Optimization of the Chain Transfer Agent Incremental Addition in SBR Emulsion Polymerization

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ABSTRACT: The incremental addition of chain transfer agent (CTA) in an emulsion styrene-butadiene polymerization reaction was optimized, using a chemometric approach that involves (a) an experimental design, in which the amount of CTA in each addition were the factors; (b) an artificial neural network modeling to obtain responses for each required processability property (i.e., Mooney viscosity and number- and weight-average molecular weight); and (c) a simultaneous desirability response, due to several properties had to be optimized at a time. As a result, an 8% increase in productivity was accomplished, and some relationships were derived among CTA additions and polymer evolution, Mooney viscosity and molecular weights. The study was carried out to further apply this strategy in the production plant. The challenge was to keep the quality of the produced polymer, particularly in terms of processability. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 3468–3477, 2012

Key words: emulsion polymerization; rubber; computer modeling; CTA; multiple response optimization

INTRODUCTION

The most important process to produce styrene-butadiene rubber (SBR) is the emulsion copolymerization of the corresponding monomers. Despite being a well established process, a number of works are still being published, in which new ways of optimization and improvements are introduced.[1]

The effects of using a chain transfer agent (CTA) in the polymerization are well known. The molecular weight distribution (MWD) in SBR emulsion polymerization is controlled by means of the CTA, commonly a thiol, which loses a labile hydrogen to the growing radical chain, leading to a dead polymer chain and starting a new propagating one from the thiol radical.[2] Thereby, the kinetic chain length is controlled by chain transfer to the CTA, which results the main termination event. However, the probability for processes such as branching and crosslinking to occur, increase with conversion. The reason is that reactions such as chain transfer to the polymer, propagation to terminal double bonds and propagation to pendant double bonds become significant as a consequence of an increase of the polymer concentration and a depletion of the CTA concentration in the polymer particle.[3]

In the SBR industry there is an increasing demand for the rise of the plant productivity, and a straightforward way to do it is to increase polymer production by enlarging the conversion in the polymerization reaction; nevertheless, this production rise must be achieved at no risk of product quality. Typical concerns about SBR quality include viscosity and processability, both properties being related with polymer structure. Viscosity is measured usually at the production site in terms of the Mooney viscosity (MV) of the polymer; this property measures, in arbitrary units based on torque, the resistance to flow of the rubber at slow shear rate.[4] Despite during rubber processing high shear rates are generally used, MV can be used as a processability parameter at the production plant, especially because it can be measured by a simple and fast procedure.[5] To further describe the rubber behavior, another processability parameter is MWD, which complements the characterization of the polymer and whose results can be applied to detect problems in the polymerization reaction.

Several strategies were introduced to increase the polymer production for the case of SBR. One

obvious option is the increment of the reaction conversion; however, for SBR emulsion polymerization, conversions no higher than 60% are desired. Above this conversion, at which the monomer droplet phase is already consumed, the side transfer reactions mentioned in a previous paragraph start to be important. The chain transfer to the polymer, caused by hydrogen abstraction from butadiene repetitive units, is the main reason for trifunctional branches to appear. On the other hand, the reaction between growing radicals and internal double bound of butadiene units is associated with tetrafunctional branches. Succesive crosslinking reactions involving the polymer chains give place to the presence of gel, which affect, in turn, the polymer quality and processability.[6] Taking a maximun value of 60% for conversion, gel content is kept to a negligible value of less than 1%.

Therefore, to enlarge the polymer production by simply increasing the conversion, some control strategy must be applied to attain rubber processability and avoid gel formation, as required. Following this approach, semicontinuous feeding of CTA has been studied.

Early works on this field were focused on apply this feeding procedure to make an efficient use of CTA, to obtain a uniform inherent viscosity during the course of polymerization, or to narrow MWD. Booth et al.[7] studied the effect of the incrementally added *tert*-dodecyl mercaptan (TDM) on MWD in the SBR emulsion polymerization. They observed that the difference between incrementally and not incrementally modified SBR was not significant; a narrower MWD could not be obtained, and this was attributed to a rate of consumption of the TDM being controlled by the rate of transfer from the monomer droplet phase to reaction loci. Uraneck and Burleigh.[8] studied the incremental addition of TDM and *tert*-nonyl mercaptan. For TDM it was found that MV and inherent viscosity were higher than the obtained when total CTA was initially added. Moreover, significant advantages in terms of CTA efficiency were found when *tert*-nonyl mercaptan was employed due to a rapid diffusion from monomer droplet to the polymer particle. Later, Uraneck[9] described that even TDM could be used for an enhancement of modification by incremental addition if enough time was given for the increment to reach the site of polymerization.

