low temperatures. (b) The ratio viscous modulus to elastic modulus, measured at 60 °C (tanδ@60 °C), which correlates with the rolling resistance, and therefore indirectly with the need of minimizing fuel consumption. (c) Mooney viscosity, which directly influences the processability of the compound. (d) The tensile strength, which is essential to know the performance of the vulcanized compound.[15]

Compounding and Measurement Procedures

Considering the properties of each polymer to be blended (see Table I), preliminary tests were carried out to evaluate their mixing ability with the different materials in the compound. The formulation used is shown in Table II. Taking into account the oil content added in the production step for SBR 1712 and SBR 1721 (typically, 27.5%), extra extender oil had to be added in some blends so that all formulations presented the same amount of total oil, preventing the oil from being a variable that affects the measured properties.

Compound mixing was carried out in a Brabender Plasti-Corder mill at 60 °C. Two batches were prepared for each formulation in order to have enough material for measuring all the properties. They were homogenized in an open mill maintaining the roll temperature at 45 ± 5 °C, according to ASTM D-3189. After obtaining the compound, two samples were cut and stored to allow testing of Mooney viscosity at 100 °C (ASTM D 1646) in an Alpha Technologies MV2000 viscometer, and vulcanization characteristics (ASTM D 5289) in an Alpha Technologies MDR2000 moving die rheometer (sealed torsion shear rotorless instrument) operating at 160 °C, frequency of 1.667 Hz and strain arc of 0.5°.

To obtain standard vulcanized sheets of the blends, the remainder of the batch was sheeted out to 2.2–2.4 mm thickness after shrinkage has taken place, allowed to cool and conditioned for 15–20 h at 23 ± 3 °C. The sheeted compound was cut into pieces to vulcanize and the direction of the milling was marked on each piece. The pieces were vulcanized at 145 °C for 22 min in a steam press, according to ASTM D 3182. The vulcanized sheets were cool in water and conditioned at 23 ± 2 °C for 24 h. From the flat sheet five specimens were cut and the tensile properties, =that is, ultimate tensile strength, elongation at break and modulus at 300% of elongation (M300%), were measured according to ASTM D 412 in an Alpha Technologies T2000 testing machine (see Supporting Information).

The measurement of tanδ@60 °C was based on rheometric analysis. Under a sinusoidal strain of the viscoelastic material, there is a phase angle shift (δ) between the complex torque response and the applied strain. The instrument separates the elastic torque (S', in phase with the applied strain) and the viscous torque (S'', 90° out of phase with the applied strain). The tan δ value is calculated as the ratio of S'' and S' according to eq. (2).

$$\tan\delta = \frac{S''}{S'} \qquad (2)$$

Rubber quality standards recommend the use of a Rubber Process Analyzer (RPA). Instead, we were able to adjust the measurement procedure in the MDR2000 rheometer, setting the temperature at 60 °C and the time limit at 3 min, allowing us to obtain the required tan δ values adequately.[16] Finally, the thermal properties, glass transition temperature (T_g) of both the compounds and the vulcanizates, were determined using a differential scanning calorimeter Perkin Elmer Jade DSC. The DSC measurement was performed under a nitrogen atmosphere on samples of 8–10 mg placed in standard aluminum pans with pierced lids. The heating and cooling cycle was between −150 and 30 °C at a scan rate of 20 °C/min. The first heating scan from −150 to 30 °C was run to eliminate the influence of thermal and mechanical history of the samples. The T_g value was determined as the temperature at the half height of the heat capacity increase (see Supporting Information).

The obtained values of each measured property in the set of 10 mixtures were tried to adjust to statistically significant models; Design Expert 7.0 software (Stat-Ease Inc., Minneapolis, MN 55413-2726, USA) was used to obtain response surfaces and to determine optimal values, with their corresponding statistical analysis. The properties that could be modeled were then used to define a desirable formulation with the optimal amount of each rubber. This was accomplished with the aid of the Desirability (included in Design Expert package), which in mathematical terms reach a compromise among the optimum values of each of the optimizable properties. Finally, in order to validate the model, a new compound was prepared with the optimized formulation, following the general mixing and vulcanization procedures previously described.

