Thermodynamic Modeling and Simulation of Styrene—Butadiene Rubbers (SBR) Solvent Equilibrium Staged Processes

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The main purpose of this paper is to describe the necessary steps to model the equilibrium based operations in styrene—butadiene rubbers (SBRs) processing. First of all, we include a brief introduction to polymer—solvent thermodynamics, so later on, we can discuss about the experimental techniques reported in literature for this kind of system, emphasizing those we have used in our work (intrinsic viscosity and inverse gas chromatography). General comments about the thermodynamic models used and experimental data treatment are also included. But, the development of an accurate simulation model which can predict the final purity of the polymer involves other thermodynamic studies, in order to determine the relative affinities of several additives with both polymer and solvent. Thus, the behavior of several polar modifiers, which are commonly employed in the synthesis process, is also reported. Experimental equilibrium data, evaluation of predictive methods, and simulation results are also reported for these additives, showing that the selection of a suitable thermodynamic model is essential for the reliability of the simulations performed.

1. Introduction

The generic term “polymer” includes a great variety of both natural, such as starch and some proteins, and synthetic materials, such as polyamides. They can be divided in two main groups depending on their mechanical behavior: plastic materials and rubbers or elastomers.1

Styrene—butadiene rubber (SBR) is the most important synthetic rubber. Due to its low manufacturing cost and its good properties, it is a good replacement for natural rubber. This material is a copolymer of both butadiene and styrene with a styrene weight fraction equal or less than 0.2—0.3.

There are two types of SBRs. The first, or random one, is obtained by polymerization of the two monomers without controlling their relative position in the final product. The second, SBS (styrene—butadiene—styrene), one is constituted by a block of styrene molecules, followed by a block of butadiene molecules, and a last block of, again, styrene molecules. From SBS rubbers, SEBS rubbers (styrene—ethylene—butadiene—styrene) can be obtained by partial hydrogenation of the double bonds of butadiene fraction.

These last compounds are mainly applied to manufacture adhesives and sealants, as plastic modifiers, or in the compounding of other products.2 In addition, other specific applications have been described for these polymers, as in the case of the pharmaceutical field3 or for asphalts modifications.4

As in a typical chemical process, the main steps of a rubber synthesis process are the raw materials fitting out, the reaction step, and the product separation. The first step is performed mainly by means of distillation or adsorption processes. The second one can be done either by an emulsion process (in aqueous media) or by an anionic polymerization process (in an organic solvent media). At last, the product separation is developed, either by devolatilization or direct evaporation or by steam stripping.

Although the raw materials fitting out and the reaction steps have widely been studied both by experimental measurements and by simulation, there is not so much work concerning the product separation step.

In a steam stripping process, polymer and solvent are separated by contact with a steam stream which vaporizes the solvent, while the condensed water remains with the polymer. Later on, both water and polymer can be easily separated in a filter, because they are absolutely immiscible, and the solvent along with the steam are separated by a flash distillation.

Although the first stripping processes were carried out in a single stage,5—8 nowadays, these processes are carried out in two following stages, so the fresh steam can be fed to the second stage and the vapor recovered from this stage can be used as a stripping agent in the first stage.

In a devolatilization process, the solvent is directly evaporated without employing any stripping agent. It has the advantage, when compared with a steam stripping process, that it is not necessary to add any equipment to recover the separated solvent. But it has the inconvenience that, due to the fact that the viscosity of the polymer crumbs increases a lot while the solvent evaporates, the separation of the last portions of solvent is very difficult (and involves a high energy consumption).

Due to the fact that both devolatilization and steam stripping are thermodynamically controlled processes, it is very important to study the thermodynamic behavior of all the components involved: polymer, organic solvent, and water.

Solvent—water mixtures are constituted by components whose molecular sizes are close to each other. Therefore, they can be studied by means of classical thermodynamics, using either equations of state (EOS) models, such as Peng—Robinson9 or Redlich—Kwong—Soave,10 or activity coefficient models, such as NRTL11 or UNIQUAC.12

But, the mixtures involving polymers can not be studied directly by means of classical thermodynamics because there is a great difference between the molecular size of the polymer and the molecular size of the other component. For this reason, a binary polymer—solvent mixture does not strongly behave as a conventional solution, and it is necessary to use specific thermodynamic models.

Several authors have proposed different models to characterize polymer—solvent mixtures. One of the most important,

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which has been mainly used in the results presented in this section, is the Flory–Huggins theory. In this theory, proposed by Flory and Huggins, the activity of the solvent in a solvent–polymer mixture is calculated as the sum of two contributions, a configurational one and an energetic one, according to eq 1.1.

\[
\ln a_i = \ln \frac{p_i}{p_i^0} = \ln(1 - \phi_2) + \left(1 - \frac{1}{T}\right)\phi_2 + \chi\phi_2^2
\]  

(1.1)

In this equation, \( p \) is the vapor pressure of the polymer solution, and \( p_i^0 \) is the vapor pressure of the pure solvent.

The first two terms in the right side of the former equation belong to the entropic configurational contribution. It takes into account the differences in size and shape of the molecules, which determine the different configurations that a molecule of polymer can adopt in the solution. This contribution is calculated as a function of the polymer volumetric fraction (\( \phi_2 \)) and the molar volume of the polymer divided by the molar volume of the solvent (\( r \)).

The last term of the equation is the energetic contribution. It is defined as a function of a nondimensional parameter called the polymer–solvent interaction parameter or Flory–Huggins parameter (\( \chi \)). This parameter, eq 1.2, has two contributions: an entropic one (\( \chi_s \), eq 1.3), whose value ranges between 0.2 and 0.5, being 0.34 the most common value, and an enthalpic one (\( \chi_h \), eq 1.4), which can be calculated from the Hildebrand and Scott theory as a function of the difference between the solubility parameters of polymer (\( \phi_2 \)) and solvent (\( \phi_1 \)) and the molar volume of the solvent (\( V_{m,1} \)).

\[
\chi = \chi_s + \chi_h
\]

(1.2)

\[
\chi_s = 0.34
\]

(1.3)

\[
\chi_h = \frac{V_{m,1}}{RT}(\phi_1 - \phi_2)^2
\]

(1.4)

The application of this model is a very easy way of obtaining experimental equilibrium data in polymer–solvent solutions, although it has a few limitations. For example, although the polymer–solvent interaction parameter was originally defined as independent of the polymer volumetric fraction, this could not be completely true. In the literature, both increasing and decreasing values of \( \chi \) with polymer composition have been reported. Besides, in solutions with very low polymer content, the theory could also fail in the calculation of the entropy and volume of mixing.