Burnett and Cameron[10] showed that an incremental addition of CTA delays the formation of branches and cross-link points to a higher conversion, obtaining SBR with an enlarged productivity and a similar processability as the normal SBR, i.e., that obtained when all CTA is added initially and the conversion is 60%.

More recently, some authors[11–13] proposed a somewhat different approach in a continuous reactor train; it has been shown through model systems that it is possible to increase the polymer production and simultaneously control molecular weights and branching by splitting both, the comonomer mixture and the total CTA feed, into two or more reactors, thus allowing to reduce the monomer phase in the first reactors of the train and, therefore, maximizing the reaction volume.

In this work, the study carried out in an emulsion-SBR production plant (Petrobras Argentina, PGSM site) is presented. Available facilities do not allow the splitting of the monomers feed along the reactor train; instead, it is possible to perform the addition of CTA at two process stages: first, at the beginning, along with monomers, activator and initiator; and second, in an intermediate point of the reactor train, in which conversion is about 30%.

Therefore, in this work, two main purposes were established: to carry out a laboratory scale approach for increasing the productivity of the SBR emulsion polymerization, by means of a multiple response optimization of the incremental addition of CTA; and to study the effect on the SBR processability properties when using this polymerization procedure.

As anticipated, main processability characteristics under study are MV and MWD. It is worth to mention that there is no mathematical model able to predict MV based only on polymerization conditions. Moreover, due to the non linear behaviour of MV, the optimization of this property is difficult to achieve. In a previous work,[14] the combined use of artificial neural networks (ANNs) and desirability function (D) was successfully employed for the modeling of SBR properties followed by a multiresponse optimization of polymerization reagents. Therefore, we proposed to broaden the optimization of the emulsion polymerization to obtain an enhanced polymer production of a typical SBR grade by a CTA incremental addition strategy. As a result, MV and number- and weight-average molecular weights (M_n and M_w) will be kept in specification whereas the conversion (x) is maximized.

EXPERIMENTAL

Polymerizations

All polymerization experiments were made in bottles at 10°C with constant rotation in a water bath. Reagents styrene (99.8%), butadiene (99.5%), soap, initiator, and redox activator were taken from production lines at Petrobras. Dodecanethiol (98%) was provided by Aldrich.

Styrene was washed with 5% Na(OH) solution to remove 4-tertbutylcatechol, used as inhibitor. Before the addition of butadiene and activator, all reagents

TABLE I
SBR Reference Polymerization Recipe

Reagent	phm
Butadiene	71.7
Styrene	28.3
Water	180
Soap	5.2
CTA	Variable
Initiator	0.022
Activator	0.016

were purged in the bottle with N_2 for oxygen elimination.

The polymerizations were carried out during 9 hour and shortstopped with hydroxylamine. In each experiment, two factors were varied: (a) the total CTA concentration and (b) the ratio initial CTA/incremented CTA. The range used for total CTA concentration was 0.381–0.407 phm (parts per hundred of monomer); the range used for the ratio initial CTA/incremented CTA was 65%/35%–85%/15%. These ranges were dictated by the central composite design employed, as explained in the next section. In Table I a reference SBR polymerization recipe can be observed. The conversion was measured on latex samples by gravimetry following the ASTM standard test method.[15] The measured properties in the obtained SBR were M_n, M_w, and MV.

MWD determinations

MWD was determined by size exclusion liquid chromatography. A Varian ProStar 210 pump with a Varian 350 refractive index detector was used. A set of four TosoHaas TSKgel columns (10^6–10^4 Da) was employed. Calibration was done with narrow polystyrene standards (Waters, Milford). 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. It is worth to mention that no evidence of filter fouling or plugging was detected for any sample, indicating that the samples are free of gel.

MV determinations

MV was measured with a MV 2000 Alpha Technologies viscometer under standard conditions.[16] For thermal stabilization, each sample was preheated during 1 min. at 100°C, and MV was measured in arbitrary Mooney units (M.U.), after 4 min stabilization time.

Processability determinations

For Black Incorporation Time tests (BIT), a Brabender Plasticorder mixer was used. The SBR polymer, carbon black, stearic acid and zinc oxide were added to the chamber. The compound was massed at 60 rpm, and BIT was determined at the time a maximum was reached in the torque graph. Gel measurements were made on raw rubber by placing 0.5 g of rubber inside of a paper filter, properly closed. Then, the sample was treated with THF for 24 hour in a soxhlet system, the insoluble residue was filtered and quantified gravimetrically.

Software

Design Expert version 7.0.3 trial (Stat-Ease, Minneapolis) was used for performing experimental design, polynomial fitting and ANOVA results. ANNs, MWD, and desirability calculations were all performed with in-house MATLAB 7.0 routines.

