Improving styrene polymerization through a commercial simulation software

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Abstract

The polymerization and impregnation of Expandable Polystyrene (EPS) requires very long batch cycles when compared to other polymerization processes. Understanding the polymerization processes could be facilitated using mathematical modeling and simulation. However, the use of commercial simulators is still underexplored because of some limitations presented since these types of software tend to be more a generalist tool. Thus, the objective of this work is improving the simulation of styrene polymerization using the Aspen Plus® commercial software modified with user-implemented correlations. The free-radical polymerization kinetics was implemented, and experimental data from the literature were used to evaluate the performance of the simulation, using the standard correlation for the gel effect and with the proposed modified correlation, which was implemented by user-model routines, considering the incorporation of the impregnating agent (*n*-pentane) in the polymeric matrix. The implemented user models for the gel effect enabled a better representation of the experimental data, with minor errors from the literature. The prediction average errors of the modified model for the gel effect are five times less than for the other models. Besides the mean-square deviation is of the order of 10 times smaller in relation to the models without the gel effect and the standard. Thus, the user-model correlations implemented in the Aspen Plus® commercial software can enable the investigation of process variables that would hardly be investigated experimentally, being a versatile tool for the study of expandable polystyrene synthesis process.

**Keywords**: Suspension polymerization, polystyrene, blowing agent, user-model routines.

* 1. Introduction

Polystyrene is a thermoplastic widely used worldwide and has been extensively studied in recent decades. Achieving improvements in polymerization processes is necessary and, in this sense, the study of new initiators and suspending agents – often expensive and difficult to obtain – is recurrent (Ambrogi et al., 2016). With the same aim, the manipulation of process variables and parameters is an economical alternative for optimizing such polymeric systems, bringing considerable reductions in batch cycles without harm or changes to the properties of the produced polymer, and without the need to introduce new reagents to the original formulation (Scorah et al., 2006). Experimental studies have brought great advances in the field of suspension polymerization with the advent of multifunctional initiators and new reactor designs and configurations specific to the process. Recent literature has also presented certain alternatives in implementing the continuous production of polymers via suspension polymerization, a process traditionally conducted in batch cycles, thus providing the technical and economic advantages inherent to continuous processes (Lobry et al., 2015).

Despite the published advances regarding suspension polymerization, there are few studies that specifically deal with the impregnation of the polymer matrix using a blowing agent. Furthermore, these few existing works do not present the investigation of parameters regarding the kinetics and properties of the final product in the presence of the expanding agent. The vast majority of works concerning the impregnation of polystyrene are experimental, however, simulation is of paramount importance in the field of polymerization processes, providing low-cost support in decision-making and in the development of new production routes (Almeida et al., 2008).

The particle size distribution in the production of polystyrene via suspension polymerization was studied by Machado et al. (2000). From the population balance equation, a model was proposed to describe the evolution of the particle size distribution, and the model was validated with experimental data. The modeling and simulation of the styrene free-radical polymerization in semi-batch was investigated by Curteanu (2003). The study led to conclusions regarding the intermediate addition of initiator as a method of controlling polymer properties. Almeida et al. (2008) developed a model for predicting the stationary and dynamic behavior of a continuous styrene polymerization process. The main parameters were estimated from data of an industrial plant. To study the physical properties of polystyrene, Srivastava and Ghosh (2010) developed a molecular dynamics model for the bulk polymerization of styrene. In this work, studies were carried out regarding the glass transition of polystyrene.

More recently, Vieira and Lona (2016) used new kinetic modeling and simulations to analyze the effect of temperature on the properties of polystyrene obtained by atom transfer radical polymerization, providing a tool for analysis and optimization of this process. Currently, there are several commercial simulators that already have implemented mathematical models validated and consolidated in the literature, such as Aspen Polymers®, which provides kinetic polymerization models associated with a vast database of common chemical species in polymerization processes of greatest commercial interest. However, the mathematical models implemented in these commercial applications are comprehensive and generic, and to overcome this, many of them allow modifications to be added to study specific cases, using user routines.