Other thermodynamic models that can also be used to reproduce the thermodynamic behavior of a polymer–solvent system are the theories of Prigogine–Flory–Patterson, Sánchez and Lacombe LF (lattice fluid), or SAFT (statistical associated fluid theory), proposed by Wertheim. In addition, predictive activity coefficient models such as UNIFAC-FV or equations of state based models such as High–Danner or the perturbed-hard-sphere-chain EoS have been developed, showing a great potential in phase-equilibria prediction involving polymer solutions.

The aim of this paper is to describe a procedure to simulate the polymer–solvent steam stripping separation step in a SEBS rubber production plant. Due to the importance of developing a thermodynamic study for this kind of simulation, in the beginning, the more important experimental methods to get equilibrium data in both polymer–solvent and conventional mixtures are described, indicating the results obtained with the two techniques employed in this work (inverse gas chromatography and intrinsic viscosity). Later on, the paper includes a description of the simulation model of the separation step considered. At last, the influence of the different thermodynamic studies over the simulation results is also discussed, in terms of the distribution of different additives in the outlet streams of the model.

2. Experimental Measurements of Polymer–Solvent Equilibria

Thermodynamics of polymer–solvent pairs is important not only from a scientific point of view but also in many interesting industrial processes. Examples of its applicability are the preparation of asymmetric membranes, the microlithography, employed in chips fabrication, or the study of the oral absorption of drugs.

Modeling polymer–solvent equilibrium requires using non-conventional techniques. Typical isothermal or isobaric vapor–liquid equilibrium (VLE) measurements can not be carried out directly, due to the specific properties of polymer solutions (high boiling point, viscosity,...). For this reason, it is difficult to characterize polymer–solvent interactions. But, these drawbacks have been overcome by applying novel experimental methods for the determination of both polymer–solvent interaction parameters and polymer solubility parameters.

There are a wide variety of methods described in literature for this purpose (Table 1), depending on the polymer composition in the mixture and the kind of polymer (glassy, amorphous, thermostable,...). Between them, intrinsic viscosity (IV) and inverse gas chromatography (IGC) are two of the most widely used due to their reliability and ease of startup.

In a rubber obtaining process, there are several steps in which the composition of the polymer solution is changing. Once the rubber is synthesized, the polymer mass fraction in the reactor is below 0.3. Later on in the process, solvent and additives are removed from polymer, a steam stripping mechanism being one of the mostly used. This step is designed to purify the final product, so the final polymer mass fraction can be greater than 0.99.

As it has been previously reported, polymer–solvents interaction parameters depend upon composition; in addition, the change in the behavior of the solvent is more important when its concentration is going to zero. Therefore, to simulate a polymer–solvent steam stripping step, a thermodynamic study of polymer solutions over a wide range of compositions is needed. There is not any experimental method covering the overall range so it is necessary to start up with two different methods.

2.1. SEBS Rubber. All the experimental measurements in this work were carried out with a SEBS (poly(styrene-b-butene/
ethylene-\(b\)-styrene) triblock copolymer) synthesized and supplied by Alfonso Cortina Technology Center of REPSOL-YPF, with a styrene content of 32\% by weight, a density of 960 kg/m\(^3\), and an average molecular weight of 86238 g/mol. This rubber is obtained by hydrogenation of poly(styrene-\(b\)-butadiene-\(b\)-styrene) triblock copolymers.

2.2. Intrinsic Viscosity Measurements. The background of the technique is the change in the viscosity by consecutive additions of polymer over the solvent. The more the viscosity increases, the more compatible polymer and solvent are.

Intrinsic viscosity \([\eta]\) is the viscosity of an infinitely diluted polymer solution. It can be calculated with the experimentally determined values of the relative (\(\eta_r\)) and specific (\(\eta_sp\)) polymer viscosities, according to the Huggins (2.1) and Kraemer (2.2) equations.

\[
\eta_sp \frac{c}{\eta} = [\eta] + K_H[\eta]^2c
\]

\[
\ln(\eta_r) \frac{c}{\eta} = [\eta] + K_K[\eta]^2c
\]

where \(c\) is the concentration of polymer solution, \(K_H\) is the Huggins coefficient, a constant for a series of polymers of different molecular weights in a given solvent and temperature, and \(K_K\) is the Kramer coefficient, where theoretically \(K_H - K_K = 0.5\).

So the intrinsic viscosity can be determined, as usual, as the common intercept of the Kraemer and Huggins relationships, using \(\eta_r\) and \(\eta_sp\) previously determined.

For the intrinsic viscosity measurements,\(^{41}\) all polymer–solvent more concentrated solutions were prepared by adding 200–300 mg polymer over approx 60 g of pure solvent and shaking until polymer dissolution. The rest of the solutions were prepared from the former ones by dilution, by adding pure solvent.

Viscosity data were carried out in a JP-Selecta Ubbelohde \(0b\) type of capillary viscosimeter. Once prepared each solution was transferred into viscosimeter and immersed in a water bath, thermostatted at 20 °C ± 0.01. The solutions were allowed to equilibrate at this temperature before starting the measurement. The accuracy of the measurements was 10⁻² s. From the flow times, relative and specific viscosities were determined.