RESULTS

Experimental design

For the CTA incremental addition strategy two considerations were taken into account. First, it was necessary to determine the number of CTA additions and the reaction time at which each addition was to be performed. As it was mentioned before, these issues were ruled by the available operating conditions in the SBR production plant. Therefore, two additions of CTA were made for the experiments; one at the beginning of the polymerization and the second at 30% conversion. To determine the necessary time for the bottle polymerization to reach a 30% conversion, a reference experiment was carried out, from which latex samples were taken at reaction times of 2, 4, 6, 7, and 8 hour. Solid content was measured for each sample and conversions were determined. Figure 1 shows the evolution of monomer conversion with time. It can be seen that the required time to achieve a conversion of 30 % is 4 hour.
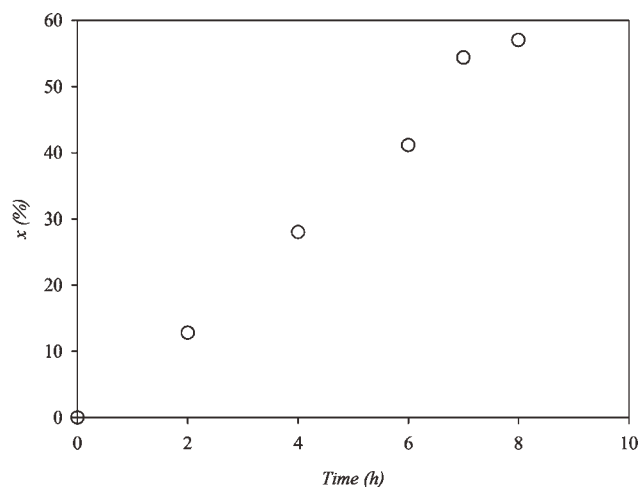

Figure 1 Conversion (x) vs. time plot for reference polymerization.

TABLE II
Experimental Design and Measured Properties

Experiment	C_t (phm)	A_0 (%)	x (%)	MV (M.U.)	M_n (Da)	M_w (Da)
1	0.385	68	66.1	142	238,190	806,580
2	0.385	82	66.5	146	264,650	840,770
3	0.394	65	66.2	147	250,990	845,590
4	0.381	75	64.5	131	213,120	758,870
5	0.394	75	66.7	137	226,240	786,990
6	0.403	68	67.2	138	223,080	797,170
7	0.403	82	67.8	111	196,380	694,110
8	0.407	75	66.2	119	204,140	758,480
9	0.394	85	68.4	134	214,080	766,770
Ref.	0.363	100	60.8	121	215,110	746,620

The second consideration for setting the incremental addition strategy is related to CTA concentration. It is necessary to determine: a) the total amount of CTA to be used, and b) the percentage of the total corresponding to each addition. For this purpose a multiresponse optimization was performed. In this methodology an experimental design is used, in which the total CTA concentration (C_t) and the initial CTA addition (A_0) are varied. From these experiments MV, M_n, and M_w are measured and properties surface response are modeled. Next, an optimization is performed using the desirability function, choosing target values for the measured properties and obtaining optimum reaction conditions.

The employed experimental design was a central composite. As it was explained above, two factors were varied: C_t and A_0; and three concentration levels were considered, giving a total number of nine experiments. Table II summarizes the experiments of the design and their respective responses x, MV, M_n, and M_w. In addition, a reference polymerization can be found where CTA addition was normal (i.e., the whole CTA was added in a single step at the beginning of the polymerization) and the reaction time was 8 hours.

Response models

Quadratic modeling

The first attempt was to fit the observed responses and the experimental factors to a second-order polynomial equation, by using a surface response methodology. Statistical parameters of the fitted models (F-Model and p-Model) are shown in Table III. 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, for none of the three studied properties any significant model could be found (p-Model >0.05). Because of the poor reliability of the fitted models, the optimization cannot be accomplished by means of quadratic polynomials. Thus, an alternative solution is the use of ANNs for the SBR properties modeling.

Artificial neural network modeling

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.[17] 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 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 y for the jth neuron in the hidden layer (y_j) equals to:

$$y_j = \frac{1}{1 + e^{\text{net}_j}} \tag{1}$$

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

$$\text{net}_j = \sum_{i=1}^{n} w_{ji} x_i \tag{2}$$

where n is the number of neurons in the input layer, w_{ji} is the connection weight from the ith neuron in the input layer to the jth neuron in the hidden layer

TABLE III
Statistical Results of Fitted Quadratic Models

Statistical parameter	MV	M_n	M_w
Fitted model	Quadratic	Quadratic	Quadratic
F-Model	8.50	1.43	2.59
p-Model	0.06	0.40	0.23
R^2 adjusted	0.82	0.21	0.49

TABLE IV
Details of ANN Models

	MV	M_n	M_w
Arquitecture	3/5/1	3/5/1	3/6/1
Epochs	4876	5300	5400
RMSEC, %	4.0	2.0	2.0

and x_i is the input to the ith 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 calibration (RMSEC), according to

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

where I is the total number of responses.

