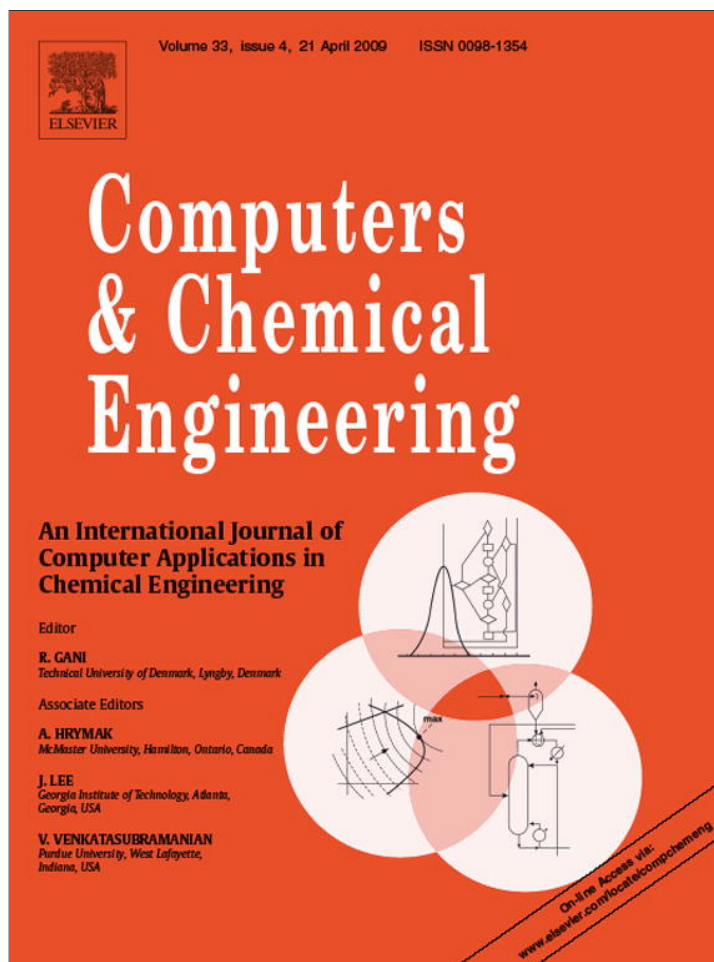


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Multiple response optimization of styrene–butadiene rubber emulsion polymerization

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ARTICLE INFO

Article history:

Received 20 December 2007
 Received in revised form 8 September 2008
 Accepted 5 January 2009
 Available online 10 January 2009

Keywords:

SBR
 Emulsion polymerization
 Artificial neural networks
 Multiple response optimization
 Desirability function

ABSTRACT

A multiple response optimization of styrene–butadiene rubber (SBR) emulsion batch polymerization is proposed. Several properties of latex and rubber were optimized to obtain a particular grade of SBR, namely 1712. Artificial neural networks (ANNs) were employed for the modelling of the following properties: solid content of latex, Mooney viscosity and polydispersity. The training was done by feeding the ANNs with experimental data obtained from a central composite design in which the concentration of some of the polymerization reagents (initiator, activator and chain transfer agent) was varied. The one-dimensional desirability function was used for optimization, in order to obtain a single set of reaction conditions for the multiple responses. With optimum conditions, polymerization experiments were carried out and good agreement was found between predicted and experimental values of the required properties.

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1. Introduction

Styrene–butadiene rubber (SBR) is one of the most important synthetic polymers. It accounts for about 40% of the total synthetic elastomer production, its major consumption being in tyres and tyre products. SBR can be obtained by styrene and butadiene emulsion copolymerization. Since its first industrial scale appearance in 1937, a high number of research studies have been aimed at producing a rubber with specific properties, suitable to each use and application (White & Soos, 1993).

The structural properties of the produced polymer represent an essential point in the production process. Such characteristics will determine the physical properties and the processability of the final rubber to be obtained, which are usually targeted to some predetermined quality specifications.

On the other hand, variations in polymer structure are the result of changes in polymerization conditions, which include the employed reagents. Therefore, for the final rubber properties to be optimized, it is necessary to control a number of process conditions; among which, the amount of key chemicals that participate in the polymerization reaction are to be considered.

In process control issues, it is necessary to take into account that most chemical process systems are nonlinear. Particularly, polymerization reactors can be among the most nonlinear, and a great deal of nonlinear control strategies has been developed in this field (Schork, Deshpande, & Leffew, 1993). Because of this nonlinearity, and in some cases, the lack of a reliable first-principle model, the use of artificial neural networks (ANNs) has shown a sustained increase in the field of polymerization control; its ability to simulate a high number of results in short computer time, and to accurately describe a system, makes ANNs particularly suitable for optimization and on-line applications (Nascimento, Giudici, & Guardani, 2000).

Some of the first illustrative examples for the use of ANNs were shown in batch systems (Joseph & Wang Hanratty, 1993); in this typical nonlinear process, it was possible to correlate certain polymer composite quality parameters with curing process variables and conditions.