RESULTS AND DISCUSSION

The values of the properties measured on each of the 10 mixtures are shown in Table IV. With these data, it was evaluated

Table IV. Properties Measured on the 10 Compounds Prepared for the Design

	Compounds									
Property	1	2	3	4	5	6	7	8	9	10
MV (arbitrary units)	63.6	65.6	67.8	65.7	64.4	65.8	67.1	65.0	64.3	63.0
Tensile strength (MPa)	23.13	21.52	22.90	20.59	21.77	22.24	20.96	21.36	20.68	20.36
% elongation	555	532	500	491	519	509	503	529	496	501
M300% (MPa)	11.45	11.43	12.77	11.70	12.04	12.77	11.39	11.46	11.78	11.65
tanδ@60 °C (compound)	0..44	0.41	0.47	0.41	0.44	0.44	0.47	0.42	0.46	0.43
tanδ@60 °C (vulcanizate)	0.19	0.2	0.18	0.19	0.18	0.18	0.18	0.2	0.18	0.17
Compound T_g (°C)	−57.75	−104.93	−102.64	−105.92	−104.83	−104.48	−104.34	−105.98	−105.3	−104.16
Vulcanizate T_g (°C)	−55.37	−90.22	−60.19	−96.85	−94.03	−93.03	−65.14	−99.16	−67.66	−96.63

in which cases a response surface could be obtained that fit a statistically significant model. This was possible for the following properties: T_g and tanδ@60 °C of the vulcanizate, tanδ@60 °C of the compound and tensile strength.

Table V summarizes some of the information from the ANOVA for each property showing statistical parameters of the fit. The model P value less than or equal to 0.05 indicates that the model will be significant with a confidence interval of 95%. In Table V is presented the polynomial equation that define the surface for each property, where $A = \%$Sty. and $B = $ pHR BR. The corresponding coefficients (a_0–a_7) are included also in Table V, along with their respective P value. The only coefficients included in each model, are those that present a P value less or equal to 0.05 or provide the required p-value for a significant model. The R^2, a term that measures the fit of the model, indicating how much of the variation can be explained by the proposed model, is also included in Table V. From the table it can be seen that, for T_g vulcanizate, tanδ@60 °C (compound) and tensile, the R^2 value for the model proposed is greater than 0.90, and implies that 90% of the variations found in each property of interest can be explained by the model. On the other hand, for the tanδ@60 °C (vulcanizate) response, the R^2 value for the model proposed is 0.63 that, despite being a relatively low value, is considered acceptable and it can be still useful to understanding the changes in the material property.[17]

The response surfaces of each property are shown in Figures 1–4, as a function of pHR BR and total %Sty. in the blend. Axis values in each figure are accommodated so that the shape of the surfaces can be clearly seen.

In Figure 1, it can be seen that the minimum value of T_g, which is desirable for a better vulcanizate performance, is given for a blend with 40 pHR BR and 21.50%Sty. From this minimum, an increment in the content of BR provides more positive values of T_g, probably because this polymer contributes with more double bonds, which implies more crosslinking sites between polymer chains. On the other hand, there is a local minimum at

Table V. Coefficients, P Value and R^2 for the Equation of the Surface, with the Form[a]: $Y = a_0 + a_1A + a_2B + a_3AB + a_4A^2 + a_5B^2 + a_6A^2B + a_7AB^2$

	Coefficients									
Modeled property	a_0	a_1	a_2	a_3	a_4	a_5	a_6	a_7	P value model	R^2
T_g (vulcanizate)	−94.43	−10.38	−14.55	1.23	5.81	8.18	9.28	−3.20	0.0046	0.9987
P value coefficients		0.0040	0.0021	0.2033	0.0100	0.0060	0.0083	0.0752		
tanδ@60 °C (vulcanizate)	0.19	6.52 E-003	-3.57 E-003						0.0584	0.6341
P value coefficients		0.0342	0.2135							
tanδ@60 °C (compound)	0.44	−0.022	-1.38 E-003	4.76 E-003	1.039 E-003	-1.97 E-003			0.0005	0.9888
P value coefficients		0.0001	0.3379	0.0480	0.5374	0.3013				
Tensile strength	21.94	−0.21	−0.75	0.49	−0.46				0.0068	0.9154
P value coefficients		0.01653	0.0025	0.0406	0.0259					

[a] For all proposed models the lack of fit was not significant, with P values of: 0.2422 for T_g (vulcanizate); 0.2965 for tanδ@60 °C (vulcanizate); 0.1985 for tanδ@60 °C (compound); 0.5630 for tensile strength. The complete ANOVA data are available in Supporting Information.