For the modeling of the properties, first it was necessary to train the ANNs. In this stage, individuals ANNs were used for each of the three studied properties. For the input layer three neurons were employed, using C_t, A_0, and x as input signals. The output layer consisted in a single neuron corresponding to the property being studied, i.e., MV, M_n or M_w. 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 relative

errors were 3% for MV and 2% for M_n and M_w. In Table IV 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 Figures 2–4. Figure 2(a) shows the surface response for MV as a function of A_0 and C_t, with x at its maximum value, and Figure 2(b) shows the predicted vs. nominal values of MV. Similarly, Figure 3(a) shows the surface response for M_n as a function of x and C_t, with A_0 at its maximum value, while Figure 3(b) shows the predicted vs. nominal values of M_n. Finally, Figure 4(a) shows the surface response for M_w as a function of x and C_t, with A_0 at its maximum value, and Figure 4(b) shows the predicted vs. nominal values of M_w. For the three properties being modeled, the differences between nominal and predicted values [Figs. 2(b), 3(b), and 4(b)] are in agreement with their respective measurement errors.

The modeled behaviour for M_n and M_w is shown in Figures 3(a) and 4(a), respectively: it can be seen that, in general, the molecular weights grow as conversion is increased, and as CTA concentration is diminished. The tendencies observed for MV in Figure 2(a) are discussed in more detail in the next section (see also Figs. 6–8).

Multiple optimization

For cases in which several properties must be simultaneously optimized it is useful to employ tools such as the Desirability function[18–20]; this 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
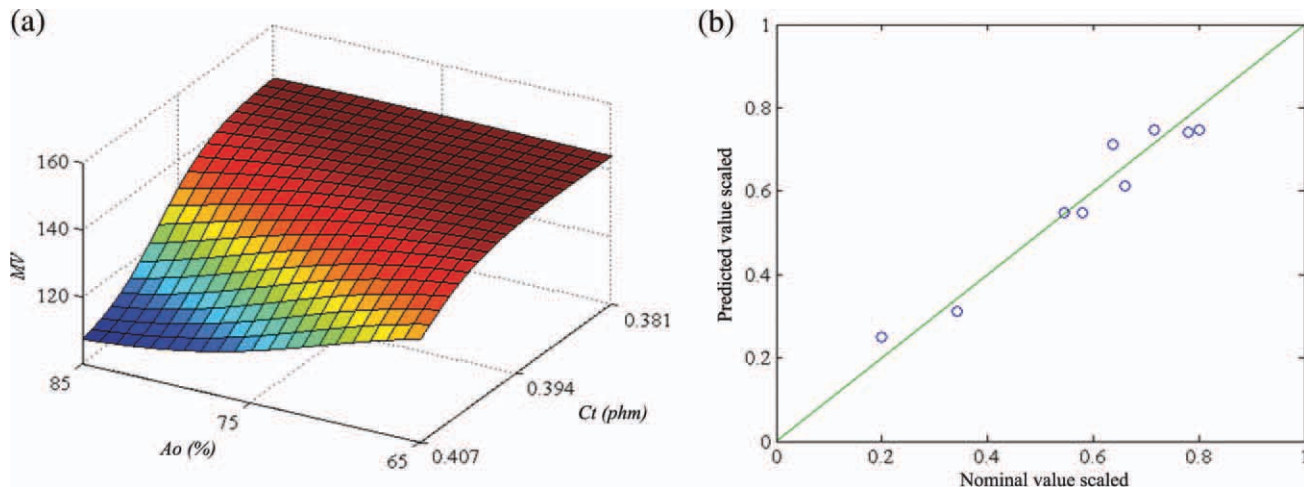