In the rubber industry, most ANN applications have been developed for the polymerization stage, and only a few were reported for rubber end-use properties and processability prediction (Schwartz, 2001).

The control of polymerization process through ANN models is a well established strategy. Tsen, Jang, Wong, and Joseph (1996) developed a methodology based on hybrid ANN models, and applied it to the emulsion polymerization of vinyl acetate. It was possible to control polymer dispersity, number average molecular weight and time in a batch reactor, and it was shown a better pre-

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dictive ability for molecular weights than employing a theoretical model.

A different and interesting approach is to define the reactor operating conditions based on some desired polymer quality. Application of ANNs to that problem has been presented for the development of polyethylene resins in a fluidized bed polymerization reactor (Fernandes & Lona, 2002). Optimal operating conditions in emulsion polymerization of vinyl acetate were also found using ANNs and polymer final properties as inputs (Fernandes, Lona, & Penlidis, 2004). In this work, a large data set was used, in which the polymer properties corresponding to each operating condition were obtained by running an extensively tested mathematical model for this emulsion system. As a result, it was possible to define the monomer, initiator and emulsifier concentration and the operating temperature, in order to obtain a given molecular weight, polydispersity, particle diameter and branching frequency. The results were compared to those predicted with the detailed model (Gao & Penlidis, 2002).

Also for emulsion polymerizations, Zhang, Morris, Martin, and Kiparissides (1998) employed the combination of multiple neural networks (stacked neural network) to simulate a batch methylmethacrylate polymerization reactor, avoiding the development of complex polymerization kinetic models. It was shown that the technique could accurately predict trajectories of polymer quality variables even in the presence of reactive impurities. The technique has been used in designing optimum recipes for a batch polymerization process. It can also be used for the prediction, control, and monitoring of batch polymerization processes.

In addition, there are studies that use hybrid models for control and optimization of polymerization reactions. Among them, DĭAnjou, Torrealdea, Leiza, Asua, and Arzamendi (2003) made use of a combination of a first-principle model and ANNs in order to predict the polymerization rate, monomer conversion and average molecular weight in emulsion polymerization. The polymerization rate and the instantaneous weight-average molecular weight were calculated by means of ANNs. This reduced model can be integrated faster than the first-principle one, making the hybrid model suitable for on-line optimization.

For solution polymerizations, Padmavathi, Mandan, Mitra, and Chaudhuri (2005) developed a reliable model that predicts product quality like Mooney and fluid viscosity in polybutadiene as a function of process parameters using neural networks, permitting an on-line implementation. From plant historical database, the values of process variables within a wide operating range, along with Mooney and solution viscosities of the corresponding samples, were collected; these values were used for the network training. Hanai, Ohki, Honda, and Kobayashi (2003) assumed that the physicochemical characteristics such as the ratio of cis form to total polymer and the polydispersity index represent the quality of polybutadiene and a fuzzy neural network (FNN) model was constructed to estimate the physicochemical characteristics and the conversion ratio from the initial conditions. Using the constructed FNN model and a genetic algorithm, the process conditions for target physicochemical characteristics were calculated finding good agreement between the calculated results and the target values, although no experimental corroboration was done.

In the present work, an SBR emulsion polymerization reaction was optimized employing chemometric tools, in order to obtain grade 1712 SBR by means of the bottle polymerization technique (Fryling, 1954). This grade of SBR represents 50% of total SBR production at Petrobras PGSM site, and thus it was chosen for this study. The properties used as quality parameter were: solid content of latex, polydispersity and Mooney viscosity. These properties were selected because they are raw polymer properties generally accepted to be directly related to processability and mixing performance (Ninomiya & Yasuda, 1969; Smith, 1976); there are some

other factors that modify the processability of a compounded rubber, but they refer to mix composition or mixing procedures, and not to the polymer itself (Norman & Johnson, 1991). It is worth to mention that there is no mathematical model able to predict Mooney viscosity, hence it is impossible to get a set of mathematically derived data points in order to train the ANNs.

For the optimization stage, Havel, Peña, Rojas-Hernández, Doucet, and Panaye (1998) proposed a powerful tool for the analytical area; in this work it was possible to predict optimal separation conditions in capillary zone electrophoresis, by the combination of experimental design and artificial neural networks with the back-propagation algorithm. This approach was found to be a general optimization methodology, and therefore its application was expanded and reported in several areas (Moreira, Micheloud, Beccaria, & Goicochea, 2007; Spanilá, Pazourek, Farková, & Havel, 2005; Wang et al., 2001).

In this work, ANNs were used for response modelling, because a surface response methodology approach, in which each response is fitted to polynomial model, was first employed with unsatisfactory results. Since several properties had to be optimized a multiple response simultaneous optimization was needed. This was accomplished by means of the desirability function (Derringer & Suich, 1980). The combined use of neural networks and desirability function constitute a methodology that allows the optimization of complex processes, which is the case of the rubber polymerization.