From our previous results,\(^{41}\) it can be concluded that, according this technique, cyclohexane shows the highest compatibility with an SEBS rubber (highest intrinsic viscosity value) and \(n\)-hexane shows the lowest (lowest intrinsic viscosity value). Besides, the lower the polymer–solvent interaction parameter, the more compatible the polymer and the solvent. This happens when enthalpic term of this parameter, proportional to \((\delta_1 - \delta_2)^2\), is the lowest. So the solubility parameter of the polymer should be close to the solubility parameter of the solvent. According to literature,\(^{42}\) this occurs when intrinsic viscosity is the highest; for this reason, the maximum of the plot intrinsic viscosity vs solubility parameter of the solvent corresponds to the polymer solubility parameter. The result obtained in our previous work\(^{41}\) is \(\delta_2 = 17.1\) MPa\(^{0.5}\).

Then, by using eqs 1.2–1.4, the Flory–Huggins interaction parameter of each polymer–solvent pair, in the range of intermediate-low polymer compositions, can be obtained. The calculation only requires the knowledge of the solubility parameter of each pure solvent, which can be easily obtained from vaporization enthalpy values.

2.3. Inverse Gas Chromatography (IGC) Measurements. By IGC measurements, the stationary phase of a chromatographic column is characterized. Using a polymer as stationary phase, measurements of the differential affinity of solvents can be performed and polymer–solvent interaction parameters can be fitted.

The background is that, once the polymer is immobilized into a packed column, small amounts of different solvents, along with air (inert component), are injected and carried through the column by the carrier gas of a typical gas chromatograph. The difference between the retention times of the air and the solvent can be related with the compatibility between the polymer and the solvent. The higher the time the solvent is in the column, the higher the affinity of the solvent and the polymer. The concept is

\[
\frac{\text{num molec mobile phase}}{\text{time molec mobile phase}} - \frac{\text{num molec stationary}}{\text{time molec stationary}} = \frac{\text{num molec mobile} + \text{num molec stationary}}{\text{time molec mobile} + \text{time molec stationary}}
\]

According to the IGC technique,\(^{43}\) the relation between the infinite dilution activity coefficient of the solvent and the retention volume is given by eq 2.5, where \(T\) is the temperature in kelvin, \(R\) is the ideal gas constant, \(M_s\) is the solvent molecular weight, and \(\ln f_r^\infty\) is the standard fugacity of the solvent. Usually, this last value is calculated by using a virial EOS truncated after the second term, as shown in eq 2.6.

\[
\ln(\Omega_r^\infty) = \ln\left(\frac{RT}{V_g M_s f_r^\infty}\right)
\]

\[
\ln(\Omega_r^\infty) = \ln\left(\frac{RT}{V_g M_s f_r^\infty}\right) - \frac{(B_{11} - V_{m,1})\rho_1}{RT}
\]

For the inverse gas chromatography measurements, Chromosorb W/\(AW-DMCS\) 80–100 mesh was used as support. The stationary was prepared by dissolving a weighted sample of the polymer in cyclohexane and depositing the solution on a weighted amount of support. The mixture was allowed to dry under vacuum by slow evaporation in a rotovapor, being stirred to ensure a homogeneous mixture; the evaporation time was 8 h. The final amount of polymer deposited in the support was 11.9\% w/w, which was determined with thermogravimetric analysis on a Seiko EXSTAR 6000 TG/DTA 6200.

Afterward, the coated support was packed into a \(\frac{1}{4}\) in. nominal diameter and 1.9 m length column, which was installed in a VARIAN 3800 gas chromatograph, equipped with a thermal conductivity detector and an electronic flow controller.

All the measurements were carried out with a helium flow of 30 mL/min, as a carrier gas, and in a temperature range between 20 and 150 °C. The amount of solvent injected was 0.2 µL along with 0.8 µL of air, as an inert component.

From the values of infinite dilution activity coefficient, the Flory–Huggins interaction parameter can be calculated by using eq 2.7,\(^{44}\) where \(r\) is the ratio between molar volume of the polymer divided by the molar volume of the solvent and \(\rho_1\) and \(\rho_2\) are solvent and polymer densities, respectively.

\[
\chi = \ln(\Omega_r^\infty) - (1 - \frac{1}{r}) + \ln\frac{\rho_1}{\rho_2}
\]

The Flory–Huggins theory, modified by Blanks and Prausnitz,\(^{16}\) allows establishing a relation between Flory–Huggins parameter (\(\chi\)) and the solubility parameters of polymer (\(\delta_2\)) and solvent (\(\delta_1\)), where \(\delta_2\) is the entropic contribution to \(\chi\), eq 2.10.
\[ \chi = \chi_S + \frac{V_{m,1}}{RT}(\delta_1 - \delta_2)^2 \]  
(2.10)

Rearranging terms, eq 2.11 is obtained. Thus, the polymer solubility parameter can be obtained in the range of infinite dilution of solvents.

\[ \left(\frac{\delta_1^2 - \chi RT}{2V_1}\right) = \delta_2^2 \delta_1 - \left(\frac{\delta_1^2}{2} + \frac{\chi RT}{2V_1}\right) \]  
(2.11)

In our previous work,45 appear the values of Flory–Huggins interaction parameters of SEBS–solvent mixtures, calculated with eq 2.7. According this technique, the value of the solubility parameter of polymer obtained is \( \delta_2 = 15.7 \text{ MPa}^{0.5} \).

2.4. Comparison between IV and IGC Experiments. As it can be seen, data of polymer solubility parameters are different depending on the technique used (17.1 MPa\(^{0.5}\) IV, 15.6 MPa\(^{0.5}\) IGC). From the literature for polydienes,40 similar results have been found (Table 2).

It could be thought that there is an influence of the temperature, but they were calculated taking into account values of the thermal expansion coefficient and this influence does not justify the results obtained. In addition, Yılmaz and Cankurtaran46 found a similar effect comparing both IV and IGC techniques, so it can be seen that there is a concentration dependence of the interaction parameters in polymer–solvent systems; therefore, it is necessary to obtain data for them in a wide range of polymer compositions.

3. Polymer–Solvent Separation Step Simulation

3.1. Introduction to Process Simulation. The importance of the simulation tools in the chemical industry has grown very much in the last two decades. With these kind of tools, preliminary tests can be carried out in order to determine the purity of the final product of a process or the behavior of a new compound introduced in this process (for example, when one additive is being replaced by another one). The availability of commercial software, such as Aspen Plus or Hysys Pro, has made it easier to obtain such models.