Figure 2 (a) Surface response model for MV; (b) Calibration plot for MV. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
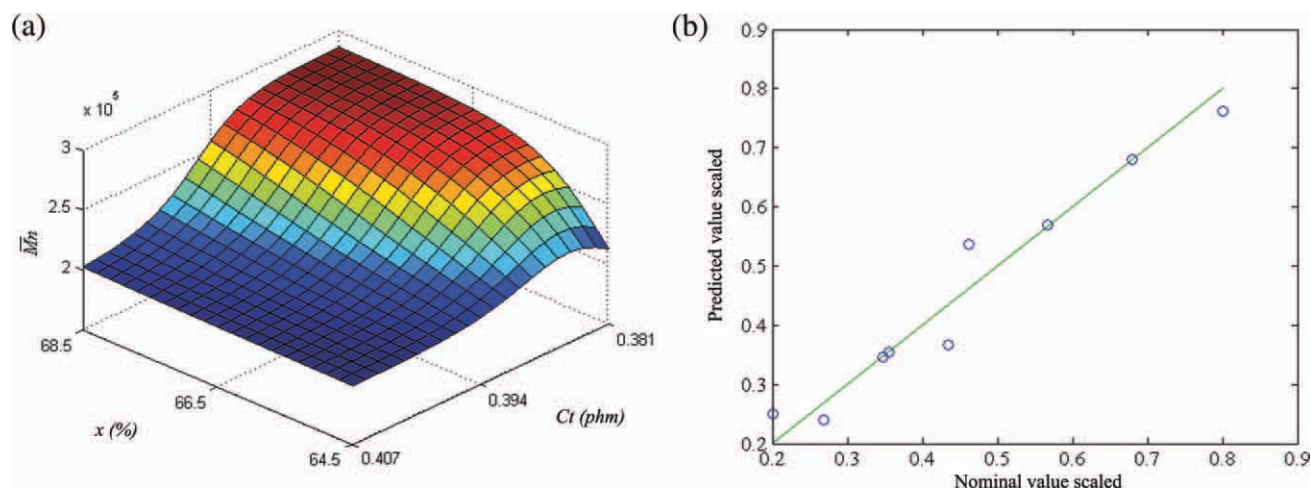
Figure 3 (a) Surface response model for M_n; (b) Calibration plot for M_n. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

from zero to one, i.e. from an unacceptable to an optimum response, respectively.

In this work, the three responses (MV, M_n, and M_w) 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:

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

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

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

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_is are affected by a weight (w_1, w_2) that emphasizes 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:

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

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_is 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.
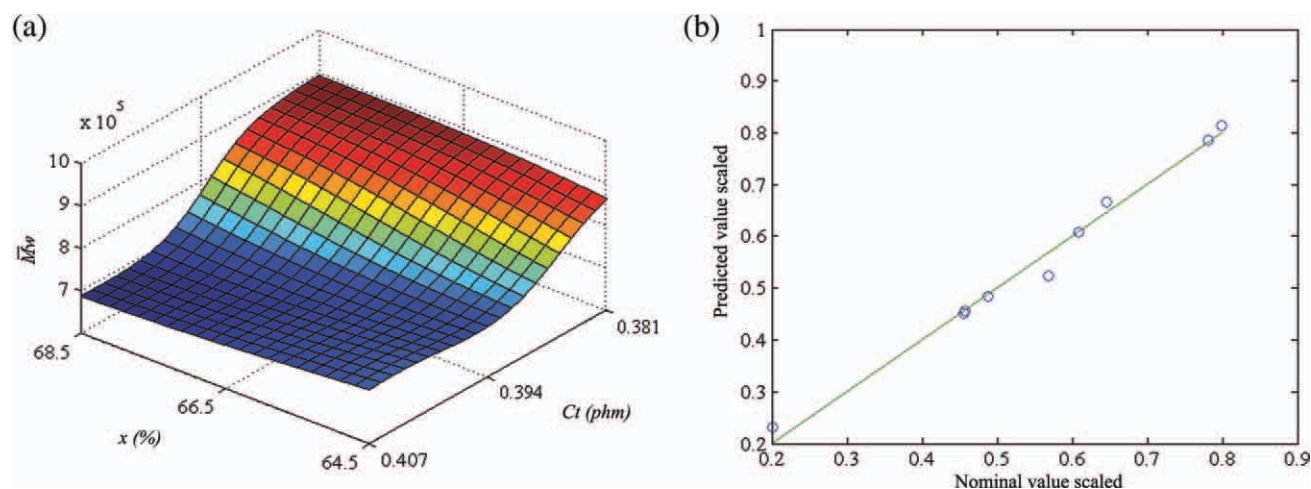