1.1. Artificial neural network

Artificial neural networks are mathematical models having the ability to learn the correlation between input and output values by means of an iterative mechanism of test and error (Zupan & Gasteiger, 1999). Neural networks are composed of basic units called neurons or nodes distributed in different layers. In this work, the architecture of the employed network consists of three layers: input, hidden and output layer. As in the nervous system, each artificial neuron receives the output from the previous neurons and each connection between neurons carries an assigned weight. For the network training the experimental data \mathbf{X} or inputs enter into the input layer, and then propagate through the network. Each neuron of the hidden layer receives and adds the outputs from all of the neurons in the input layer. After that, the resulting summation is passed through a transfer function, commonly a sigmoid function, which means that the output for the j th neuron in the hidden layer (y_j) equals to:

$$y_j = \frac{1}{1 + e^{-net_j}} \quad (1)$$

being net_j the net input to the j th neuron in the hidden layer, which is given by the expression:

$$net_j = \sum_{i=1}^n w_{ji}x_i \quad (2)$$

where n is the number of neurons in the input layer, w_{ji} is the connection weight from the i th neuron in the input layer to the j th neuron in the hidden layer and x_i is the input to the i th neuron in the input layer.

For the network training, a back-propagation learning algorithm was used. In this method, the error between the output vector of the network (out_{calc}) and the experimental vector (out_{exp}) is calculated and then all weights are corrected throughout the entire network from the last layer to the first one. After weight correction, the procedure is repeated until an acceptable error is reached. The error is calculated as the root mean square error of correlation (RMSEC),

according to:

$$RMSEC = \frac{\sqrt{\sum (out_{calc} - out_{exp})^2}}{I} \quad (3)$$

where I is the total number of responses.

1.2. Multiple optimization

The usual method to optimize a response or property is the step by step procedure, which consists in modifying one factor while holding the others constant, and observing the effect that this modification produces. Another approach is to make an optimization using experimental designs and a surface response analysis, determined by least-squares fit, in order to set the conditions in which the response takes a certain value, either a maximum or a minimum one. This approach also considers possible interactions among the studied factors. Such analysis may not be enough for a process involving rubber, because at the time of being compounded the rubbery behaviour cannot be accurately predicted from a single property. In this case it is useful to employ a simultaneous property optimization by means of tools such as the Desirability Function (Del Castillo, Montgomery, & McCarville, 1996; Derringer & Suich, 1980; Harrington, 1965); this function transforms a problem of multiple responses 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, i.e. from an unacceptable to an optimum response, respectively.

In this work, the three responses (solid content, Mooney viscosity and polydispersity) are required to take a certain target value each (t_i). Therefore, to set the d_i values it is necessary to define the following continuous function:

$$d_i = 0 \quad \text{if } y_i \leq \min_i \text{ or } y_i \geq \max_i \quad (4)$$

$$d_i = \left[\frac{y_i - \min_i}{t_i - \min_i} \right]^{w_1} \quad \text{if } \min_i < y_i < t_i \quad (5)$$

$$d_i = \left[\frac{\max_i - y_i}{\max_i - t_i} \right]^{w_2} \quad \text{if } t_i < y_i < \max_i \quad (6)$$

where y_i is the predicted response of the fitted model, and \min_i , \max_i represent the minimum and maximum acceptable value of y_i , respectively. The d_i s are affected by a weight (w_1 , w_2) that emphasize either the target value or the minimum and maximum limits.

For a process with n responses, the simultaneous desirability is a geometric mean of all transformed responses:

$$D = (d_1^{r_1} \times d_2^{r_2} \times \dots \times d_n^{r_n})^{1/\sum_{i=1}^n r_i} = \left(\prod_{i=1}^n d_i^{r_i} \right)^{1/\sum_{i=1}^n r_i} \quad (7)$$

where r_i is a relative importance assigned to each transformed response d_i . Notice that if any of the responses is unacceptable, that is $d_i = 0$, the overall function becomes zero.

The values assumed by the rubber responses are continually related to the initial conditions in the polymerization reaction; with the d_i s being a function of those responses, thus it can be established that the simultaneous function D is also a continuous function of the initial reaction conditions. As a result, a shift from multivariate to univariate optimization problem is achieved, and the optimum polymerization conditions can be set now by standard techniques.

2. Software

Design Expert version 7.0.3 trial (Stat-Ease Inc., Minneapolis, USA) was used for performing experimental design, polynomial fit-

ting and ANOVA results. ANN and desirability calculations were all performed with in-house MATLAB 7.0 routines.

3. Experimental

All polymerization experiments were made in bottles at 10 °C with constant rotation in a water bath. Reagents styrene (98%), butadiene (98.5%), soap, chain transfer agent (CTA), initiator and redox activator were taken from production lines at Petrobras. Styrene was washed with 5% Na(OH) solution to remove 4-tert-butylcatechol, used as inhibitor. Before the addition of butadiene and activator, all reagents were purged in the bottle with N₂ for oxygen elimination.