3.2. Polymer–Solvent Separation by Means of a Steam Stripping Process. In several patents,5,6 many methods of developing a steam stripping process in one or more stages and with or without steam recirculation have been described, although in the scientific literature there are few references concerning this topic.

As a first approach, each steam stripping stage can be considered as a flash stage in which polymer, solvent, and water are separated in three streams: one vapor stream which contains steam, water, and solvent; one organic liquid stream which contains the polymer and the solvent nonflashed; and one aqueous stream which contains the condensed water. In a second approach, a more complex model should involve two stages, each one assimilated to a flash stage, and maybe it could be adequate to study the possibility of mass transfer limitations.

In the experimental sections, cyclohexane, methylcyclohexane, and cyclopentane were selected as the most compatible solvents for an SEBS rubber. In this chapter, to compare the behavior of these three solvents in a steam stripping process, Aspen Plus was used to simulate one separation stage between polymer and solvent by means of a steam stripping process.

3.3. Thermodynamic Study to Simulate a Steam Stripping Process. To accurately simulate the process, an exhaustive thermodynamic study with the three components involved in the system, solvent (1), polymer (2), and water (3) is required. For this reason, NRTL interaction parameters of all binary mixtures have been obtained.

The NRTL activity coefficient model11 can describe both vapor–liquid (VLE) and liquid–liquid (LLE) equilibrium of strongly nonideal solutions, such as polymer–solvent solutions. For binary mixtures, this model has three binary interaction parameters: \( r_{12}, r_{21}, \) and \( r_{13} \). The first two are normally fitted and have a temperature dependence according to eq 3.1. The third one (\( r_{13}, \) nonrandomness parameter) usually ranges between 0.2 and 0.47; but, 0.3 is an acceptable value for nonpolar mixtures, and 0.2 is an acceptable value for polar systems.11

\[ r_{ij} = a_{ij} + b_{ij} \]  
(3.1)

Concerning solvent (1)–polymer (2) mixtures (cyclohexane–SEBS, methyclyclohexane–SEBS, and cyclopentane–SEBS), from the values of polymer solvent interaction parameter at 293.15 K (0.455 for the SEBS–cyclohexane couple, 0.459 for the SEBS–methylcyclohexane couple, and 0.460 for the SEBS–cyclopentane couple) experimentally determined in our previous works,41,45 \( P–xy \) data (pressure, liquid phase mass fraction, vapor phase mass fraction) have been obtained, according the procedure showed in Figure 1 and based on Flory–Huggins theory.

In a first step, fixing different values of SEBS volume fraction and using SEBS density (960 kg/m\(^3\), data supplied by the REPSOL-YPF Company) and solvent density (data taken directly from the bottle), the liquid mass fraction of both compounds can be obtained. On a second step, the pressure of polymer solution for different polymer fractions can be obtained from the pure solvent vapor pressure values, polymer solvent interaction parameter, and polymer volume fraction, applying the Flory–Huggins equation, eq 1.1.

In this way, \( P–xy \) data can be obtained from polymer solvent interaction parameter at a given temperature (293.15 K). The procedure is valid for mixtures which are completely miscible, as it happens in the case of SEBS–cyclohexane, SEBS–cyclopentane, and SEBS–methylcyclohexane, but not for mixtures partially miscible, as it could happen with other organic solvents.

Table 3 shows the \( P–xy \) data obtained, following the procedure previously described, for all binary mixtures, using

![Figure 1](Image 370x551 to 502x684)
the values obtained for polymer–solvent interaction parameters. Because the polymer content in the vapor phase has been considered to be equal to zero, this variable does not appear in the table. At 293.15 K, the vapor pressure of cyclohexane, methylcyclohexane, and cyclopentane are 10.4, 4.8, and 34.5 kPa, respectively.47 As it can be seen in Table 3, Flory–Huggins theory predicts that the decrease of the solvent vapor pressure due to polymer is important only at elevated polymer compositions (polymer volume fraction higher than 0.6).

With Table 3 values and considering the vapor polymer fraction equal to zero, nonlinear fittings to the NRTL model were done. For this purpose, Aspen Plus commercial software was employed. In the three cases studied, good fits (a residual root-mean-square error of 7.7% in the case of cyclohexane, 8.7% in the case of cyclopentane, and 8.7% in the case of methylcyclohexane) were obtained, both in the low polymer concentration zone as well as in rich polymer concentration one, indicating that the procedure employed is valid. In all the cases, \( \alpha_{12} \), \( b_{12} \), and \( b_{21} \) parameters of NRTL equation were adjusted, while keeping \( \alpha_{12} \) parameter constant and equal to 0.3. With them, activity coefficient (\( \gamma \)) can be obtained, in order to predict the vapor–liquid equilibrium.

Figure 2 shows the results in terms of \( x_1 - P \) (SEBS mass fraction versus pressure) curves at constant temperature. As it can be seen, due to the fact that cyclopentane has the higher vapor pressure at 293.15 K, the decreasing pressure is more important in the mixture of SEBS with this solvent than in the cases of the mixtures with the other two ones.

For solvent (1)–water (3) systems, NRTL binary interaction parameters obtained from the LLE-Aspen Plus database48 were used. This database has been demonstrated to be appropriate for predicting both liquid–liquid and liquid–vapor equilibrium for water–hydrocarbon mixtures when comparing prediction with experimental solubility data obtained from the literature.49,50 Table 4 shows the NRTL binary interaction parameters of this database, being, \( \alpha_{12} \) a parameter equal to 0.2. With these parameters, the predicted solubility of water in cyclohexane at 298.15 K is \( 1.127 \times 10^{-8} \) w/w, the literature value being equal to \( 1.001 \times 10^{-8} \) w/w.49 The predicted inverse solubility (cyclohexane in water) result is \( 5.44 \times 10^{-8} \) w/w, which shows a very small deviation in comparison with literature \((5.5 \times 10^{-8} \) w/w).50

Finally, a polymer–water mixture was studied considering that they are both completely immiscible with each other and obtaining NRTL parameters accordingly. This is a good approach because the polymer can be considered as an aliphatic chain of infinite length and it is demonstrated experimentally49,50 that an increasing chain length gives a decreasing water solubility due to the decreasing polarity.