Figure 4 (a) Surface response model for M_w; (b) Calibration plot for M_w. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
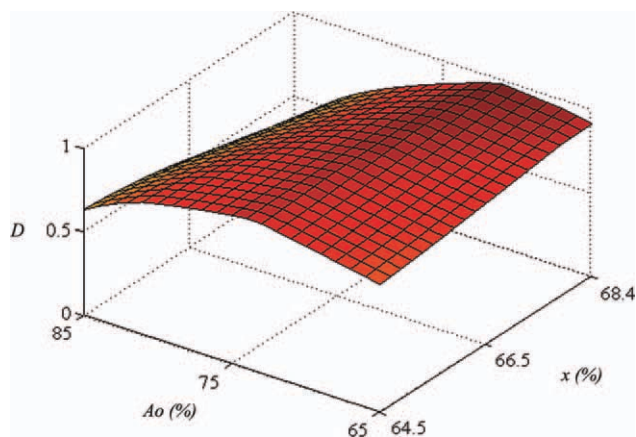
Figure 5 Surface response for D as a function of A_0 and x, with C_t at its optimum value. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

With the obtained surface response models, theoretically produced data were used to calculate associated desirabilities d_i [see eqs. (4)–(6) and Table V for parameter values] and simultaneous desirability D. It should be noted, that the used target values t_i were those obtained from the reference polymerization.

The optimum value for simultaneous desirability was found to be $D = 0.96$, which corresponds to 0.400 phm for C_t and 72% (0.288 phm) for A_0, leading the reaction to 68.3% conversion. Figure 5 shows the surface response for D as a function of A_0 and x, with C_t at its optimum value. Once these optimum factor values were obtained, a new bottle polymerization was carried out following the general procedure described above, and setting C_t and A_0 factors at their optimum values. The accomplished conversion was 67%. The obtained polymer was analyzed
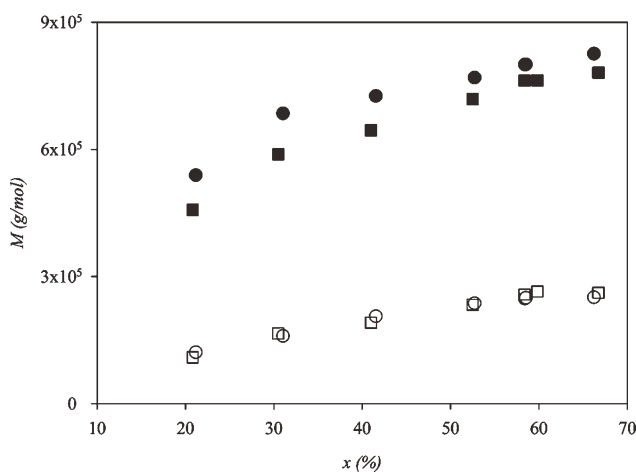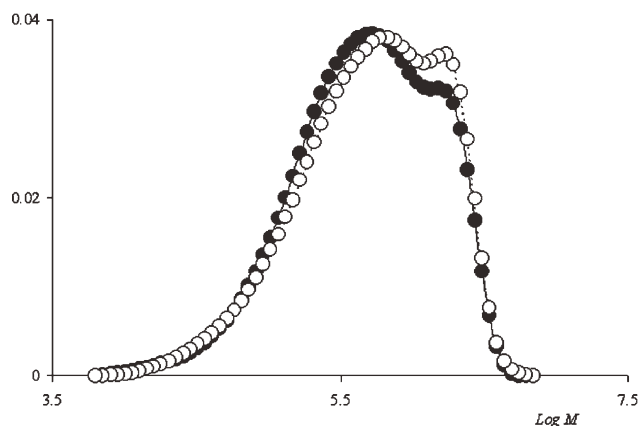

Figure 7 MWD for the obtained polymers. ---○: experiment 3 (C_t: 0.394 phm, A_0: 65%); ---●: experiment 5 (C_t: 0.394 phm, A_0: 75%).

and the experimental values for optimized properties are shown in Table VI.

Processability tests

A BIT test was done to compare the processability of the SBR produced by CTA incremental addition and the one obtained by normal addition. The results are shown in Table VII. It can be seen that the incorporation time of fillers for the optimized rubber is shorter than the reference rubber, showing an adequate processability for the incremental rubber. This test results should be considered as merely comparative, as routine test on production lines involves the addition of processing oils, thus lowering the resulting BIT for most SBR rubber. A second processability comparison between reference and optimized SBR was carried out by measuring gel content. The obtained values were about 0.5% for
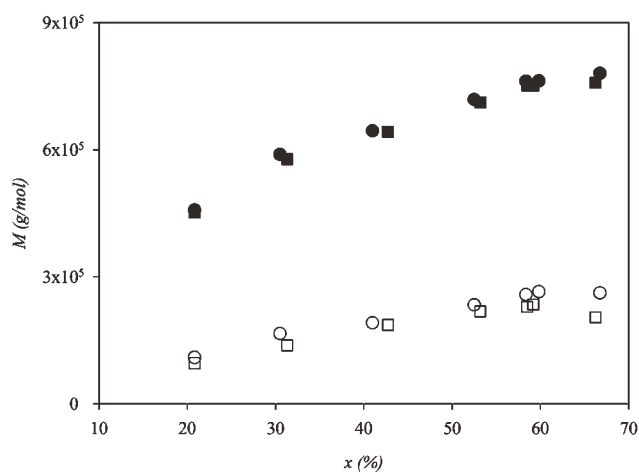