The investigation of polymerization processes using commercial simulators as tools has recently gained prominence. Lesage et al. (2012) identified reaction kinetic parameters in the Aspen Custom Modeler® with the dynamic simulation of a CSTR for propylene polymerization in the gas phase to produce polypropylene, an extremely versatile thermoplastic polymer (Drummond et al., 2019). Funai et al. (2014) used Aspen Polymers® to validate a model of the Nylon® hydrolytic polymerization process in a semi-batch reactor. Kusolsongtawee and Bumroongsri (2017) presented a mathematical model of a fluidized bed polymerization reactor applied in the production of low-density polyethylene using the Aspen Custom Modeler® software to obtain polymer characteristics and investigate the flow behavior in the reactor.

In this context, the present work aims to improve styrene polymerization using Aspen Polymers® commercial software. For this purpose, the standard model of the software was modified with innovative user-model routines to consider the effect of the blowing agent in the polymerization process. After implementing the EPS impregnation model so that the effect of the blowing agent is considered, the simulation will be validated using experimental data published in the literature.

* 1. Methodology
		1. Simulation design

The styrene suspension polymerization process was modeled in the Aspen Polymers® software using the batch reactor unit, as shown in the Figure 1. Benzoyl peroxide (BPO) (initiator), styrene (dispersed phase, monomer), water (continuous phase), and *n*-pentane (blowing agent) were added. The polymerization reactions occur in the organic liquid phase (drops of monomer/polymer) (Machado et al., 2007). The software's standard kinetic mechanism is implemented based on free-radical polymerization. The set of reactions included chain initiation, propagation reaction, at least one termination step and chain transfer or inhibition reaction to produce the dead polymer, with these reactions occurring simultaneously during polymerization. The parameters required for calculating the reaction rate constants, the pre-exponential factors and the activation energies were taken from Villalobos et al. (1991), Choi et al. (1988), and Mahabadi and O’Driscoll (1977). For predicting physical properties, the thermodynamic model of liquid activity coefficient of polymeric system (POLYNRTL) was used. The physicochemical properties of the polymer were calculated using Van Krevelen's group contribution method.



**Figure 1**. Block diagram of the simulation assembled in Aspen Polymers®.

* + - 1. Modifications implemented to address the gel and glass effects

The standard gel effect correlations of Aspen Polymers® are empirical models adjusted from experimental data. These refer only to the gel effect in polymerization reactions without impregnation and do not represent the glass effect. However, *n*-pentane (*n*P5) is the EPS solvent and rubberizes the polymer matrix. It is known that the addition of a solvent to the system alters the global free volume, and this alteration has a direct influence on the polymerization kinetics leading to different behaviors regarding the gel and glass effects. Therefore, in the present work, the correlations expressed in Equation (1) and Equation (2) were incorporated in Aspen Polymers® through user-model routines written in programming language, as these are based on the theory of free volume. By using user correlations, the model captures the influence of the impregnating agent on the polymeric matrix. The Equation (1) was specified to modify the termination rate constant (*k*tc) due to the gel effect, and Equation (2) to adjust the propagation rate constant (*k*p) due to the glass effect.

|  |  |
| --- | --- |
| $$k\_{tc}\left(X\right)=k\_{tc0}∙\left(1+δ∙\left[P\right]\left(X\right)\right)∙\left(\frac{M\_{wcr}}{M\_{w}\left(X\right)}\right)^{N}∙exp\left[-A∙\left(\frac{1}{VF\left(X\right)}-\frac{1}{VF\_{cr1}}\right)\right]$$ | (1) |
| $$k\_{p}\left(X\right)=k\_{p0}∙exp\left[-B∙\left(\frac{1}{VF\left(X\right)}-\frac{1}{VF\_{cr2}}\right)\right]$$ | (2) |

* + 1. Experimental validation

To validate the mathematical model and the modifications proposed in the simulator, part of the work presented by Villalobos et al. (1993) was replicated. The authors presented a study on the effect of adding the impregnating agent in several stages of the experimental reaction. Suspension polymerization and impregnation of polystyrene with *n*-pentane were carried out in a 3.2 L reactor with Rushton stirrer type at 350 rpm at 90 °C and an initiator concentration (BPO) of 0.01 mol·L-1 of styrene. The suspending agent was tricalcium phosphate (TCP) at a concentration of 7.5 g·L-1.