3.4. Simulation Results. This process can be assimilated to an adiabatic liquid–liquid–vapor equilibrium flash stage, without considering mass transfer phenomena. For this purpose, a FLASH3 model was employed; this model represents a single liquid–liquid–vapor equilibrium stage, so the three outlet streams are in equilibrium.

The flow diagram is shown in Figure 3. In this process, a mixture of SEBS and solvent (cyclohexane, cyclopentane, or methylcyclohexane) is fed to the FLASH3 block (SEBS + sol stream), along with steam (steam stream). The block has three outlet streams: vapour, which contains steam, along with the evaporated solvent, polymer, which contains the organic phase (SEBS with solvent left), and aqueous, which contains mainly the liquid water.

To compare the behavior of the solvents, three simulations were done with Aspen Plus. The conditions specified for the FLASH3 model were 160 kPa of pressure and a duty equal to zero (adiabatic equipment).

In such processes, the temperature is controlled by varying the amount of steam introduced in the stripping stage.5,51 To simulate this situation, a design specification was included in the FLASH3 block which calculates the necessary amount of steam to reach a temperature specification of 368.15 K in the block. Typical conditions of the stripping process are 160 kPa pressure and 368.15 K temperature.5 A greater separation could be achieved by decreasing the pressure, but in this case, the amount of necessary steam would be much greater.

Table 3. \( P-x \) Obtained from the Polymer Solvent Interaction Parameter

<table>
<thead>
<tr>
<th>SEBS–methylcyclohexane</th>
<th>SEBS–cyclohexane</th>
<th>SEBS–cyclopentane</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \phi_2 )</td>
<td>( P ) (kPa)</td>
<td>( x_2 )</td>
</tr>
<tr>
<td>0</td>
<td>4.8</td>
<td>0</td>
</tr>
<tr>
<td>0.20</td>
<td>4.8</td>
<td>0.236</td>
</tr>
<tr>
<td>0.40</td>
<td>4.6</td>
<td>0.451</td>
</tr>
<tr>
<td>0.60</td>
<td>4.1</td>
<td>0.649</td>
</tr>
<tr>
<td>0.80</td>
<td>2.9</td>
<td>0.832</td>
</tr>
<tr>
<td>0.90</td>
<td>1.7</td>
<td>0.917</td>
</tr>
<tr>
<td>0.99</td>
<td>0.2</td>
<td>0.992</td>
</tr>
</tbody>
</table>

Figure 2. Experimental (dot) and regressed data for SEBS–solvent mixtures at 293.15 K.

Table 4. NRTL Binary Interaction Parameters for Water–Solvent Mixtures

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Water–cyclohexane</th>
<th>Water–cyclopentane</th>
<th>Water–methylcyclohexane</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a_{ij} )</td>
<td>( b_{ij} )</td>
<td>( c_{ij} )</td>
<td>( b_{ij} )</td>
</tr>
<tr>
<td>7.4</td>
<td>-9.7</td>
<td>0.2</td>
<td>13.1</td>
</tr>
</tbody>
</table>

Figure 3. Flow diagram of a single stripping stage.
In all simulations, the conditions of the SEBS + sol stream were kept constant at 298.15 K, 200 kPa, 15% mass of SEBS, and 3 kg/s mass flow. The conditions of the other inlet stream (steam) were in all cases saturated vapor at 1000 kPa pressure.

The temperatures and pressures of all streams are summarized in Table 5. Table 6 shows the overall flow rate, water, and solvent flow rates and solvent (w1), polymer (w2), and water (w3) mass fractions in all the streams of Figure 3.

Comparing the composition of the polymeric phase (polymer stream) in the three simulations, it can be seen that, when using cyclohexane and methylcyclohexane, the mass fraction of solvent in this phase (0.0503 for cyclohexane and 0.130 for methylcyclohexane) is higher than when using cyclopentane (3.11 × 10⁻⁵); this is due to the highest volatility of cyclopentane compared with the other two solvents.

The difference between cyclohexane and methylcyclohexane can be explained according the same vapor pressure phenomena (cyclohexane has slightly high volatility). This reasoning is valid because the Flory–Huggins parameter of SEBS with the three solvents is quite similar, so when obtaining equilibrium P–xy data from the Flory–Huggins parameter and from pure vapor pressure, the main difference between one data set and the others is due to vapor pressure.

From these studies, it can be seen that, with cyclopentane as solvent, the purity of the final product is really high but involves a large amount of steam consumption to reach the temperature specification. With methylcyclohexane as solvent, the amount of steam is smaller, but the purity of the final product is very low. With cyclohexane as solvent, the steam consumption is just 9% higher than in the case of methylcyclohexane, but the purity of the final product is 95%, which is an adequate value, and really higher when comparing with the final purity using methylcyclohexane as solvent.

### Table 5. Temperature and Pressure of All Streams, in a Single Stage Process

<table>
<thead>
<tr>
<th>Stream</th>
<th>SEBS + sol</th>
<th>steam</th>
<th>vapor</th>
<th>polymer</th>
<th>aqueous</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (kPa)</td>
<td>100</td>
<td>1000</td>
<td>160</td>
<td>160</td>
<td>160</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>298.15</td>
<td>453.1</td>
<td>368.15</td>
<td>368.15</td>
<td>368.15</td>
</tr>
</tbody>
</table>

### Table 6. Simulation Results with All Solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Cyclohexane</th>
<th>Methylcyclohexane</th>
<th>Cyclopentane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam flow (kg/h)</td>
<td>4011</td>
<td>3669</td>
<td>4682</td>
</tr>
<tr>
<td>Water flow (kg/h)</td>
<td>2194</td>
<td>1841</td>
<td>2665</td>
</tr>
<tr>
<td>w1</td>
<td>0.806</td>
<td>0.829</td>
<td>0.775</td>
</tr>
<tr>
<td>w2</td>
<td>0.053</td>
<td>0.130</td>
<td>0.050</td>
</tr>
<tr>
<td>w3</td>
<td>1.58 × 10⁻⁵</td>
<td>2.04 × 10⁻⁵</td>
<td>3.11 × 10⁻⁵</td>
</tr>
</tbody>
</table>

In this section, a first step to develop a more complex simulation model has been described. With this model, it is possible to estimate the amount of each compound that remains in the polymer phase, in order to assess the quality product specifications.

