

Quantification of Styrene–Butadiene Rubber Swelling as a Function of the Toluene Content in Gasoline: A New Method to Detect Adulterations of Fuels

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ABSTRACT: The swelling of styrene–butadiene rubber (SBR) when exposed to organic solvents was measured and mathematically correlated to the toluene concentration in a complex mixture such as gasoline. This relation enables inferences to be made regarding the composition and quality criteria of the fuel and represents a new method to detect adulterations. Changes in the mass and volume were measured by gravimetric and hydrostatic techniques. A simplex-lattice experimental mixture design was carried out in mixtures with toluene, heptane, and type C gasoline (a blend of gasoline with ethanol) and the mass swelling was statically analyzed for 5 and 15 min of continuous immersion in the mixtures of the solvents. For the experimental design two cubic equations were obtained with a high value for R^2 -adjusted (>0.98) at $25^\circ\text{C} \pm 1^\circ\text{C}$ correlating mass swelling of SBR and the content of solvents. For both immersion times, the greatest and most important effect over the mass swelling was the content of toluene, with the mass variations increasing proportionally with toluene content in the gasoline. The analysis of variance applied to the mass swelling data verified that it is possible to obtain good mathematical equations to associate the rubber swelling with the solvent composition and concentration. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Rubbers are characterized by a long range of elasticity.¹ The elasticity is increased after submitting the rubber to vulcanization process, which creates the crosslinks in the polymeric chains. When a crosslinked polymer is placed in a solvent, the solvent molecules penetrate into the network and it swells. After certain time, an equilibrium state becomes established when network forces and osmotic pressure balance each other.²

The degree of interaction between polymeric matrices and solvents, and therefore the degree of swelling, is dependent on the several criteria: the mass ratio between monomers in a copolymer,³ the degree of crosslinking,⁴ solvent and polymer chemical composition, the functionality of the junction units between polymeric chains, and other intrinsic parameters related to the polymer such as molecular mass, polydispersity index, spatial

orientation, glassy transition temperature, tacticity, and free volume of the polymer.⁵ External parameters such as temperature,⁶ agitation, and exposure to radiation can also have an influence on the interaction.⁵

It is well known from the literature that the swelling degree increases with the time of immersion in the solvent.^{1,7,8} However, the degree of rubber swelling is also a function of the characteristics of the solvents such as molecular weight, polarity, and molar volume.

This reflects a polymer's particular selectivity for establishing several degrees of interaction with solvents according to the respective polymer-solvents affinities. Rubbers have the same selective behavior toward solvents as crosslinked polymers.^{3,9,10–13}

This study was designed to investigate the swelling behavior of styrene–butadiene rubber (SBR) in response to its preferential

interaction with toluene over heptane in a blend of gasoline and ethanol anhydrous.

Gasoline is a mixture of several volatile petroleum hydrocarbons with between 4 and 12 carbon atoms, whose distillation range varies between 30 and 225°C under atmospheric pressure.¹⁴ The hydrocarbons present in gasoline may be classified into four basic classes: paraffins (normal and branched), cycloparaffins, olefins, and aromatics and its exact composition of gasoline varies considerably depending on the nature of the petroleum from which it originates, the process through which the gasoline is obtained, the end use for which it is produced and the legislation in place at the location of production and distribution (permitted contents of benzene, sulfur, lead, etc.).¹⁵

The addition of ethanol to refinery gasoline in Brazil is mandatory and the content can oscillate between 20 and 25 ± 1% by volume, according to the availability of the raw material for its production and oscillations in the price of alcohol and sugar on the internal and external markets. The sale of refinery gasoline is not permitted in gas stations in Brazil. Type C gasoline is the designation for the mixture of ethanol and refinery gasoline, according to specifications determined by local legislation.¹⁵

Organic solvents are sometimes added to gasoline to reduce its price at the gas stations, since they are cheaper than the fuel. This addition is obviously illegal and must be controlled. The adulterated fuel can cause many problems to the engine; also, it causes an increase in the emission of toxins and pollutant gases. The adulteration by addition of solvents can involve both aliphatic, (e.g., hexane) and aromatic (e.g., toluene and xylenes) substances. Commercial solvents, such as kerosene, thinner, and even diesel oil have been used in this practice.^{16–18}

The high miscibility of organic solvents in gasoline, their chemical similarities, and the fact that most of the substances used for adulteration are normal constituents of refinery gasoline hinder the detection of the adulterating substances.¹⁹ There are many laboratory methods that can be used to determine adulterations in gasoline. One of the techniques commonly applied in this area is gas chromatography (GC), which can be coupled with mass spectrophotometer (MS) to give a more detailed analysis.¹⁹ Although chromatographic analysis is a very efficient analytical method it can be slow when many samples have to be analyzed, and it is also expensive.¹⁷

In this study, it is shown that it is possible to establish a clear mathematical relation between the rubber swelling and the content of a certain chemical substance or class of substances, since rubber has a stereo chemical affinity in a complex mixture such as gasoline. This relation enables inferences to be made regarding the composition and quality criteria of the fuel. The aim is to establish a new method to detect fuel adulterations using polymers as sensors due to different chemical affinities of polymer to solvents expressed by his degree of swelling.

An experimental mixture design was applied, where the components, presented in % v/v, were type C gasoline, heptane, and toluene. The response variables statistically analyzed were the mass swelling of the SBR samples after 5 and 15 min of exposure to the different solvent blends according to the experimental design.