All polymerizations were carried out during 8 h and short-stopped with hydroxylamine. In each case initiator, activator and CTA concentrations were varied. The used ranges were 0.008–0.027 phm (parts per hundred of monomer) for initiator, 0.010–0.017 phm for activator and 0.188–0.425 phm for CTA. These ranges were dictated by the central composite design employed, as explained in the next section.

The properties measured for the obtained SBR were solid content on latex, polydispersity and Mooney viscosity.

Solid content measurement technique (ASTM D1417, 1993) consists in taking a latex sample from the bottle at a reaction time of 8 h. Butadiene was eliminated under vacuum and then a weighted latex aliquot was precipitated with isopropyl alcohol and placed in oven at 145 °C for styrene and water removal, until constant weight was obtained. Solid content was calculated as weight ratio.

Molecular weight distributions were determined by size exclusion liquid chromatography. A Varian ProStar 210 pump with a Varian 350 refractive index detector was used. A set of four Tosoh-Haas TSKgel columns (10⁶ to 10⁴ Da) was employed. Calibration was done with narrow polystyrene standards (Waters Corp., Milford, USA). Mobile phase was THF at 1 mL/min flow rate. SBR samples were dissolved in THF and filtered through 0.45 μm membrane before injecting 200 μL into the columns.

Mooney viscosity was measured with a MV 2000 Alpha Technologies viscometer under standard conditions (ASTM D1646, 1993). For thermal stabilization, each sample was preheated during 1 min at 100 °C, and Mooney viscosity was measured 4 min after stabilization.

4. Results

SBR 1712 is a polymer with a typical Mooney viscosity between 110 and 120. In addition, it is advisable for the polymerization reaction to be stopped at conversions not much higher than 60% (Quirk & Morton, 1994). Larger values decrease rubber processability since chain branching becomes important. This conversion value represents a solid content on latex of ca. 25 wt%.

On the other hand, in order to have suitable processability it is required the presence of short chains that act like plasticizers or lubricants, which can be accommodated between the longest chains and favor the mixing process with fillers (Hoffman, 1989). As a consequence, a convenient polydispersity value of 3 is assumed for emulsion SBR, which affords a compromise between good mechanical properties and adequate processability for rubber compounding.

Therefore, the optimization target values required to obtain SBR 1712 are 115 for Mooney viscosity, 25% for solid content at 8 h reaction time and 3 for polydispersity.

In order to perform a multiple optimization, a relationship between polymerization reagents and properties under optimization must be established. For that purpose a central composite design with three factors (initiator, activator and CTA) was applied. The criterion to use this design was to obtain the maximum useful

Table 1
Complete set of polymerizations and experimental responses.

Experiment	Initiator (mL)	Activator (mL)	CTA (mL)	Solid content (wt%)	Mooney	D
1	0.030	2.00	0.60	23.9	147.9	2.92
2	0.080	2.00	0.60	22.8	153.6	3.09
3	0.055	2.00	0.40	21.8	158.9	3.08
4	0.055	2.00	0.80	21.4	59.4	3.06
5	0.055	1.50	0.60	17.2	157.0	2.81
6	0.055	2.50	0.60	23.0	47.1	3.46
7	0.040	1.70	0.48	16.9	79.2	3.28
8	0.070	1.70	0.48	18.0	48.9	3.61
9	0.040	1.70	0.72	17.0	21.3	3.14
10	0.070	1.70	0.72	18.0	26.7	3.06
11	0.040	2.30	0.48	21.3	145.2	3.44
12	0.070	2.30	0.48	24.9	160.1	3.48
13	0.040	2.30	0.72	20.6	68.7	3.19
14	0.070	2.30	0.72	23.3	105.0	3.23
15	0.055	2.00	0.60	23.3	160.7	2.80
16	0.090	2.67	0.78	25.6	106.8	3.04
17	0.090	2.50	0.65	26.5	133.2	3.42
18	0.098	2.50	0.78	27.5	99.6	3.09
19	0.085	2.40	0.70	26.3	119.2	3.32
20	0.090	2.50	0.78	27.3	97.1	3.71
21	0.085	2.40	0.85	25.9	71.0	3.23
22	0.095	2.40	0.85	25.9	59.0	3.40
23	0.082	2.50	0.78	24.5	94.8	3.59
24	0.090	2.50	0.90	27.2	97.3	3.33
25	0.085	2.60	0.85	26.8	105.6	3.20
26	0.095	2.60	0.85	27.2	108.0	3.27
27	0.090	2.33	0.78	24.4	83.4	3.11
28	0.095	2.40	0.70	26.1	114.3	2.91
29	0.095	2.60	0.70	27.8	129.4	3.20
30	0.085	2.60	0.70	26.0	141.3	2.89

information with the minimum number of experiments. A single point was used in the center of the design, making a total of 15 experiments.

In a first attempt, the experimental design ranges were selected from standard polymerization conditions employed in rubber plants (i.e. initiator: 0.030–0.080 mL; activator: 1.5–2.5 mL; CTA: 0.4–0.8 mL). The corresponding measured properties for this set were not suitable for the optimization; for example, too high or too low Mooney values were found, both far from the target. Therefore, it was decided to expand the experimental set with a second central composite design, changing all factor ranges for the next 15 experiments (initiator: 0.082–0.098 mL; activator: 2.33–2.67 mL; CTA: 0.65–0.90 mL).