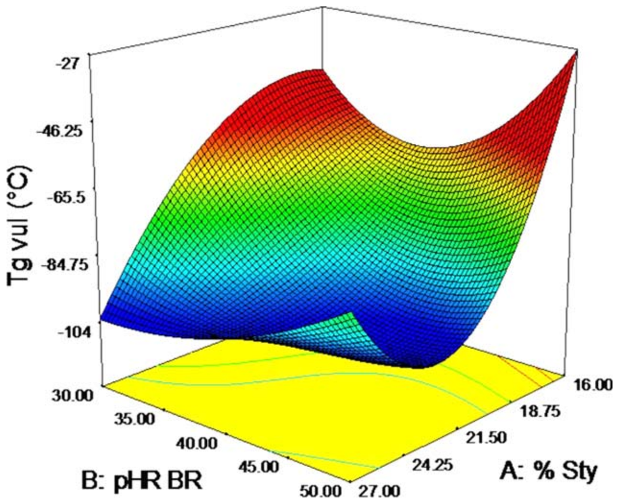

Figure 1. Response surface for T_g of the vulcanizate. [Color figure can be viewed at wileyonlinelibrary.com]

relatively high values of %Sty., which is explained by the presence of interaction terms (a_3, a_6, a_7, see Table V) in the equation of the response surface for T_g. This seems to be contradictory with the idea that at higher quantities of styrene the thermal properties will deteriorate and therefore a more detailed morphology study should be undertaken to address such behavior. It is worth mentioning; however, that in all the vulcanized compounds only one glass transition temperature was observed, indicating a good miscibility between the three types of rubber in the blend.

Figure 2 shows the response surface for tanδ@60 °C of the vulcanizate; it can be seen that as pHR BR increases, the value of this property takes lower values. The tendency is in agreement with the negative value for a_2 coefficient in the corresponding model equation (Table V). In addition, it is coincident with the fact that BR rubber improves the elastic modulus in the vulcanizate, so the tanδ@60 °C of the vulcanizate get smaller. For a compound used in the tread of a tire, the observed decrease in this property will improve the rolling resistance.[18]

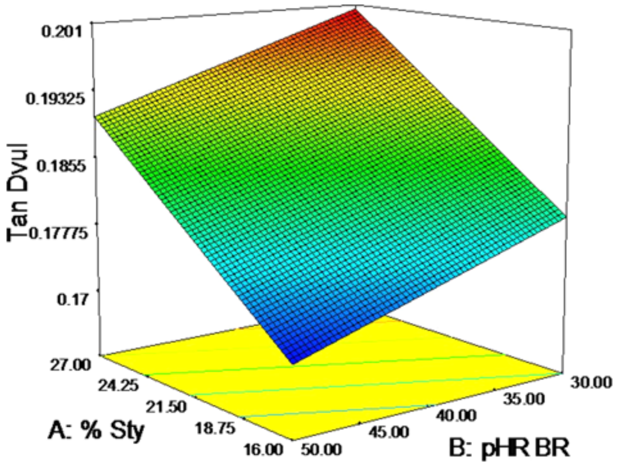

Figure 2. Response surface for tanδ@60 °C of the vulcanizate. [Color figure can be viewed at wileyonlinelibrary.com]