EXPERIMENTAL MIXTURE DESIGN

A simplex-lattice experimental mixture design for three components (% v/v type C gasoline, % v/v toluene, and % v/v heptane) was used in this study. A mixture design is a special type of response surface experiment in which the factors are ingredients or components of a mixture, and the response is a function of the proportions of each ingredient. In a mixture problem with “ q ” components, a simplex-lattice is a uniformly spaced set of points in a regular-sided figure with q vertices in $(q-1)$ dimensions.²⁰ More details are available in the literature.^{20–23}

The response surface fits for mixture designs are presented in eqs. (1)–(4). Considering a mixture with “ q ” components expressed by the independent terms x_i , y is the dependent variable and β_{ij} and γ_{ij} are the coefficients for terms x_i .

- Linear Model

$$y = \sum_{i=1}^q \beta_i x_i \quad (1)$$

- Quadratic Model:

$$y = \sum_{i=1}^q \beta_i x_i + \sum_{i<j}^q \sum_j \beta_{ij} x_i x_j \quad (2)$$

- Special Cubic Model:

$$y = \sum_{i=1}^q \beta_i x_i + \sum_{i<j}^q \sum_j \beta_{ij} x_i x_j + \sum_{i<j}^q \sum_{j<k}^q \sum_k \beta_{ijk} x_i x_j x_k \quad (3)$$

- Complete Cubic Model:

$$y = \sum_{i=1}^q \beta_i x_i + \sum_{i<j}^q \sum_j \beta_{ij} x_i x_j + \sum_{i<j}^q \sum_{j<k}^q \sum_k \beta_{ijk} x_i x_j x_k + \sum_{i<j}^q \sum_j \gamma_{ij} x_i x_j (x_i - x_j) \quad (4)$$

In this study, \mathbf{x} is the vector of the independent variables with three components, i.e., $x_i = [A, B, C]$ where A represents the % v/v type C gasoline, B is the % v/v toluene, and C is the % v/v heptane, respectively.

EXPERIMENTAL

Materials

The refinery gasoline was donated by Repar Petrobras Refinery and stored in a freezer at 0°C to prevent evaporation losses. The chemical composition of the gasoline was determined via Varian CP-3800 gas chromatography with flame ionization detector (GC-FID) using a 100 m × 0.25 mm × 0.5 μm column connected to a mass spectrometer (MS) Varian Saturn 2000. The injected volume was 0.3 μL. Individual components of the

Table I. Composition of the Refinery Gasoline Sample

Hydrocarbon contents by group type			
Hydrocarbon type	wt %	vol %	mol %
Total aromatics	22.389	18.641	18.547
Total iso-paraffins	20.845	22.846	21.815
Total naphthenes	21.679	20.664	20.892
Total olefins	15.879	17.303	20.146
Total oxygenates	0.237	0.214	0.300
Total paraffins	14.835	16.186	15.495
Total unknowns	4.136	4.146	2.806
Ethanol	0.000	0.000	0.000
Total	100.00	100.00	100.00

gasoline sample were characterized using detailed hydrocarbon analysis software (StarDHATM). Table I shows the composition of the refinery gasoline used in this study.

The pro-analysis grade solvents heptane, toluene, anhydrous ethanol, and acetone were used without further purification. The type C gasoline was obtained by mixing 75% v/v refinery gasoline with 25% v/v anhydrous ethanol (>99.5% purity) at 25°C ± 1°C.

A sheet of a common type of styrene-butadiene rubber produced by OrionTM was obtained on the local market, classified as M2AA-703A13-EA-14-Z1 according to ASTM D2000.²⁴

Methods

The tests were performed at the Laboratory of Mass Transfer – LABMASSA/UFSC. The methodology of the experiments was based on the ASTM D471 and ASTM D6814 standards.^{25,26} The OrionTM SBR samples were cut from the sheet of SBR mentioned above, obtained locally, with the dimensions 2.5 cm × 5.0 cm × 2.0 mm, as recommended in ASTM D471. The cross-linking density was determined as described at ASTM D6814 using the Flory-Rehner equation and toluene as solvent. The value estimated was 0.4192×10^{-3} mol/cm³.

These samples were immersed in acetone at room temperature for the extraction of components remaining from the vulcanization process, such as plasticizers, sulfur, accelerators, antioxidants, process improvers, and other extractable materials entrapped by the crosslinked matrix, which could be extracted by solvents during the swelling tests, affecting the results and the swelling equilibrium.^{3,27,28}

The extraction process consisted of the immersion of five rubber samples in 150 mL of acetone in a sealed glass bottle at room temperature for five consecutive days. During this period the acetone was recycled using a rotary evaporator and replaced in the bottle with the samples. After the extraction, the samples were placed to evaporate the acetone for 1 week, until they reach constant weight. At the end of this period, a reduction in the volume of around 18% and an 8.5% increase in the average density of the samples were noted. After the acetone extraction, the density of the rubber samples had increased from 1.6060 g/cm³ to 1.7422 g/cm³, with a standard deviation of 0.0048.

According to the standard ASTM D471, the swelling experiments should be carried out in triplicate and the mean obtained, and the three specimens must be swollen at the same time and inside the same recipient. Also, there should be no direct contact of the samples with each other or with the walls of the recipient. Thus, a 2.45 mm diameter hole was made on the top of each sample. The hole allowed a wire to be passed through the samples to suspend them from a support fixed under the lid of the bottle, to prevent contact between the samples and the recipient walls. Also, between each rubber sample, a glass bead was placed to ensure their separation.

The immersion tests were carried out in the absence of direct light, inside a closed recipient of glass containing 150 mL of solvent. The flasks containing the solvents were previously placed in an acclimated room at a temperature of 25°C ± 1°C to ensure the correct dosage of the blends of the gasoline with the solvents.

In this study, 14 blends were prepared containing type C gasoline, toluene and heptane in the volumetric proportions given in Table II, and the dosage of solvents was performed at 25°C using volumetric pipettes. To prevent problems associated with the varying quality of the gasoline from gas stations, the type C gasoline was prepared in the laboratory by mixing 75% (v/v) of refinery gasoline with 25% (v/v) of anhydrous ethanol.