The conditions of the entire set of experiments and their respective responses are detailed in Table 1.

After all polymerization experiments were completed, the obtained experimental data were subjected to a multiresponse optimization, in order to obtain the conditions in which the involved factors determine the target values.

A surface response methodology was used for the properties being modelled. In this method, the functional relationship between the observed response and the experimental factors takes the form of a second-order polynomial equation:

$$Y_i = \beta_0 + \sum_{i=1}^3 \beta_i X_i + \sum_{i=1}^3 \beta_{ii} X_i^2 + \sum_{i=1}^2 \sum_{j=i+1}^3 \beta_{ij} X_i X_j + \varepsilon_i \quad (8)$$

where Y_i represents the optimized responses, X_i the analyzed factors (initiator, activator and CTA), β_0 is a constant intercept, β_i , β_{ii} and β_{ij} represent the coefficients of linear, quadratic and cross-product terms and ε_i is the experimental error. Statistical parameters of the fitted models (F-Model and P-Model) are shown in Table 2. For the model to be significant, that is, not generated by noise, P-Model values should be less than 0.05. As it can be seen, the only significant model was the solid content (P-Model < 0.05) while for Mooney viscosity and polydispersity the models were not

Table 2
Statistical results of fitted quadratic models.

Statistical parameter	Solid content	Mooney viscosity	Polydispersity
Fitted model	Quadratic	Quadratic	Quadratic
F-Model	21.93	1.42	0.70
P-Model	<0.0001	0.24	0.69
R ² adjusted	0.8747	0.1237	−0.1093
R ² predicted	0.6867	−1.3865	−1.0603

significant (P-Model > 0.05). Based on these results, the optimization cannot be accomplished by means of quadratic polynomials because of the poor reliability of the fitted models.

Following the same methodology, and taking into account that the number of experimental data was sufficiently large, a cubic model fitting was also tried; however, P values less than 0.05 for Mooney viscosity and polydispersity were obtained, indicating that the models were not significant.

As the surface response methodology showed poor fitting results, probably due to the complex behaviour of the Mooney viscosity and polydispersity, an alternative approach was required. The use of artificial neural networks was recently employed for the modelling of properties in multiresponse optimization problems (Moreira et al., 2007).

First, it was necessary to establish the architecture of the employed artificial network. As usual, the number of neurons in the input layer is the same as the number of factors in the design. In this case three neurons were used, corresponding to initiator, activator and CTA. In addition, to determine the number of output nodes, two strategies can be considered: Schmidt, Cornejo-Ponce, Bueno, and Poppi (2003) tested two variations of Back Propagation, BP-SC (for a single component) and BP-MC (for multiple component) in ANN training. Best performance was achieved when the network was built with a single output for each application, rather than when a single network was employed to correlate all responses at the same time. Therefore, three neural networks were built with

only a neuron in the output layer, corresponding to solid content, Mooney viscosity and polydispersity, respectively.

To decide the number of neurons in the hidden layer, the criterion employed was to train each network with a different number of neurons until the *RMSEC* (Eq. (3)) decreased to a value close to the property measurement error, using the minimum possible number of training epochs. Estimated measurement errors were 3% for solid content, 4% for Mooney viscosity and 6% for polydispersity.

For each of the three studied properties, one network was trained using the experimental design of Table 1 as input signals, and the values of solid content, Mooney viscosity and polydispersity as output values. In Table 3 the architecture and resulting *RMSEC* values of the trained ANNs are shown.

Employing the trained networks, response models were made for each property, with the corresponding graphical results shown in Figs. 1–3. Fig. 1(a) shows the surface response for solid content

Table 3
Details of ANN models.

	Solid content	Mooney viscosity	Polydispersity
Net architecture ^a	3/6/1	3/6/1	3/4/1
Epochs	30,000	10,000	30,000
Learning rate	0.5	0.5	0.5
Momentum coefficient	0.5	0.5	0.5
RMSEC %	3	4	6

^a Net architecture is expressed as: input neurons/hidden neurons/output neurons.

as a function of initiator and activator, with CTA at its optimum value, and Fig. 1(b) shows the predicted vs. nominal values of solid content. Similarly, Fig. 2(a) shows the surface response for Mooney viscosity as a function of activator and CTA, with initiator at its optimum value, while Fig. 2(b) shows the predicted vs. nominal values