### 3.5. Influence of Additives in the Separation Process

As previously said, styrene–butadiene rubbers (SBR) are mainly produced by a block polymerization process of monomers, catalyzed with alkyl lithium compounds in the presence of an organic solvent (i.e., cyclohexane). In a strongly nonpolar media, the organometallic catalyst molecules tend to form oligomers by association with other ones. Therefore, a polar modifier is added to the polymerization reactor in order to stabilize the alkyl lithium compounds, improving the efficiency of the catalyst. Polar modifiers can also change other polymer properties as their microstructure and glass transition temperature.

Generally, these process additives have a hydrocarbon chain and a polar domain, which perform chelant activity with the catalyst. A wide variety of compounds have been tried as polar modifiers, being ethers and amines the most widely studied.

This point is focused in the behavior of these compounds in a SEBS rubber–solvent separation step by means of a steam stripping process. For several additives, some experimental equilibrium data of their binary mixtures with cyclohexane (solvent), polymer, and water have been obtained; later on, these data have been fitted to the NRTL equation, and the binary parameters obtained have been used in a simulation model. For another group of additives, the Aspen Plus database includes the values of the NRTL interaction parameters of the binary mixtures of these additives with both water and cyclohexane, so it is not necessary to obtain experimental data.

The NRTL binary interaction parameters either experimentally determined or taken from the Aspen Plus database were introduced in a steam stripping simulation model developed with Aspen Plus. For this purpose, a two-stage model was employed, according the diagram which appears in Figure 4. In this model, a stream from the polymerization reactor, consisting of polymer and solvent goes to the steam stripping process. Later on, the condensed bottom water is separated from the final polymer by sedimentation, whereas top steam carrying the solvent is condensed and two liquid phases (aqueous and organic) are separated by decantation.

The objective is to determine the distribution of each compound in the different outlet streams of the process. The additives from whom experimental vapor–liquid or liquid–liquid equilibrium data were obtained are ethyl tetrahydrofurfuryl ether (ETE), triethylene glycol dimethylether (TEGDME), and really higher when comparing with the final purity using methylcyclohexane as solvent.

---

**Figure 4. Two-stage steam stripping process scheme.**

In this section, a first step to develop a more complex simulation model has been described. With this model, it is possible to estimate the amount of each compound that remains in the polymer phase, in order to assess the quality product specifications.
N-N'-N'-tetramethylethylene diamine (TMEDA), tetrahydrofurfurylamine (THFAM), and 4-ethylmorpholine (4EMORF). The additives whose binary interaction parameters were taken from the Aspen Plus database are 1,4-dioxane (DIOX), ethyleneglycol dimethylether (EGDME), and tetrahydrofuran (THF). The source of the binary interaction parameters of the NRTL model for each binary mixture is shown in Table 7.

The vapor-liquid experiments were performed using the isobaric ebullometric technique in the range of low additive compositions (the typical compositions used in the industrial process are below 1000 ppm). The apparatus has been previously used for similar purposes. In this equipment, entirely made of glass, both the liquid and vapor phases are continuously recirculated, in order to provide mixing of the phases and to ensure that equilibrium is established. The vapor condenser is connected to a constant-pressure system controlled by a Cartesian manostat, so the pressure could be kept constant at 101.32 kPa, with an accuracy of ±0.1 kPa. The equilibrium temperatures were measured with a certified thermocouple type J with an accuracy of ±0.1 °C. Both samples were analyzed with a Perkin-Elmer A/S gas chromatograph with a flame ionization detector. In this apparatus 4EMORF–cyclohexane, 4EMORF–water, THFAM–cyclohexane, THFAM–water, TEGDME–cyclohexane, TEGDME–water, TMEDA–cyclohexane, and TMEDA–water equilibria were measured. For the mixture of the heaviest additive studied (TEGDME, the one with the lowest composition in the vapor phase) with cyclohexane, the uncertainties (in terms of standard deviation/average of the mole fraction) of the VLE data were 7.8% for the vapor phase composition and 3.8% for the liquid phase composition.

<table>
<thead>
<tr>
<th>Additive systems</th>
<th>Additive-cyclohexane systems</th>
</tr>
</thead>
<tbody>
<tr>
<td>a)</td>
<td>b)</td>
</tr>
<tr>
<td>THF</td>
<td>DIOX</td>
</tr>
<tr>
<td>Chex</td>
<td>lit</td>
</tr>
<tr>
<td>water</td>
<td>lit</td>
</tr>
</tbody>
</table>

Table 7. Source of the NRTL Binary Interaction Parameters of Each Mixture

*a* All of these were also estimated using the UNIFAC method (exp parameters obtained from experimental fitting, lit Aspen Plus database).

Figure 5. $y-x$ equilibrium curves predicted with the binary parameters obtained from the Aspen Plus database and those predicted with the UNIFAC method at 101.32 kPa. (a) THF–water. (b) THF–cyclohexane. (c) EGDME–water. (d) EGDME–cyclohexane. (e) DIOX–water. (f) DIOX–cyclohexane.
Figure 6. VLE and LLE experimental and predicted data of heavy polar modifiers, at 101.32 kPa. (a) TMEDA–water. (b) TMEDA–cyclohexane. (c) 4EMORF–water. (d) 4EMORF–cyclohexane. (e) ETE–water. (f) THFAM–water. (g) THFAM–cyclohexane. (h) TEGDME–water. (i) TEGDME–cyclohexane.
model, along with the equilibrium curve predicted by the binary parameters obtained by fitting experimental data to NRTL into the ebullometer and then vacuum was set. The temperature and a vacuum controller. The pure substances were introduced ebullometer previously described, by setting a vacuum pump pressure of the system, the experiments were carried out in the organic carbon (TOC) measurements (Shimazdu VCSH).