The swelling temperature was established as 25°C ± 1°C and it was controlled using an ultra thermostated water bath during the first day of the swelling to prevent temperature alterations due to sample manipulation during mass measurements. At the end of the first day and until the end of the experiment, that is, on the seventh day, the flasks containing the solvent and the samples were stored in an acclimated room at 25°C ± 1°C in the absence of light.

The mass and volume swelling measurements were obtained through the difference in the mass before and after immersion

Table II. Mixture Experimental Design

Experimental cases	Type C gasoline (% v/v)	Toluene (% v/v)	Heptane (% v/v)
M1	16.67	66.67	16.67
M2	66.67	0.00	33.33
M3	33.33	33.33	33.33
M4	66.67	16.67	16.67
M5	16.67	16.67	66.67
M6	0.00	66.67	33.33
M7	100.00	0.00	0.00
M8	33.33	0.00	66.67
M9	0.00	33.33	66.67
M10	33.33	66.67	0.00
M11	33.33	33.33	33.33
M12	66.67	33.33	0.00
M13	0.00	100.00	0.00
M14	0.00	0.00	100.00

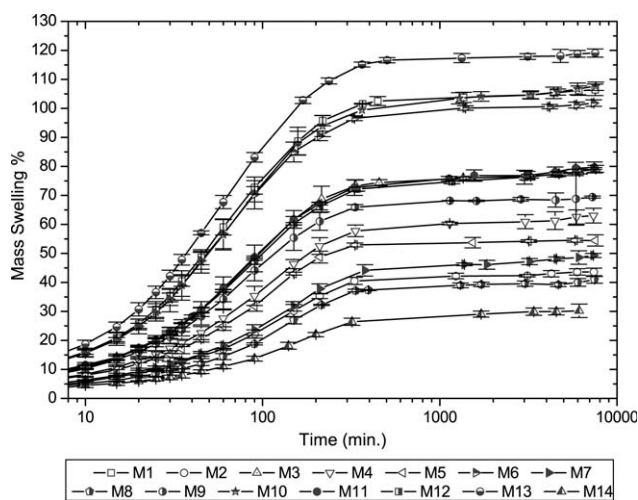


Figure 1. Mass swelling versus immersion time for samples of SBR immersed in several mixtures of gasoline and solvents, whose compositions are indicated in Table II. Each point represents the mean and 95% confidence intervals for the average behavior of three samples. The magnified curve on the right shows greater detail for shorter times.

in the test liquid, as recommended in ASTM D471. All measurements were performed on a Shimadzu analytical balance, model AW220, with a resolution of 0.1 mg. The procedure to obtain the experimental gravimetric data was based on the “Archimedes method” or the hydrostatic weighing method, which is one of the best known density measurement techniques.

Mass measurements in air and water were taken at regular periods of time after the sample immersion in the test liquid. After a certain period of swelling, the three samples of rubber were removed from the test liquid and wiped with a towel paper to remove the solvent excess and immediately weighed, individually, on the analytical balance to determine the weight in air. The samples were then dipped in alcohol to prevent bubbles, wiped with a towel paper to remove the excess alcohol, and weighed again, individually, in water to obtain the density and volume of the swollen rubber. Several measurements were taken up to the seventh day of continuous swelling, when no further notable mass variation was observed. There was no solvent renewal during the swelling experiments (a common practice in swelling experiments) because the intention of this study was to verify the possibility of using the degree of SBR swelling as a tool to estimate the concentrations of the aromatic compounds in a complex mixture, such as gasoline. Thus, when the solvent is renewed daily during the swelling experiments, the rubber equilibrium condition is changed as the concentrations of the different compounds in the solvent medium are kept almost constant.

The rubber density, ρ_R , was determined by the hydrostatic weighing method. In this method, the weight of a specimen is measured in two different media, air (W) and water (W_{water}). The weight measured in water is generally known as the apparent mass and results from the balance between buoyancy and

gravimetric forces. The density is obtained from eq. (5) using the water density ρ_{water} .

$$\rho_R = \frac{W}{W - W_{\text{water}}} \rho_{\text{water}} \quad (5)$$

The mass swelling in air ΔMass (%w/w) was calculated according to eq. (6), where W_0 is the rubber weight at zero time or under the initial conditions before swelling and W is the rubber weight at any time t , both measured in air:

$$\Delta\text{Mass \%} = \frac{(W - W_0)}{W_0} \cdot 100 \quad (6)$$

The volume swelling ΔVolume (% v/v) was calculated using the rubber density obtained from eq. (5) according to eq. (7), where V_0 is the rubber volume at zero time, or under the initial conditions before swelling, and V is the rubber volume at time t :

$$\Delta\text{Volume} = \frac{(V - V_0)}{V_0} \cdot 100 \quad (7)$$

RESULTS AND DISCUSSION

The aim of this first study was to evaluate the possibility of using the swelling of SBR (styrene-butadiene rubber) to estimate the content of toluene, an aromatic compound, in gasoline, a complex mixture of more than one hundred compounds. This relation enables inferences to be made regarding the composition and quality criteria of the fuel. The rubber SBR was chosen because it is one of the cheapest rubber sheets found on the local market and, according to the manufacturer OrionTM, this rubber presents considerable swelling when exposed to aromatic compounds.