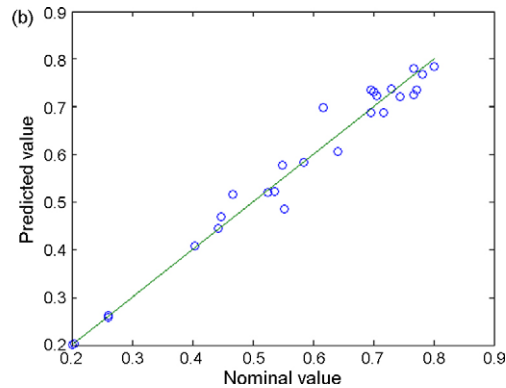
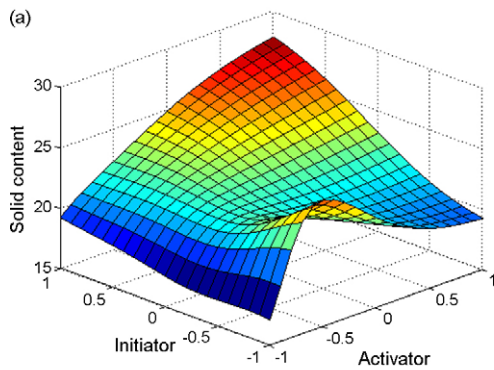


Fig. 1. Graphical results for solid content: (a) surface response; (b) predicted vs. nominal values; symbols: ○, training; —, ideal.

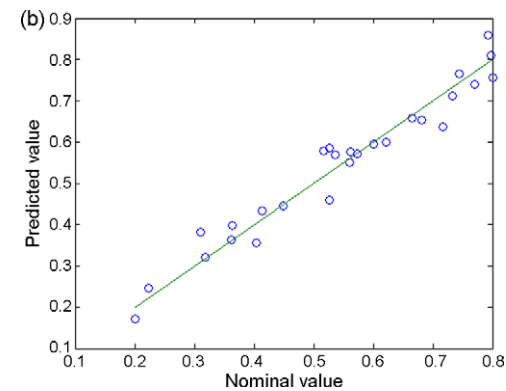
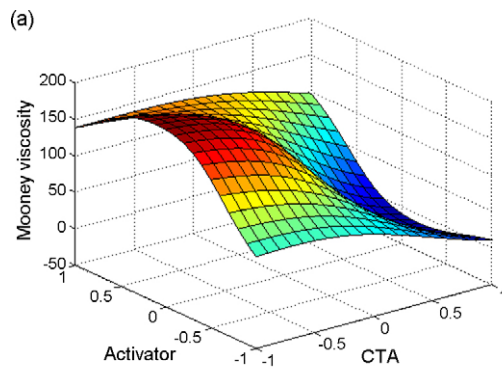


Fig. 2. Graphical results for Mooney viscosity: (a) surface response; (b) predicted vs. nominal values; symbols: ○, training; —, ideal.

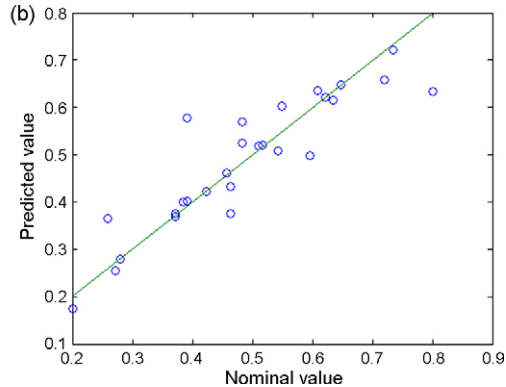
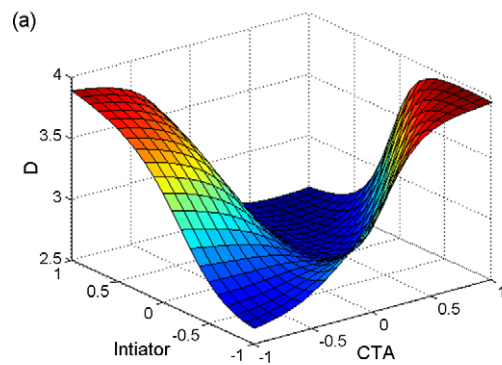


Fig. 3. Graphical results for polydispersity: (a) surface response; (b) predicted vs. nominal values; symbols: ○, training; —, ideal.

Table 4
Desirability function parameters (see Eqs. (4)–(6)).

Parameter	w_1	w_2	\min_i	\max_i	t_i
Solid content	1	1	16.9	27.8	25
Mooney viscosity	1	1	-13	192.5	115
Polydispersity	1	1	2.5	3.9	3

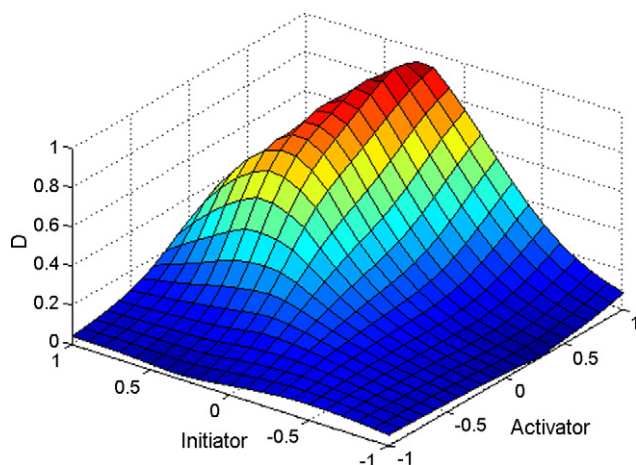


Fig. 4. Simultaneous desirability surface response with CTA at its optimum value.