A sample of the aqueous phase was taken and analyzed by total water were added until two phases were observed. Later on, a additions of small quantities of ETE over a great amount of tank in a thermostatically controlled bath is needed. Thus, systems. If two liquid phases are present, then a simple stirred not adequate because it can be only used in homogeneous additive

dispersion method. It can be observed that the higher the contribution method.57 It can be seen that the results are very different when using UNIFAC parameters instead of the ones obtained by fitting experimental data.

For synthetic rubber processing, it is recommended to get experimental VLE or LLE data of mixtures in which heavy polar additives are involved. UNIFAC properly predicts the behavior of these substances only when they are light enough. Additive−water pair interactions seem to have a bigger influence than additive−cyclohexane ones over the simulation results. This could be due to hydrogen bonding that it is not taken into account by the UNIFAC model.

4. Conclusions

In this paper we present a new procedure to model the equilibrium-staged operations for synthetic SEBS rubber processing, with Aspen Plus.

Concerning polymer−solvent mixtures, from the results it can be seen that it is necessary to carry out experimental measurements in the overall polymer composition range.

The results show that all the solvents have a good behavior in a one stage steam stripping process at moderate temperature and pressure conditions, cyclohexane being the most suitable. Employing this solvent in the stripping process, the amount of polymer in the organic phase is high enough and the steam consumption is acceptable.

With this modeling procedure, the behavior of some additives in the separation process can be also analyzed.

But, the most important conclusion is that, by applying the methodology described in the paper, it is possible to estimate the amount of a component which remains with the polymer after the separation, in order to assess quality specifications to employ it, for example, as a recipient for drinks. Another application could be optimizing the conditions (temperature, pressure, and amount of vapor) of the operation. This is the first step to develop a more complex model of the polymer−solvent steam stripping separation process.

Nomenclature

\( a_i \) = activity of component \( i \)

\( a_{oi} \) = first NRTL binary interaction parameter of components \( i \) and \( j \)

\( b_{ij} \) = temperature-dependent NRTL binary interaction parameter of components \( i \) and \( j \)

\( B_{v2} \) = solvent second term of the virial EOS, cm³/mol

\( c \) = concentration of polymer solution, g/dL

\( f_{li} \) = standard fugacity of the i component, Pa

\( F \) = carrier gas flow rate, cm³/s

\( j \) = retention volume correction factor

\( K_H \) = Huggins coefficient

\( K_K \) = Kraemer coefficient

\( M_i \) = i average molecular weight

\( N_A \) = Avogadro number

\( P \) = pressure, Pa

\( p \) = vapor pressure of polymer solution, Pa

Table 8. Simulation Results of the Stripping Process for Heavy Polar Modifiers in Terms of Separation Degree (Additive Mass Flow in Each Outlet Stream Divided by Additive Mass Flow in the Inlet Stream), As a Function of the NRTL Parameters Employed for Both Additive−Cyclohexane and Additive−Water Mixtures

<table>
<thead>
<tr>
<th>additive</th>
<th>binary mixtures</th>
<th>outlet streams</th>
<th>final solvent</th>
<th>top water</th>
<th>bottom water</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMEDA</td>
<td>exp exp</td>
<td>0.6</td>
<td>80.8</td>
<td>11.1</td>
<td>7.5</td>
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<tr>
<td>exp UNIFAC</td>
<td>0.9</td>
<td>37.9</td>
<td>23.9</td>
<td>37.3</td>
<td></td>
</tr>
<tr>
<td>UNIFAC</td>
<td>exp UNIFAC</td>
<td>0.6</td>
<td>85.3</td>
<td>6.7</td>
<td>7.4</td>
</tr>
<tr>
<td>exp UNIFAC</td>
<td>0.9</td>
<td>45.0</td>
<td>16.8</td>
<td>37.2</td>
<td></td>
</tr>
<tr>
<td>4EMORF</td>
<td>exp exp</td>
<td>0.8</td>
<td>79.4</td>
<td>8.6</td>
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</tr>
<tr>
<td>exp UNIFAC</td>
<td>1.0</td>
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<td>11.5</td>
<td>38.6</td>
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</tr>
<tr>
<td>UNIFAC</td>
<td>Exp</td>
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<td>75.2</td>
<td>13.2</td>
<td>10.8</td>
</tr>
<tr>
<td>UNIFAC</td>
<td>UNIFAC</td>
<td>1.0</td>
<td>44.1</td>
<td>16.4</td>
<td>38.4</td>
</tr>
<tr>
<td>ETE</td>
<td>exp exp</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>exp UNIFAC</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td></td>
</tr>
<tr>
<td>UNIFAC</td>
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<td>87.6</td>
<td>11.4</td>
<td>88.0</td>
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<tr>
<td>exp UNIFAC</td>
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<td>2.5</td>
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<tr>
<td>THFAM</td>
<td>exp exp</td>
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<td>19.5</td>
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<td>11.8</td>
<td>77.3</td>
</tr>
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<td>12.0</td>
<td>67.7</td>
</tr>
<tr>
<td>TEGDME</td>
<td>exp exp</td>
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<td>0.5</td>
<td>89.3</td>
</tr>
<tr>
<td>exp UNIFAC</td>
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<td>16.9</td>
<td>0.3</td>
<td>75.9</td>
<td></td>
</tr>
<tr>
<td>UNIFAC</td>
<td>exp UNIFAC</td>
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<td>UNIFAC</td>
<td>6.9</td>
<td>15.7</td>
<td>1.8</td>
<td>75.7</td>
</tr>
</tbody>
</table>

*Exp parameters obtained from experimental fitting; UNIFAC parameters obtained with the UNIFAC group contribution method.