Samples of SBR were immersed in pure solvents (type C gasoline, heptane and toluene) and in several mixtures of them, and the consequent swelling was evaluated for different sequential

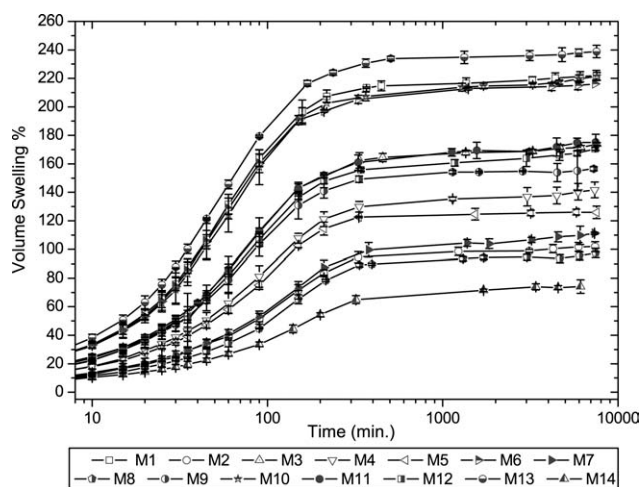


Figure 2. Volume swelling versus immersion time for samples of SBR immersed in several mixtures of gasoline and solvents, whose compositions are given in Table II. Each point represents the mean and the 95% confidence intervals for the average behavior of three samples.

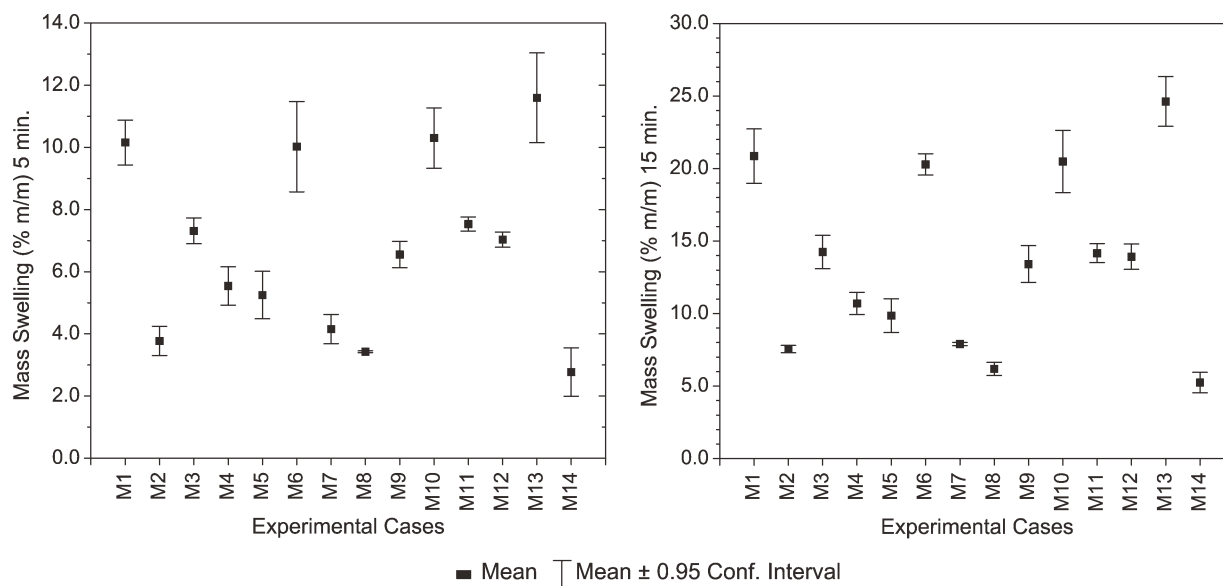


Figure 3. Mass swelling box plots for 5 and 15 min after SBR immersion in several mixtures (compositions given in Table II).

time periods. The rubber swelling was measured via gravimetric and hydrostatic experiments.

A simplex-lattice experimental mixture design for the three components (% v/v type C gasoline, % v/v toluene, and % v/v heptane) was applied. The design had three interior points and one central point replicated once, and is shown in Table II. The experiments were random and carried out in triplicate.

Figures 1 and 2 show the mass and volume swelling, respectively, versus immersion time in minutes for samples of SBR immersed in different solvent mixtures, as described in Table II. Each point represents the mean and the 95% confidence intervals for the average behavior of three samples exposed to identical experimental conditions. The log scale in Figures 1 and 2 makes evident that there are distinctive effects on the rubber swelling depending on the kind of compounds which are present in the mixture. For a few exceptions, the confidence intervals are narrow, presenting low standard deviations, and demonstrating visually that each different solvent composition produces a real and distinctive statistical effect on the degree of rubber swelling, even in short time periods.

The amplitude of volume swelling is larger than the mass variations. At around 9 h, the slopes of all the swelling curves change and the swelling process continues to increase slowly. In short time periods, the mass and volume swelling of rubber samples immersed in the solvents occurs rapidly, and is controlled by diffusion, while over longer immersion times a further slow increase in the swelling occurs caused by network degradation.^{1,4} The degradation is caused/promoted by the solvent effect combined with environmental factors (heat, light, oxygen) on polymer chemical structure, which breaks chemical bonds forming new structures. As the degradation continues, cracking and chemical disintegration occurs in the rubber.

An important aspect to note in Figures 1 and 2 is that all mixtures tested produced some degree of swelling of the SBR, but, the intensity of this swelling is dependent on the quantity of aromatic compounds present in the solvent mixture.