Table 5
Comparison between expected and experimental values obtained with optimized conditions (initiator = 0.08 mL; activator = 2.50 mL; CTA = 0.85 mL).

Response	Target value	Experimental value
Solid content	25	25.1 ± 0.5
Mooney viscosity	115	114.8 ± 3.4
Polydispersity	3	3.1 ± 0.2

of Mooney viscosity. Finally, Fig. 3(a) shows the surface response for polydispersity as a function of initiator and CTA, with activator at its optimum value, and Fig. 3(b) shows the predicted vs. nominal values of polydispersity.

Theoretically produced data were used to calculate associated desirabilities d_i (see Eqs. (4)–(6) and Table 4 for parameter values) and simultaneous desirability D (taking $r_i = 1$ in Eq. (7)).

The optimum D value was found to be 0.94, which corresponds to 0.08 mL of initiator, 2.50 mL of activator and 0.85 mL of CTA. Fig. 4 shows the surface response for D as a function of initiator and activator, with CTA at its optimum value.

Once the optimum factor values were obtained, a new bottle polymerization was carried out in duplicate following the general procedure described above, and setting the three factors at their optimum values. As it can be seen in Table 5, experimental results for solid content, Mooney viscosity and polydispersity were in agreement with the target values, and the differences that were found are in the order of the analytical measurement error.

5. Conclusions

A multiple response optimization of SBR emulsion polymerization is shown, having used experimental design, ANNs, surface response and the desirability function.

Application of ANNs is a well established methodology for optimization problems; nevertheless, its use on emulsion SBR, supported by experimental results, is a strong point in the present work. This experimental verification confirms that the employed strategy is suitable for the modelling of latex solid content, polydispersity and Mooney viscosity.

The ANN methodology might not be the first option for this problem but, as it is demonstrated in the work, surface response with polynomial models gave unsatisfactory results for the above-mentioned properties.

Particularly for Mooney viscosity, the challenge was to get a reliable set of calibration data, which is known to be a critical point for ANN training (Nascimento et al., 2000). Considering that there is no first-principle model from which Mooney viscosity data could be derived, it was necessary to get experimental results. For this reason, the training was done by feeding the ANNs with bottle polymerization data, working under standard industrial laboratory conditions, taking the reagents and solutions directly from the production plant, and using routine analytical methods of process control from the same laboratory. Furthermore, the bottle polymerization is the method of choice when testing new reagents or conditions for the production scale.

Following this point of view, the aim of the optimization was placed on end-use properties like processability and Mooney viscosity; these properties, despite being related with polymer structure at molecular level, appear more feasible to be modelled by a black box strategy than by a first-principle model.

The possibility to estimate reaction conditions based on required final properties has been exemplified on other polymers (Fernandes et al., 2004). In the present work, a simultaneous optimization stage has been added to the ANN model, using the information obtained from the surface response and the desirability function. The analytical methodology followed here on SBR emulsion is novel in the area of polymerization optimization.

Finally, optimized polymerization conditions for SBR 1712 were experimentally tested, and good agreement between target values and experimental results was achieved.

To sum up, the combination of chemometric tools and multiple response optimization showed its effectiveness to model and control molecular properties. Considering that the input variables chosen for optimization, i.e. initiator, activator and CTA, are individually added and easily controlled at production scale, it is therefore possible to set these reaction conditions, according to the required quality for every different SBR grade to be made. In this way, a quality focused production strategy is established.

Acknowledgements

Petrobras and CONICET (Consejo Nacional de Investigaciones Científicas y Técnicas) are acknowledged for financial support. G. Martinez Delfa thanks CONICET and Petrobras for a fellowship. We thank Petrobras for agreeing to publication of some of the experimental results from its Pilot Plant at PGSM site.

References

- ASTM D1417. (1993). *Annual Book of ASTM Standards*. Philadelphia: ASTM., p. 253.
- ASTM D1646. (1993). *Annual Book of ASTM Standards*. Philadelphia: ASTM., p. 319.
- DiAnjou, A., Torrealdea, F. J., Leiza, J. R., Asua, J. M., & Arzamendi, G. (2003). Model reduction in emulsion polymerization using hybrid first-principles/artificial neural network models. *Macromolecular Theory and Simulations*, 12, 42–56.
- Del Castillo, E., Montgomery, D. C., & McCarville, D. R. (1996). Modified desirability functions for multiple response optimization. *Journal of Quality Technology*, 28, 337–345.
- Derringer, G. C., & Suich, R. (1980). Simultaneous optimization of several response variables. *Journal of Quality Technology*, 12, 214–219.
- Fernandes, F. A. N., & Lona, L. M. F. (2002). Application of neural networks for the definition of the operating conditions of fluidized bed polymerization reactors. *Polymer Reaction Engineering*, 10, 181–192.
- Fernandes, F. A. N., Lona, L. M. F., & Penlidis, A. (2004). Inverse modeling applications in emulsion polymerization of vinyl acetate. *Chemical Engineering Science*, 59, 3159–3167.
- Fryling, C. F. (1954). Emulsion polymerization systems. In G. S. Whitby, C. C. Davis, & R. F. Dunbrook (Eds.), *Synthetic Rubber* (pp. 238–243). New York: John Wiley & Sons.