Figure 6 MWD evolution for experiments 3 and 5. Legend: (○ and ●) M_n and M_w, respectively, for C_t: 0.394 phm, A_0: 65%; (□ and ■) M_n and M_w, respectively, for C_t: 0.394 phm, A_0: 75%.

Figure 8 MWD evolution for experiments 5 and 8. Legend: (○ and ●) M_n and M_w, respectively, for C_t: 0.394 phm, A_0: 75%; (□ and ■) M_n and M_w, respectively, for C_t: 0.407 phm, A_0: 75%.

TABLE V
Desirability Function Parameters [See Eqs. (4)–(6)]

Parameter	w_1	w_2	min_i	max_i	t_i
MV	1	1	111	147	121
M_n	0.5	0.5	196,380	264,650	215,110
M_w	0.5	0.5	694,110	845,590	746,620

both, which is comparable with typical gel content accepted for SBR in the production plant. These results are in agreement with BIT measurements, in which complete filler incorporation was achieved, with no observation of heterogeneous dispersion in the resulting compounds.

DISCUSSION

Following the aims of the present work, the topics to be analyzed are the use of multiple response optimization for increasing SBR productivity, and the effect of CTA incremental addition on the SBR processability properties.

Table VI shows the experimental results of the optimized polymerization. It can be seen that the experimental results are in agreement to the target values. This means that the incremental rubber keeps the properties of the reference polymer, whereas the conversion was raised from 60% (which corresponds to the reference) to 67%. The main difference can be found on MV with a low experimental value of 117; this is probably because the accomplished conversion was 67%, a value lower than the target one dictated by the desirability. It might be expected that if the conversion had been larger, then MV would have been increased too and would have become closer to the target value. However, it is worth mentioning that the MV value for the optimized rubber falls within the production specification of the reference SBR. On the other hand, the suitable processability found in BIT test, shows that the rubber obtained by the CTA incremental addition strategy does not present difficulties for the incorporation of fillers. Although the BIT value for the optimized rubber was lower than that of the reference, it is difficult to assign this difference to an improvement of the rubber quality or to the four points of difference on MV. In any case, the results obtained in all the processability properties measured showed that the

TABLE VI
Comparison Between Target and Measured Values in the Optimized Polymerization

Response	Target value	Experimental value
MV	121	117
M_n	215,110	215,120
M_w	746,620	726,000

TABLE VII
BIT Test Results

Sample	BIT (min)
Reference SBR	8.25
Optimized SBR	6.25

increase in conversion did not allow a lowering in rubber quality.

Now, it is interesting to analyze the set of experimental results presented in Table II. As it was previously shown, a relationship between MV and the factors of the CTA incremental addition strategy (A_0 and C_t) can be observed. It is worth to analyze these observations in terms of MWD and its evolution with conversion, although it must be pointed out that a reliable description of MV behavior is difficult to achieve solely based on this approach.

In Figure 2(a), different tendencies for MV can be observed. There is a decrease on the MV values when A_0 is increased, for a given C_t level. Nevertheless, it could be seen that this tendency is less pronounced as C_t decreases from 0.407 phm to 0.381 phm. Analyzing the MWD evolution (Fig. 6) for experiments 3 and 5 (A_0: 65 and 75%, respectively, and C_t: 0.394 phm for both), major differences on M_w at early stage of the polymerization can be observed. When A_0 is higher, the development of low molecular weight chains is favored due to a higher initial concentration of CTA in the polymer particle; then, after 50% conversion, the difference is less pronounced because of the CTA increment, which is higher for polymerization 3. This behavior produces in the overall MWD a shift to high molecular weights and a more marked shoulder when A_0 decreases (Fig. 7), which correlates also with the higher MV observed.

In second place, it could be seen [Fig. 2(a)] that MV decreases as C_t increases, for a given A_0, and this trend is less pronounced as A_0 reduces from 85% to 65%. In Figure 8 the evolution of molecular weights for experiments 5 and 8 (C_t: 0.394 phm and 0.407 phm, respectively, A_0: 75% for both) shows that M_n and M_w, curves have similar tendencies, but for experiment 8 all values are slightly minor, corresponding to the higher CTA concentration used.