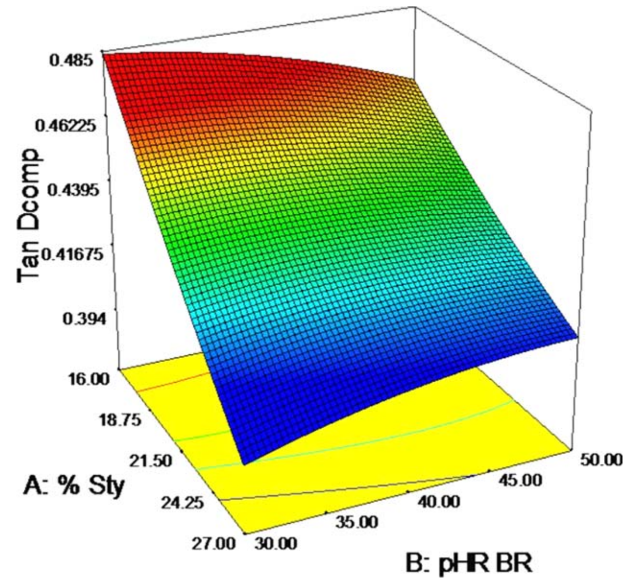

Figure 3. Response surface for tanδ@60 °C of the unvulcanized compound. [Color figure can be viewed at wileyonlinelibrary.com]

In Figure 3, it can be seen the response surface for tanδ@60 °C of the unvulcanized compound, and in Figure 4 the corresponding to the tensile strength. For these responses, the interactive terms play a key role in the proposed models (a_3 coefficients, see Table V), because they allow access to information that was not trivial when developing the experiments. For the tanδ@60 °C of the unvulcanized compound, both a_1 and a_2 terms are negative, but the higher absolute value of a_1 makes the property decreasing with the rise of %Sty., at any BR content.

For the tensile strength, the equation of the response surface presents only the quadratic term a_4 for %Sty., causing it to have

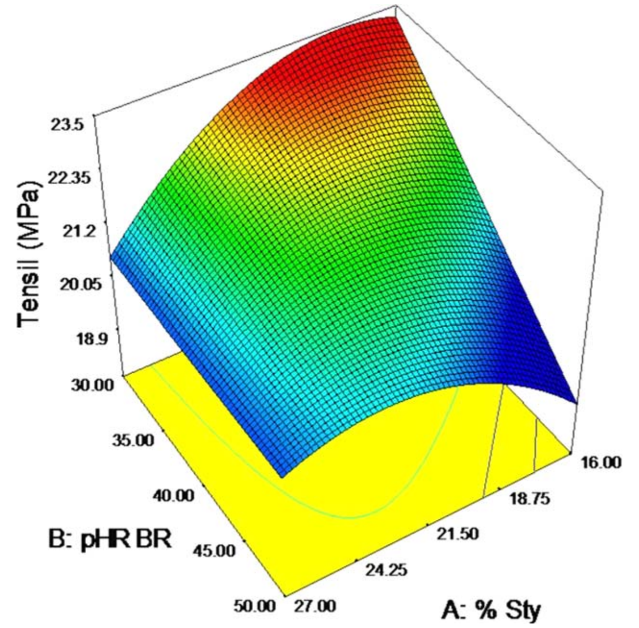

Figure 4. Response surface for ultimate tensile strength. [Color figure can be viewed at wileyonlinelibrary.com]

Table VI. Parameters Defined for the Desirability Function

Property	Goal	Weight lower (*w*1)	Weight upper (*w*2)	Importance (*ri*)
T_g (vulcanizate)	Minimize	1	5	5
tanδ@60 °C (vulcanizate)	Minimize	1	0.1	1
tanδ@60 °C (compound)	Maximize	1	1	3
Tensile strength	In rank	1	1	3

a dominant effect on this property. The lower values of %Sty. indicates that the compound has a higher proportion of rubber E-SBR 1712, and it is known that this rubber has a tensile value higher than the corresponding to E-SBR 1721 or BR rubbers.[19] Therefore, it is expected that, at low %Sty. content, the rubber E-SBR 1712 dominates, thus increasing the tensile strength of the vulcanizate, as we can see in Figure 4. On the other hand, when %Sty. is high, the tensile value is not sensitive to the amount of BR. It is observed that the region of higher tensile values corresponds to a low pHR BR and an amount of styrene between 19 and 20%.

The four modeled properties were employed to obtain an optimum formulation and thus to evaluate the proposed experimental design. The required optimum formulation was determined with the aid of the desirability function, in order to achieve a compromise between the optimal values of each of the four properties.