Samples of SBR immersed in heptane underwent lower mass and volume swelling, unlike samples subjected to toluene, which showed the greatest degree of swelling. Type C gasoline (curve M7) induced slightly greater mass and volume variations than

Table III. Analysis of Variance of Statistical Models to Find the Best Fit for the Variable Mass Swelling of SBR After 5 and 15 min of Immersion in Several Solvents

Variable	Statistics	Linear model	Quadratic model	Special cubic model	Complete cubic model
Mass swelling 5 min	<i>P</i> value (model)	0.000000	0.000000	0.278823	0.007206
	<i>R</i> ²	0.96292	0.98650	0.98695	0.99099
	Adjusted <i>R</i> ²	0.96102	0.98462	0.98471	0.98846
	<i>P</i> value (lack of fit)	0.000001	0.041985	0.038468	0.623979
Mass swelling 15 min	<i>P</i> value (model)	0.000000	0.000000	0.885262	0.001971
	<i>R</i> ²	0.981851	0.993340	0.993344	0.995783
	Adjusted <i>R</i> ²	0.980920	0.992414	0.992202	0.994597
	<i>P</i> value (lack of fit)	0.000001	0.033111	0.020331	0.836526

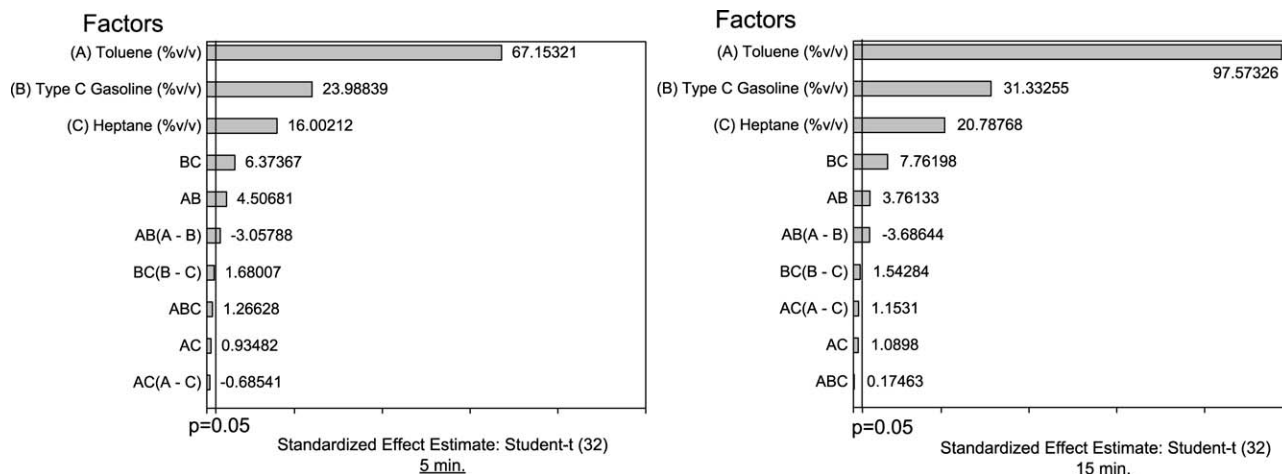


Figure 4. Pareto Charts of standardized effects for the complete cubic model for the variable mass swelling of SBR [Δ Mass (% w/w)] at 5 min (left) and 15 min (right) of immersion in solvents.

heptane. Refinery gasoline contains many different hydrocarbons in varying percentages but, in general, the proportion of aliphatic compounds is the highest. Table I shows that the gasoline sample used contains around 56% (v/v) of aliphatic and 19% of aromatic compounds. The formulation of type C gasoline with anhydrous ethanol has a lower proportion of aromatic compounds due to the dilution with ethanol and, thus, when SBR samples are immersed in this mixture a rubber swelling close to (but slightly higher than) the effect produced by heptane.

The experimental cases M3 and M11 have the same composition of solvents and represent replicates at the central point (1/3, 1/3, 1/3), which permits an estimate of the curvature in the response surface. In Figures 1 and 2 it can be observed that the central point replicates are fairly similar, demonstrating good experimental procedures.

Mixtures containing heptane and type C gasoline (2/3 type C gasoline + 1/3 heptane and 2/3 heptane + 1/3 type C gasoline) showed levels of swelling between those of pure heptane and type C gasoline. Also, mixtures of type C gasoline and toluene (2/3 type C gasoline + 1/3 toluene and 1/3 type C gasoline + 2/3 toluene) showed levels of swelling between pure toluene and type C gasoline. This verifies that the gasoline composition dilu-

tion affects the rubber swelling depending on the kind of solvent used.

Experimental Design Analysis

To perform the statistical analysis and plot the response surfaces only two time periods were selected from the complete swelling curves: 5 and 15 min of SBR immersion in the several mixtures detailed in Table II. These time intervals were selected to assess the performance of the proposed method at very short time periods; this is, to estimate the aromatic compounds content in a mixture with gasoline by measuring the SBR swelling. The response variables statistically analyzed for the experimental mixture design in this study were mass swelling after 5 and 15 min. The mean values for each experimental case are the average of three SBR samples immersed in the same solvent mixture. The confidence intervals were calculated using a two-tailed Student-t frequency distribution and a 95% confidence level. These data are plotted in Figure 3 which shows the mass swelling box plots for 5 and 15 min of SBR immersion in several solvent mixtures, whose compositions are given in Table II.

For mass swelling, the minimum and maximum experimental values observed were: 2.45% w/w and 12.13% w/w for 5 min of immersion; 4.93% w/w and 25.38% w/w for 15 min of

Table IV. Analysis of Variance for Significant Statistical Cubic Model for Mass Swelling [Δ Mass (% w/w)] of SBR After 5 and 15 min of Exposure

Variables	Statistics	SS	DF	MS	F	P value	R ²	Adjusted R ²
Mass swelling 5 min	Model	315.8662	5	63.17324	633.5066	0.000000	0.988762	0.987202
	Total Error	3.5899	36	0.09972				
	Lack of fit	0.8797	7	0.12567	1.3447	0.265737		
	Pure Error	2.7102	29	0.09346				
	Adjusted Total	319.4561	41	7.79161				
Mass swelling 15 min	Model	1448.857	5	289.7714	1419.244	0.000000	0.994952	0.994251
	Total Error	7.350	36	0.2042				
	Lack of fit	1.385	7	0.1979	0.962	0.476510		
	Pure Error	5.965	29	0.2057				
	Adjusted Total	1456.207	41	35.5173				