As it was previously mentioned, a less pronounced effect on MV could be observed when C_t is low, regardless the A_0 value, and also when A_0 is low, regardless the C_t value [see Fig. 2(a)].

For both tendencies, a possible explanation is that for these conditions the initial CTA concentration is low, and the formed polymer chains have a molecular weight so high that the further addition do not lead to a significant change in the molecular weight and therefore, in MV.

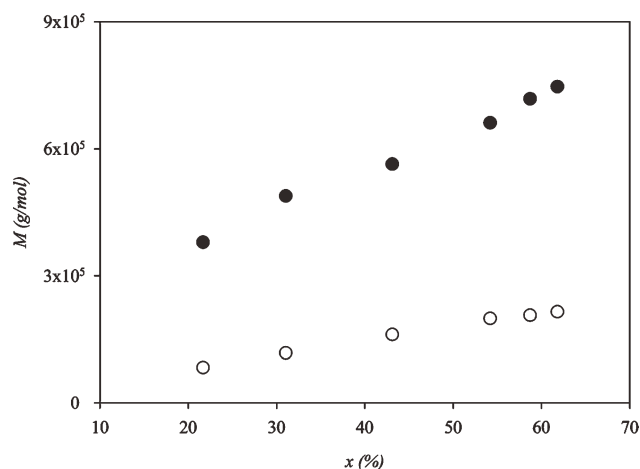In the set of experiments in Table II it is observed a growing relationship between MV and M_w. Then,

Figure 9 MWD evolution for reference polymerization. Legend: ($\bigcirc$ and $\bullet$) M_n and M_w, respectively, for C_t: 0.363 phm, A_0: 100%.

what can be stated is that there is no evidence for the obtained polymers to be significantly different in terms of degree of branching, or gel content. If that difference existed, we could have found experiments with similar M_w, but variable MV values, which are produced because of different gel content for each polymer. In fact, as mentioned earlier, we did not find any gel during sample filtration for MWD determinations.

Another highlight is the change in the evolution of MWD with conversion, when comparing the normal and the incremental CTA additions. Figure 9 shows the evolution of MWD for the reference polymerization. It could be seen that M_w increases in the course of polymerization, demonstrating a continuous depletion of CTA concentration in the polymer particle since the mass transfer rate is insufficient to compensate its consumption; moreover, this behavior continues even when monomer droplet phase disappears, at around 50% conversion, and the monomer concentration in the polymer particle start to decay. However, for experiments 3, 5, and 8, the M_w plots (Figs. 6 and 8) show a softened growing trend from 40% conversion thereafter, compared with reference evolution, due to the effect of the CTA increment. It is expected that the effects of the incremental addition does not take place immediately, since CTA is added in styrene solution and some time is required to emulsify the droplets and hence, to increase the interfacial area of the monomer droplet which leads to a better diffusion of CTA.

CONCLUSIONS

A multiple response optimization of CTA incremental addition for a SBR emulsion polymerization at laboratory scale was shown, making use of a methodology which combines 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 system, supported by experimental results, is a strong point in the present work.

Since surface response with polynomial models gave unsatisfactory results, using an ANN methodology to correlate non linear properties with initial reaction conditions turned to be a proper alternative. Suitable black box models for MV and MWD were obtained supported by experimental data. Particularly, for MV estimation, it must to be emphasized that no first principle model is available. The ANN modeling presented in this work has proved to be an appropriate tool to overcome this problem, allowing to generate surface response that shows a novel correlation between the factors of the incremental addition strategy and MV. In addition, the experimental results were analyzed in terms of MWD evolution, and it was possible to find some tendencies between MV and MWD.

Optimized conditions for CTA addition in SBR polymerization were experimentally tested, and good agreement between target values and experimental results was achieved, moreover, all measured properties gave acceptable process values. As BIT test has shown, it was found that polymer processability was not affected when increasing the reaction conversion, and therefore, the multiresponse optimization-ANN model is useful to set the conditions of the incremental addition strategy for improving productivity. The accomplished conversion represents an 8% increase in SBR production, with respect to normal polymerization, by only using a 12% additional CTA. It should be highlighted that a reaction conversion higher than 68% was not looked after, since polymer chemical composition would change at such conversion. It has been shown that for larger conversion increments, a change in the composition of the comonomer mixture should be considered.

Finally, the bottle polymerization technique is the method of choice when testing new reagents or conditions for the production scale. Although results produced in batch systems, like the obtained by bottle polymerization, cannot be directly transferred to a train of continuous stirred tank reactors, the accomplished study at laboratory scale, aided by chemometric tools, does encourage the scaling-up of the proposed CTA dosing strategy to the production lines to take advantage of the installed capabilities of the plant.

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