The Desirability function transforms a problem of multiple responses optimization into a single response case, denoted as simultaneous desirability (D). In this method the values of each estimated response is transformed into a dimensionless desirability value d_i. These latter values range from zero to one, that is, from an unacceptable to an optimum response, respectively. The d_is can be affected by a weight (w_1, w_2) that emphasizes either the minimum or the maximum limits. In the problem presented here, an optimum must be obtained for four responses, and the simultaneous desirability D will be the geometric mean of the four transformed responses d_i, each affected by a relative importance r_i. Table VI shows the parameters used in the construction of the desirability function.[20–22]

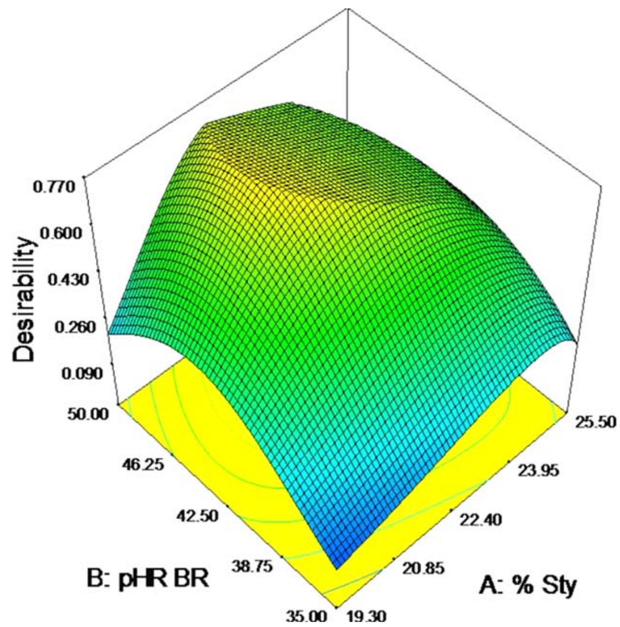

Figure 5. Response surface for simultaneous desirability. [Color figure can be viewed at wileyonlinelibrary.com]

It can be seen from Table VI that the required values for the responses include a minimum value for T_g and tanδ@60 °C of the vulcanizate, and a maximum for tanδ@60 °C of the compound. Regarding the tensile it is expected that the optimum falls within the range of values of the model. The mathematical treatment of the desirability function aims to find a unique value for the independent variables, % Sty. and pHR BR, capable of produce such desired objective values in the final properties.

The surface of the simultaneous desirability is shown in Figure 5. The maximum of this surface corresponds to the optimized values of the variables: 21.41%Sty. and 45 pHR BR. In terms of the used formulation (see Table II), these values represent 52 pHR of E-SBR 1712, 66 pHR of E-SBR 1721 and 45 pHR of BR.

It can be seen in Figure 5 that the optimum blend is the region presented at intermediate %Sty. values, and at high pHR BR content, in relation to the ranges used for each of these variables.

In the validation step, the values predicted by the model were compared to those obtained in experimental determinations carried out on the optimized compound. Table VII shows both, the predicted and experimental values for each property. Experimental values were obtained by averaging the results on two compounds with the optimum ratio of the three rubbers, prepared separately. Comparing these experimental values with those predicted from every response surface in the model, it is possible to conclude that the differences are not significant and can be considered within the experimental errors.

On the other hand, the values of the optimized properties shown in Table VII can be compared with those found in the literature corresponding to the tread of tires. The value of tan δ of vulcanizate for commercial passenger tires is in the range

Table VII. Predicted and Measured Values of the Properties in the Optimized Compound

Property	Predicted	Measured
T_g (vulcanizate) (°C)	−100.00	−99.9 ± 3.8
tanδ@60 °C (vulcanizate)	0.179	0.184 ± 0.005
tanδ@60 °C (compound)	0.437	0.438 ± 0.005
Tensile strength (MPa)	21.4	20.8 ± 0.6