- Gao, J., & Penlidis, A. (2002). Mathematical modeling and computer simulation/database for emulsion polymerizations. *Progress in Polymer Science*, 27, 403–535.
- Hanai, T., Ohki, T., Honda, H., & Kobayashi, T. (2003). Analysis of initial conditions for polymerization reaction using fuzzy neural network and genetic algorithm. *Computers and Chemical Engineering*, 27, 1011–1019.
- Harrington, E. C. (1965). The desirability function. *Industrial Quality Control*, 21, 494–498.
- Havel, J., Peña, E. M., Rojas-Hernández, A., Doucet, J.-P., & Panaye, A. (1998). Neural networks for optimization of high-performance capillary zone electrophoresis methods. A new method using a combination of experimental design and artificial neural networks. *Journal of Chromatography A*, 793, 317–329.
- Hoffman, W. (1989). *Rubber technology handbook*. Munich: Hanser Verlag, p. 50.
- Joseph, B., & Wang Hanratty, F. (1993). Predictive control of quality in a batch manufacturing process using artificial neural network models. *Industrial and Engineering Chemistry Research*, 32, 1951–1961.
- Moreira, G. A., Micheloud, G. A., Beccaria, A. J., & Goicoechea, H. C. (2007). Optimization of the *Bacillus thuringiensis* var. *kurstaki* HD-1 δ -endotoxins production by using experimental mixture design and artificial neural networks. *Biochemical Engineering Journal*, 35, 48–55.
- Nascimento, C. A. O., Giudici, R., & Guardani, R. (2000). Neural network based approach for optimization of industrial chemical processes. *Computers and Chemical Engineering*, 24, 2303–2314.
- Ninomiya, K., & Yasuda, G. (1969). Processibility of rubbers and usefulness of the mooney viscometer. *Rubber Chemistry and Technology*, 42, 714–734.
- Norman, R. H., & Johnson, P. S. (1991). Processability testing. *Rubber Chemistry and Technology*, 54, 493–534.
- Padmavathi, G., Mandan, M. G., Mitra, S. P., & Chaudhuri, K. K. (2005). Neural modelling of Mooney viscosity of polybutadiene rubber. *Computers and Chemical Engineering*, 29, 1677–1685.
- Quirk, R. P., & Morton, M. (1994). Polymerization. In J. E. Mark, B. Erman, & F. R. Eirich (Eds.), *Science and technology of rubber* (p. 50). San Diego: Academic Press.
- Schmidt, F., Cornejo-Ponce, L., Bueno, M. I. M. S., & Poppi, R. J. (2003). Determination of some rare earth elements by EDXRF and artificial neural networks. *X-Ray Spectrometry*, 32, 423–427.
- Schorf, F. J., Deshpande, P. B., & Leffew, K. W. (1993). *Control of polymerization reactors*. New York: Marcel Dekker, p. 270.
- Schwartz, G. A. (2001). Prediction of rheometric properties of compounds by using artificial neural networks. *Rubber Chemistry and Technology*, 74, 116–123.
- Smith, B. R. (1976). Measurement of Molecular weight distribution of SBR and prediction of rubber processability. *Rubber Chemistry and Technology*, 49, 278–290.
- Spanilá, M., Pazourek, J., Farková, M., & Havel, J. (2005). Optimization of solid-phase extraction using artificial neural networks in combination with experimental design for determination of resveratrol by capillary zone electrophoresis in wines. *Journal of Chromatography A*, 1084, 180–185.
- Tsen, A. Y.-D., Jang, S. S., Wong, D. S. H., & Joseph, B. (1996). Predictive control of quality in batch polymerization using hybrid ANN models. *AIChE Journal*, 42, 455–465.
- Wang, H., Zhou, Y., Zhao, Y., Li, Q., Chen, X., & Hu, Z. (2001). Optimization of on-line microwave flow injection analysis system by artificial neural networks for the determination of ruthenium. *Analytica Chimica Acta*, 429, 207–213.
- White, J. L., & Soos, I. (1993). The development of elastomer rheological processability quality control instruments. *Rubber Chemistry and Technology*, 66, 435–454.
- Zhang, J., Morris, A. J., Martin, E. B., & Kiparissides, C. (1998). Prediction of polymer quality in batch polymerization reactors using robust neural networks. *Chemical Engineering Journal*, 69, 135–143.
- Zupan, J., & Gasteiger, J. (1999). *Neural networks in chemistry and drug design* (2nd ed.). Weinheim: Wiley VCH.