In order to model the VLE, a valid vapor pressure equation is needed. Parameters for Antoine expression of water, cyclohexane, ETE, TEGDME, TMEDA, THF, DIOX, and EGDME are available in commercial databases (in this work the Aspen Plus database was used). However, THFAM and 4EMORF vapor pressure experiments were performed. To vary the pressure of the system, the experiments were carried out in the ebullometer previously described, by setting a vacuum pump and a vacuum controller. The pure substances were introduced into the ebullometer and then vacuum was set. The temperature of both vapor and liquid was measured after 30 min.

For liquid−liquid experiments, the ebullometric technique is not adequate because it can be only used in homogeneous systems. If two liquid phases are present, then a simple stirred tank in a thermostatically controlled bath is needed. Thus, ETE−water LLE measurements were performed. Consecutive additions of small quantities of ETE over a great amount of water were added until two phases were observed. Later on, a sample of the aqueous phase was taken and analyzed by total organic carbon (TOC) measurements (Shimazdu VCSH).

Figure 5 shows the \( y-x \) equilibrium curve predicted with the binary parameters taken from the Aspen Plus database, along with the equilibrium curve predicted by UNIFAC group contribution method. It can be observed that the higher the boiling point of the additive, the worse the UNIFAC predictions.

Figure 6 shows the \( y-x \) equilibrium curve predicted with the binary parameters obtained by fitting experimental data to NRTL model, along with the equilibrium curve predicted by the UNIFAC group contribution method. It can be seen that additive−water mixtures are even worse predicted than additive−cyclohexane ones. Therefore, it is necessary to obtain experimental data of VLE or LLE to get a reliable thermodynamic model, when working with heavy polar modifiers.

The NRTL binary interaction parameters of polymer−additive mixtures were obtained following the same procedure described in section 3.3 with the polymer−solvent interaction parameter determined by means of eq 1.2, with the values of the solubility parameter of both polymer (experimentally determined) and solvent (taken from literature).

Concerning simulation results, Table 8 quantifies the distribution of the heavy polar modifiers, from whom experimental data have been obtained, in the different streams of the process, as a function of the NRTL parameters employed (experimental fitting or UNIFAC predictions). The results are shown in terms of separation degree (mass flow of additive in the stream/mass flow of additive in the inlet stream times 100). As it can be seen, the results are very different when using UNIFAC parameters instead of the ones obtained by fitting experimental data.

Concerning simulation results, Table 8 quantifies the distribution of the heavy polar modifiers, from whom experimental data have been obtained, in the different streams of the process, as a function of the NRTL parameters employed (experimental fitting or UNIFAC predictions). The results are shown in terms of separation degree (mass flow of additive in the stream/mass flow of additive in the inlet stream times 100). As it can be seen, the results are very different when using UNIFAC parameters instead of the ones obtained by fitting experimental data.
\( P_i^s \) = vapour pressure of component \( i \), Pa  
\( r = \) molar volume of polymer to molar volume of solvent ratio  
\( R = \) ideal gas constant  
\( \tau = \) flow time of the polymer solution, s  
\( \tau_0 = \) flow time of the pure solvent, s  
\( \tau_m = \) inert component retention time, s  
\( \tau_t = \) solvent retention time, s  
\( T = \) temperature, K  
\( V_p = \) retention volume, cm³/g  
\( V_{mol} = \) molar volume of \( i \), cm³/mol  
\( W = \) amount of polymer packed in the column, g  
\( x = \) liquid phase mass fraction  
\( y = \) vapour phase mass fraction  

**Greek Symbols**  
\( \alpha_{ij} = \) nonrandomness parameter of NRTL equation  
\( \delta_i = \) solubility parameter of component \( i \), MPa⁰.¹⁵  
\( \delta_i^* = \) solubility parameter of component \( i \) obtained in infinite dilution conditions MPa⁰.¹⁵  
\( \Delta H_1 = \) solvent heat of solution, kJ/mol  
\( \Delta_{mix} H = \) solvent partial molar heat of mixing, kJ/mol  
\( \Delta_{vap} H_i = \) solvent heat of vaporization, kJ/mol  
\( \chi = \) polymer–solvent interaction parameter  
\( \zeta = \) enthalpic contribution of polymer–solvent interaction parameter  
\( \zeta_s = \) entropic contribution of polymer–solvent interaction parameter  
\( \Omega^* = \) infinite dilution activity coefficient of \( i \)  
\( \rho_i = \) density of \( i \), g/cm³  
\( [\eta] = \) intrinsic viscosity, dL/g  
\( \eta_i = \) relative viscosity  
\( \eta_0 = \) specific viscosity  
\( \zeta_s = \) entropic contribution of polymer–solvent interaction parameter  
\( \zeta_{in} = \) enthalpic contribution of polymer–solvent interaction parameter  
\( [\eta]_\theta = \) intrinsic viscosity at theta conditions, dL/g  
\( \Phi_0 = \) universal viscosity constant, 1/mol  
\( \nu_i = \) partial specific volume of \( i \)  
\( \tau_0 = \) NRTL binary interaction parameter of components \( i \) and \( j \)  

**Subscripts**  
1, 2, 3 = solvent, polymer, water  
4EMORF = 4-ethylmorpholine  
DIOX = 1,4-dioxane  
EGDME = ethylene glycol dimethylether  
EOS = equation of state  
ETE = ethyl tetrahydrofuranyl ether  
IGC = inverse gas chromatography  
IV = intrinsic viscosity  
LF = lattice fluid  
LLE = liquid–liquid equilibrium  
SAFT = statistical associated fluid theory  
SBR = styrene–butadiene rubber  
SBS = styrene–butadiene–styrene rubber  
SEBS = styrene–ethylene–butadiene rubber  
TEGDME = triethylene glycol dimethylether  
THF = tetrahydrofuran  
THFAM = tetrahydrofuranylamine  
TMEDA = N,N,N′,N′′-tetramethyethylene diamine  
VLE = vapor–liquid equilibrium

**Literature Cited**


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