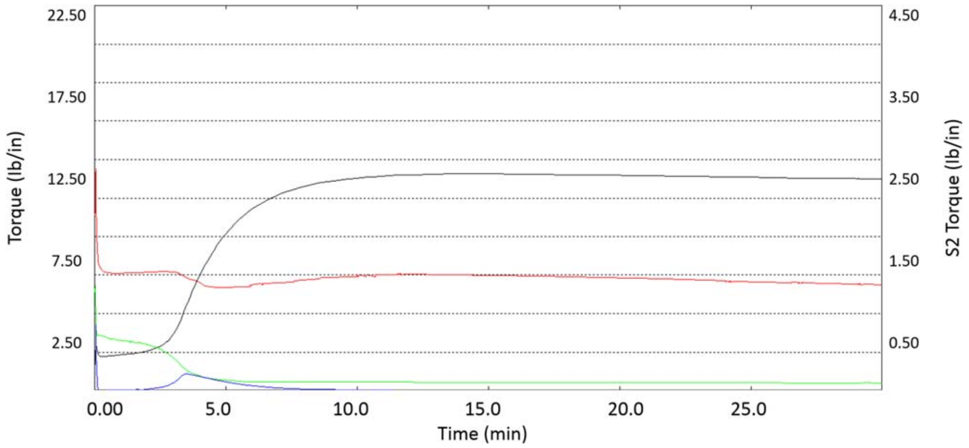

Figure 6. MDR rheometric curve of the optimized compound; black line: S' torque (elastic torque); red line: S'' torque (viscous torque); green line: tan δ (S''/S' ratio). Measurements were performed according to ASTM D 5289. [Color figure can be viewed at wileyonlinelibrary.com]

0.150–0.256.[23] The measured value in the ternary blend of rubbers is 0.184, which is within that range and towards the lowest values. With regard to tensile strength, values as high as 19.8 MPa have been reported,[24] so that the value obtained in the optimized compound is slightly higher than those reported, and is still a useful value for this application. With respect to glass transition T_g, the smaller its value the better, since this property is related to the flexibility of the tire at low temperatures.[24] On the other hand, a high value in the tan δ of the compound makes easier the extruding and molding operations of the raw compound to give the definitive shape.

Figure 6 shows the rheometric curve (black line) measured on the optimal compound prepared. This compound, with the best combination of three rubbers, has a time scorch (*ts*) of 2.7 min. We can compare such *ts* with those from compounds having only one of the studied rubbers. In additional experiments, we prepared three compounds, each with only one type of rubber (i.e., one compound using SBR 1712, a second one with SBR 1721, and a third one with BR alone). The compound with E-SBR 1712 has a *ts* of 3.69 min, the compound with E-SBR 1721 has a *ts* of 4.24 min and the compound with BR has a *ts* of 1.89 min. So the optimal blend reach a ts lower than any SBR, allowing a faster vulcanization and therefore lower energy requirement. We can observe in the curve a slope downwards, indicating a reversion stage. This means that if performing the vulcanization beyond the time when reversion occurs, a loss of properties will be produced. Reversion is typical for compounds using BR alone.[25] For the optimized blend, reversion appears later, and the vulcanization time of 22 min is well before the reversion occurs.

A more detailed analysis of this cure curve, along with the comparison of its characteristic times and torques, is important and can be performed from a theoretical and experimental approach.[26–29] In such references, the use of kinetic models is described, as well as the simulation of a rheometer curve using a few parameter data, fitting the curve with parabolic and hyperbolic functions.

CONCLUSIONS

A formulation could be developed consisting of a blend of three different types of rubbers, widely used in tire compounds. Using an experimental design, the optimization of properties involved in the tread of a tire was achieved. By means of the desirability function, an optimum blend was obtained with a defined amount of each type of rubber, which presented maximum values for tensile and tanδ@60 °C of the compound, whereas for T_g and tanδ@60 °C of the vulcanizate provided minimum values. With the optimum formulation, the model could be validated by comparison between the values predicted and the experimental values measured on new prepared compounds. In addition, the four modeled properties in the material with the optimum blend of rubbers, present values comparable to those found in compounds of commercial tire treads. It would be possible to consider other important properties on tires that could be optimized following a similar approach. Some examples include viscoelastic properties (creep and stress relaxation test, tear strength, storage modulus, loss modulus) or end-use characteristics (wet traction, dry traction, winter, or ice traction), which can be measured either on laboratory-scale compound or on the tire itself, using specific equipment. The focus of the present work is to show the feasibility of the methodology, that uses combined DoE and multiple responses optimization. This strategy was adequate to address a common problem in the production of rubber materials, which involves the compound development stage, reaching a satisfactory result.

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