Table V. Coefficients of the Independent Variables for the Cubic Model for the Mass Swelling [Δ Mass (% w/w)] of SBR After 5 min of Exposure

Factors	Coefficient	Standard error	t(36)	P value	−95% Confidence limit	+95% Confidence limit
(A) Type C gasoline (% v/v)	4.23939	0.149451	28.36647	0.000000	3.93629	4.54249
(B) Toluene (% v/v)	11.61147	0.173536	66.91099	0.000000	11.25953	11.96342
(C) Heptane (% v/v)	2.82606	0.143275	19.72480	0.000000	2.53549	3.11664
AB	3.77066	0.718802	5.24576	0.000007	2.31286	5.22846
BC	5.25150	0.721436	7.27923	0.000000	3.78836	6.71464
AB(A-B)	−5.11901	1.531630	−3.34220	0.001948	−8.22530	−2.01272

immersion, respectively. The average standard deviations were: 0.26 for Δ Mass (% w/w) 5 min and 0.40 for Δ Mass (% w/w) 15 min. Some large standard deviations were obtained for the greater levels of mass swelling measured, due to difficulties associated with manipulating quickly the swollen rubber pieces of larger dimensions, which occurred when the experimental cases contained the greatest percentages of toluene. Nevertheless, the experimental data were pre-tested and shown to be appropriate for the statistical analysis of variance described below.

Analysis of Variance

For the following analysis a 95% confidence limit and significance level of 5% were used. According to the analysis using an experimental mixture design, first, the most appropriate statistical model to describe the collected data needs to be found, as stated in eqs. (1)–(4).

The four models [eqs. (1)–(4)] were tested and the best fits for the mass swelling after 5 and 15 min of immersion were chosen according to the criteria: a model which is significant (model P -value < 5%) and without lack of fit (P -value > 5%). According to these criteria the special cubic model was not significant for the two variables analyzed. The other models were significant, but only the complete cubic model did not presented a lack of fit. Therefore, the complete cubic model offered statically the most suitable fit to describe the mass swelling of SBR after 5 and 15 min of immersion in the mixtures described in Table II. Table III summarizes the statistical analysis of variance for the sequential fitting of the models of increasing complexity, showing the principal parameters used to find the best and most significant fit.

Figure 4 shows the Pareto charts of the standardized effects according to the Student-t values for the complete cubic model for the variable mass swelling of SBR [Δ Mass (% w/w)] after 5 min (left) and 15 min (right) of immersion in the solvents. In

these charts, the effects are organized according to their magnitude of Student-t probability over the variable mass swelling. It is evident, for both immersion times, that the toluene content in the solvent mixtures has the greatest and most significant effect on the mass swelling of the SBR specimens. The next most important effects relate to the type C gasoline and heptane contents, respectively, in order of significance. The interaction effects were found to be of minor significance and some of them were not significant, that is, the P value was below 5%. An interesting aspect to note is that the interaction between type C gasoline and heptane was not significant, this is, this combination did not affected the SBR swelling in a relevant way, only second-order interactions involving toluene being significant.

The non significant effects must be removed from the complete cubic model to obtain a more correct statistical model. Table IV shows the analysis of variance after removing the non significant effects from the models for the variables mass swellings after 5 and 15 min. Despite this simplification, the models continue to be significant and present high adjusted correlation coefficients (~ 0.98 for 5 min and ~ 0.99 for 15 min).

After obtaining the most suitable adjusted models to express the mass swelling of the SBR samples, the next step was to calculate the coefficients for each independent variable and their confidence limits. The results are shown in Table V (for 5 min) and Table VI (for 15 min), which also give the standard error and the P value for all coefficients.

The principal factors A, B, and C (% v/v type C gasoline, % v/v toluene, % v/v heptane, respectively) and their interactions (AB and BC) had positive effects on the SBR swelling. On the other hand, the second-order interaction AB(A-B) had a negative influence on the swelling. The effects of all factors on the mass swelling at 15 min are greater than at 5 min.

Table VI. Coefficients of the Independent Variables for the Cubic Model for the Mass Swelling [Δ Mass (% w/w)] of SBR After 15 min of Exposure

Factors	Coefficient	Standard Error	t(36)	P value	−95% Conf. Limit	+95% Conf. Limit
(A) Type C gasoline (% v/v)	8.15842	0.213849	38.15043	0.0009000	7.7247	8.59213
(B) Toluene (% v/v)	24.69380	0.248312	99.44660	0.000000	24.1902	25.19740
(C) Heptane (% v/v)	5.21667	0.205011	25.44578	0.000000	4.8009	5.63245
AB	4.00222	1.028531	3.89121	0.000414	1.9163	6.08818
BC	8.83882	1.032301	8.56226	0.000000	6.7452	10.93243
AB(A-B)	−8.30270	2.191604	−3.78841	0.000556	−12.7475	−3.85792