To validate the proposed modified model, the mean-squared error (MSE) was calculated to measure the agreement between simulated data and experimental values obtained from Villalobos et al. (1991), as shown by Equation (3).

|  |  |
| --- | --- |
| $$MSE=\frac{1}{n}\sum\_{i=1}^{n}\left(Y\_{i}-\hat{Y}\_{i}\right)^{2}$$ | (3) |

The mean-absolute percentage error (MAPE) was also calculated, according to Equation (4), as the average between the errors of the simulated points.

|  |  |
| --- | --- |
| $$MAPE=\frac{1}{n}\sum\_{i=1}^{n}\left(\frac{Y\_{i}-\hat{Y}\_{i}}{Y\_{i}}\right)∙100$$ | (4) |

* 1. Results and discussions

To evaluate the simulation built with the modified model, part of the work by Villalobos et al. (1993) was reproduced. Figure 2 shows the comparison between the experimental data for 7.5% *n*P5 with the simulations (i) without gel effect correlation, (ii) with the software's default correlation, and (iii) with the model's implemented user correlation.



**Figure 2**. Comparison between the simulated and the literature data obtained.

Table 1 shows the statistical treatment data for the simulations produced without correlation for the gel effect and with the correlation implemented in the Aspen Polymers® software. In the work by Tefera et al. (1997), which deals with the selection of mathematical models, four models for polymerization via free-radicals were evaluated, and all presented errors of up to 10% in the simulations used to estimate the parameters. Therefore, according to this criterion, the model with the implemented user correlation was the only one that presented MAPE lower than 10%, considered acceptable.

**Table 1**. Comparative statistical analysis between the simulated models.

|  |  |  |  |
| --- | --- | --- | --- |
| **Time (min)** | **(i) Without gel** | **(ii) Standard model** | **(iii) Modified model** |
| ***MSE*** | ***MAPE*** | ***MSE*** | ***MAPE*** | ***MSE*** | ***MAPE*** |
| **60** | 0.000006 | 2.8% | 0.000002 | 1.6% | 0.0000061 | 2.8% |
| **120** | 0.000359 | 10.3% | 0.000002 | 0.8% | 0.0003187 | 9.7% |
| **180** | 0.001454 | 12.1% | 0.001020 | 10.1% | 0.0003959 | 6.3% |
| **240** | 0.004892 | 16.4% | 0.006790 | 19.4% | 0.0003887 | 4.6% |
| **270** | 0.016587 | 24.0% | 0.014713 | 22.6% | 0.0016061 | 7.5% |
| **300** | 0.022769 | 25.3% | 0.039578 | 33.3% | 0.0003719 | 3.2% |
| **330** | 0.038509 | 29.9% | 0.037961 | 29.7% | 0.0018003 | 6.5% |
| **390** | 0.069667 | 35.3% | 0.032371 | 24.0% | 0.0042173 | 8.7% |
| **420** | 0.072480 | 35.3% | 0.035132 | 24.6% | 0.0022415 | 6.2% |
| **480** | 0.084570 | 36.4% | 0.030752 | 21.9% | 0.0005177 | 2.8% |
|  | **0.031129** | **22.8%** | **0.019832** | **18.8%** | **0.0010786** | **5.8%** |

Therefore, it can be observed that the implemented user-models for the gel effect in the commercial simulator enable a good representation of the experimental data, where the modified model with the user correlation proposed being that with the minor error about the experimental data. The average error of the predictions of the modified model for the gel effect is four times less than for the other models; besides the mean-square deviation is of the order of 10 times smaller in relation to the models without gel effect and standard. Thus, the user-model correlations implemented in the commercial software enables to investigate process variables that would hardly be investigated experimentally, being a versatile tool for the study of expandable polystyrene synthesis process.

* 1. Conclusions

The simulation of the EPS polymerization and impregnation process was built using the Aspen Polymers® software. The software's standard model was modified with user-model routines, so the simulation was able to represent the effect of the blowing agent on the process dynamics. The simulation with the modified model was validated using experimental data obtained from the literature. Errors of up to 10% proved the representativeness of the model. A comparison was made between the modified model, the software standard and those without gel effect, demonstrating that the simulation was an efficient tool. Therefore, this commercial simulator with modified correlation can be a versatile and efficient tool for studying EPS synthesis processes. The application allowed the mathematical model to be adapted to this specific application, which makes future investigations and manipulations of process variables less costly.

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