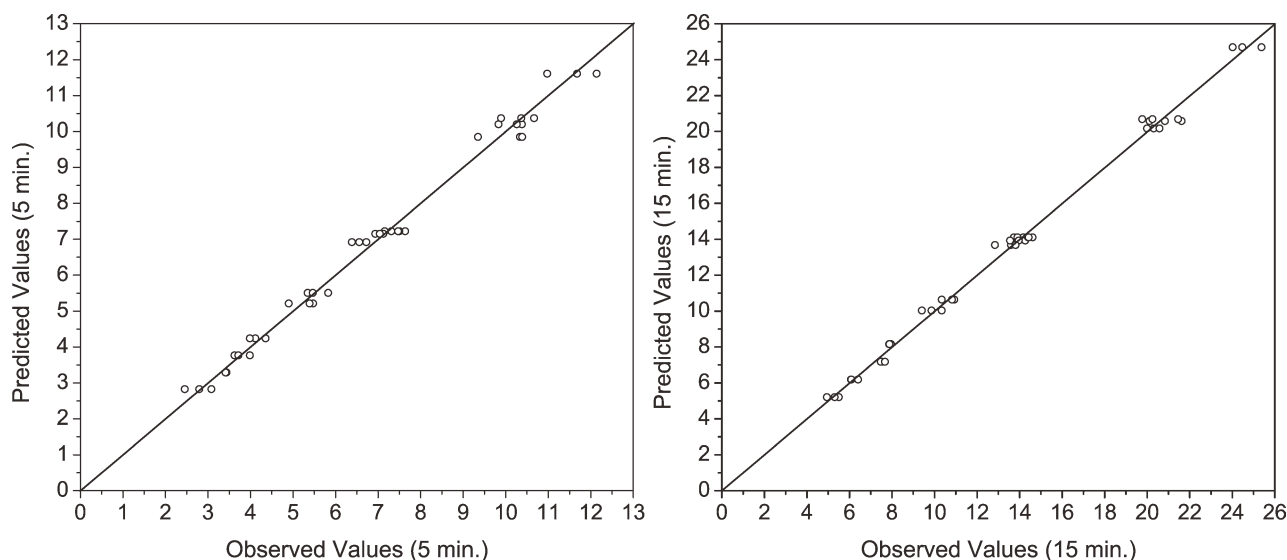


Figure 5. Observed values versus values predicted using the adjusted cubic model for the mass swelling of SBR [Δ Mass (%w/w) after 5 min (left) and 15 min (right) according to eqs. (8) and (9)].

From the experimental mixture design analysis of variance, and using the results given in Tables V and VI, two adjusted cubic equations for the mass swelling of SBR were obtained according to the volumetric content of the three solvents A, B and C (type C gasoline, toluene and heptane, respectively) at $25^{\circ}\text{C} \pm 1^{\circ}\text{C}$.

The equation obtained to model the mass swelling of SBR after 5 min of exposure to the solvents, with an adjusted correlation coefficient of 0.9872, is presented in eq. (8).

$$\Delta\text{Massa (\%m/m) 5 min.} = +4.24A + 11.61B + 2.83C + 3.77AB + 5.25BC - 5.12AB(A - B) \quad (8)$$

The equation obtained to model the mass swelling of SBR after 15 min of exposure to the solvents is presented in eq. (9), with

an adjusted correlation coefficient of 0.9943. Figure 5 shows the good linear correlation between observed x predicted values for both adjusted cubic models according to eqs. (8) and (9).

$$\Delta\text{Massa (\%m/m) 15 min.} = 8.16A + 24.69B + 5.22C + 4.00AB + 8.84BC - 8.30AB(A - B) \quad (9)$$

Response Surface Fits

Using the adjusted cubic models obtained, response surface fits for the mass swelling of SBR at 5 min and 15 min were obtained, as shown in Figures 6 and 7, respectively. The first aspect to note is the similarity of the shapes in Figure 6 for 5 min and Figure 7 for 15 min of swelling, the magnitudes being different but the behavior being the same.

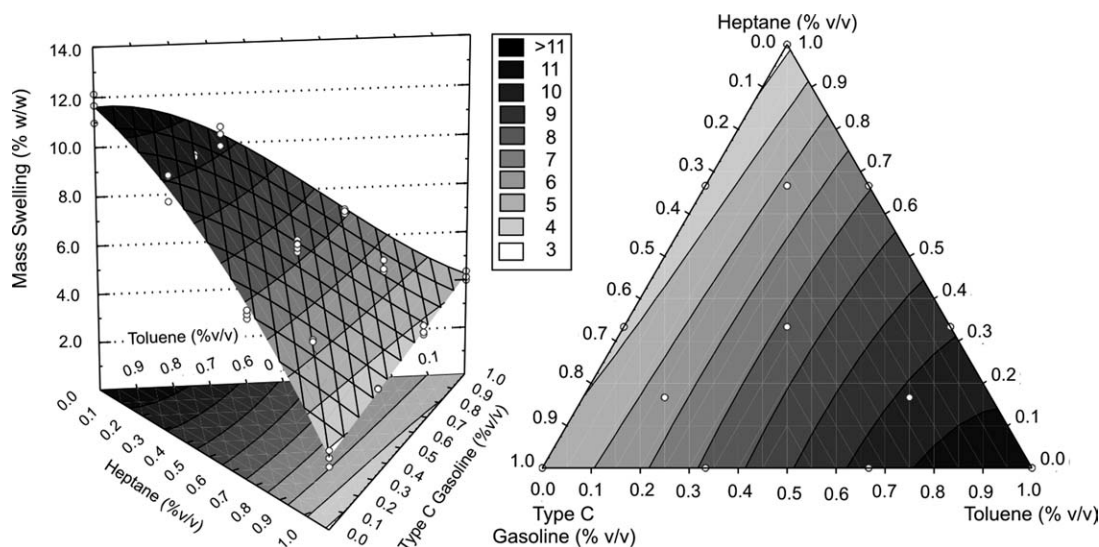


Figure 6. Response surface for mass swelling [Δ Mass (%w/w)] of SBR after 5 min of exposure to a mixture of solvents (type C gasoline, toluene, and heptane).

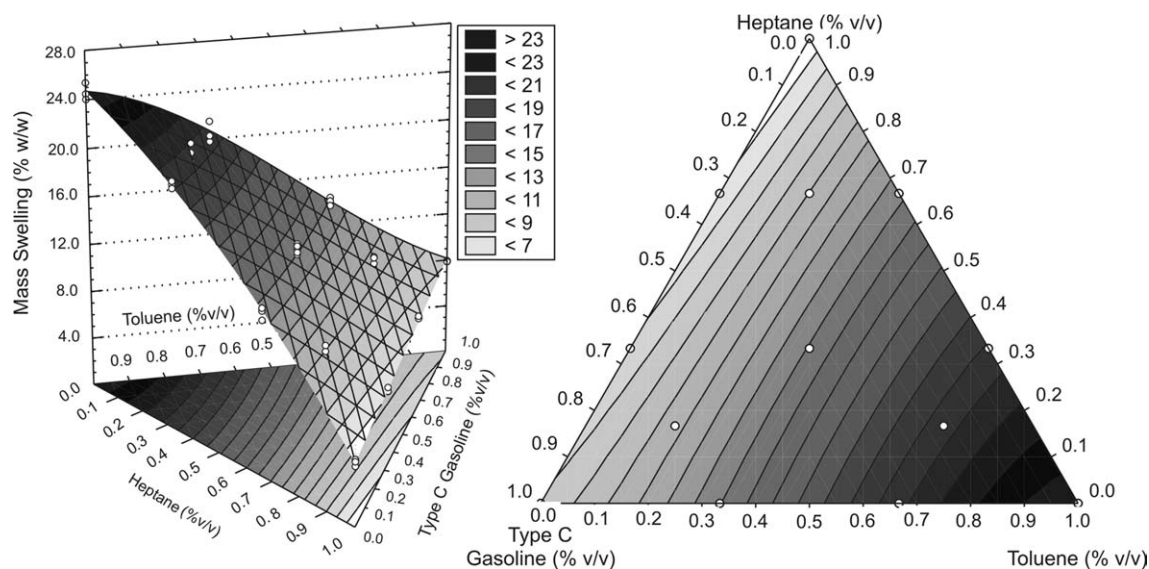


Figure 7. Response surface for mass swelling [ΔMass (%w/w)] of SBR after 15 min of exposure to a mixture of solvents (type C gasoline, toluene, and heptane).

From these figures it can be seen that the swelling increases with an increase in the toluene content of the mixture, the maximum swelling value being observed for pure toluene for both immersion times (5 and 15 min). The minimum swelling value was found when the SBR specimens were exposed to pure heptane and the rubber samples exposed to type C gasoline presented slightly higher values than those exposed to heptane. The curvatures observed on the response surfaces in Figures 6 and 7 result from the effect of the interactions between factors. According to these figures, the mass swelling values are restricted to between 2.5 and 12% after 5 min and between 5 and 25% after 15 min of SBR exposure to solvent mixtures.

Because of the good statistical models and fits obtained to describe the mass swelling of the SBR samples immersed in several mixtures of type C gasoline, toluene, and heptane for 5 and 15 min, it is possible to consider the existence of a pattern in the swelling according to the content of aromatic and aliphatic compounds present in the gasoline composition.

This analysis verifies that it is possible to determine mathematical equations to describe the relation between rubber swelling and the solvent composition and this opens a new line of research with many practical and experimental applications for this area.

CONCLUSIONS

This study evaluated statically the possibility for the use of SBR (styrene–butadiene rubber) swelling as a tool in the analysis of fuel quality, through quantifying the swelling as a function of the content of toluene, an aromatic compound, in gasoline. The rubber swelling was measured via gravimetric and hydrostatic experiments. A simplex-lattice experimental mixture design for three components (% v/v type C gasoline, % v/v toluene, and % v/v heptane) was applied. The design had three interior points and one central point replicated once. The confidence

intervals for the measurements were narrow, with low standard deviations, demonstrating that each different solvent mixture results in real and statistically distinctive effects on the degree of rubber swelling, even within short time intervals. The minimum and maximum experimental values for mass swelling observed were: 2.45% w/w and 12.13% w/w for 5 min of immersion; and 4.93% w/w and 25.38% w/w for 15 min of immersion, respectively. The average standard deviations for ΔMass (% w/w) were: 0.26 for 5 min and 0.40 for 15 min. The amplitude of volume swelling was larger than that of mass swelling. At around 9 h, all the slopes of the swelling curves changed and the swelling process continued to increase slowly. Samples of SBR tested in heptane had lower mass and volume swelling compared with the swelling of the rubber samples tested in toluene. The swelling results for type C gasoline showed slightly higher variations of mass and volume than those induced by heptane. It was demonstrated that the dilution of gasoline with different mixtures of heptane and toluene quantitatively affects the rubber swelling (mass and volume) for all immersion times, and that this is mainly dependent on the toluene content. The response variables statistically analyzed for the experimental mixture design were mass swelling after 5 and 15 min for SBR. Two adjusted cubic equations for mass swelling, at $25^\circ\text{C} \pm 1^\circ\text{C}$, gave the fits statically most suitable to describe the mass swelling of SBR, presenting no lack of fit, with a high value for R^2 -adjusted (>0.98). The principal factors A, B, and C (% v/v type C gasoline, % v/v toluene, % v/v heptane, respectively) and their interactions (AB and BC) had positive effects on the SBR mass swelling, making it increase. On the other hand, the second-order interaction AB(A–B) had a negative influence on the swelling. For all factors the effect on the mass swelling at 15 min was greater than at 5 min. The response surface methodology enabled the representation of the mass swelling equations according to the type C gasoline, toluene, and heptane content in the solvent mixtures, where it could be seen that the swelling increases with increasing toluene content in the mixture, the

maximum value for mass swelling being obtained with pure toluene for both immersion times (5 and 15 min). The analysis of variance for the mass swelling verified that it is possible to find good mathematical equations to describe the relation between rubber swelling and solvent composition. This finding opens a new line of research with many potential practical and experimental applications.

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