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MATHEMATICAL SIMULATION OF THE STYRENE-BUTADIENE RUBBER'S PRODUCTION IN THE CASCADE OF REACTORS BY THE MONTE CARLO METHOD

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ABSTRACT

In the paper, the algorithm of modeling of continuous low-temperature free-radical butadiene-styrene copolymerization process in emulsion based on the Monte Carlo method is offered. This process is the cornerstone of industrial production butadiene - styrene synthetic rubber, which is the most widespread large-capacity rubber of general purpose. Modeling is carried out taking into account residence-time distribution of particles in system that gives the chance to research the process proceeding in the battery of consistently connected polymerization reactors. At the same time, each polymerization reactor represents the continuous stirred tank reactor. The constructed model allows to research molecular-weight and viscous characteristics of the formed copolymerization product, to predict the weight content of butadiene and styrene in copolymer, and to carry out calculation of molecular-weight distribution of the received product at any moment of conducting process.

Key words: Copolymerization, Butadiene, Styrene, Monte Carlo method, Residence-time distribution, Molecular weight distribution.

INTRODUCTION

Synthetic rubbers constitute extensive group of petrochemical products and are polymers that can be processed into the rubber during vulcanization. Currently, it produced wide range of synthetic rubbers differing on application properties that depends on used monomers: butadiene, styrene, isoprene, etc. Their combination and method of conducting polymerization defines properties of the received product and it's function.

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Styrene-butadiene synthetic rubbers are one of the most widespread large-capacity synthetic rubbers of general purpose. Process of the low-temperature free-radical styrene-butadiene copolymerization in emulsion is the basis of the industrial production. Studying of this process becomes possible at creation of mathematical model. In turn, simulation will allow to predict properties and modify quality indicators of the received product that is an actual task today.

EXPERIMENTAL

Beforehand, it is necessary to write out the kinetic scheme of styrene-butadiene copolymerization process. Let us assume that reactivity of the active center of the growing chain is determined by the nature of the end unit. Then the kinetic scheme of the process consists of the following stages:

Initiator decay

$$\mathrm{I} \xrightarrow{\mathrm{k_d}} 2\mathrm{R},$$

Initiation of active centers

$$R + M^{\beta} \xrightarrow{k_{i\beta}} P^{\beta}_{A(\beta),B(\beta)},$$

Chain propagation

$$P^{\alpha}_{n,m} + M^{\beta} \xrightarrow{k_{p\alpha\beta}} P^{\beta}_{n+A(\beta),m+B(\beta)},$$

Chain transfer

$$P^{\boldsymbol{\alpha}}_{n,m} + S \xrightarrow{k_{reg\boldsymbol{\alpha}}} Q_{n,m} + R,$$

Chain termination by disproportionation

$$P^{\alpha}_{n,m} + P^{\beta}_{r,q} \xrightarrow{k_{d\alpha\beta}} Q_{n,m} + Q_{r,q},$$

Chain termination by recombination

$$P^{\alpha}_{n,m} + P^{\beta}_{r,q} \xrightarrow{k_{r\alpha\beta}} Q_{n+r,m+q},$$

Here $\alpha,\beta=\overline{1,2}$; M^1 and M^2 are the monomers of the first and second type; $P^{\alpha}_{n,m}$ and $Q_{n,m}$ are the active and inactive polymer chains with length $m+n$, comprising m units of the M^1 monomer and n units of the M^2 monomer; $k_i, k_p, k_{reg}, k_d, k_r$ are the reaction rate constants of initiation, chain propagation, transfer, disproportionation and recombination elementary stages, respectively; $A(\beta)=\{1, \text{if } \beta=1; \text{else } 0\}$; $B(\beta)=\{1, \text{if } \beta=2; \text{else } 0\}$[1].

Earlier, Mustafina et al.[2] was considered algorithm of simulation batch process of styrene-butadiene copolymerization, based on the Monte Carlo method. But the production of styrene-butadiene rubber is a continuous process that occurs in several reactors, combined in cascade. It is related to an increase in productivity, stable indicators of the received product and economic efficiency.

At the modeling of periodic polymerization process, all particles of system throughout the simulation time are in the same reactor. In this case, each reaction is characterized by time of modeling, which is calculated according to the formula[3]:

$$\Delta t=\frac{1}{R_{sum}}\ln\left(\frac{1}{r_p}\right) \qquad \ldots(1)$$

Here R_{sum} – the sum of the rates of possible elementary reactions of the kinetic scheme of copolymerization process and r_p – random number generated in the interval [0,1]. But in the case of the continuous process worth talking about some average residence time as a random variable, which is characterized by a probability distribution function[4].

According to the literature[5,6], the probability that a particle spends time from t to $t+dt$ in the current reactor is $p(t)dt$, but since considered polymerizers are continuous stirred tank reactors, for them value $p(t)$ is calculated by the formula:

$$p(t)=\left(\frac{n}{\tau}\right)^n\frac{t^{n-1}}{(n-1)!}e^{-\frac{nt}{\tau}} \qquad \ldots(2)$$

Here n – count of reactors in the system, τ – average residence time of the reaction mixture in a single reactor (h).

Fig. 1 shows the residence time distribution of the particles of the reaction mixture in the cascade of 12 polymerizers by volume $V = 10.8\ m^3$ with volumetric flow rate C_f =

9.5982 m^3/h. In this case, average residence time of reaction mixture in polymerizer equals 1.125 hour.

Thus, for modeling a continuous polymerization process, which takes place in the cascade of continuous stirred tank reactors, each particle of the system (molecule or macromolecule) must be characterized by the residence time in the reactor, which is determined using the distribution (2). It is necessary to choose the subinterval *dt*, to the sum of the probabilities for each variant of the residence time for the time interval from *0* to t_{max} was equal to one.

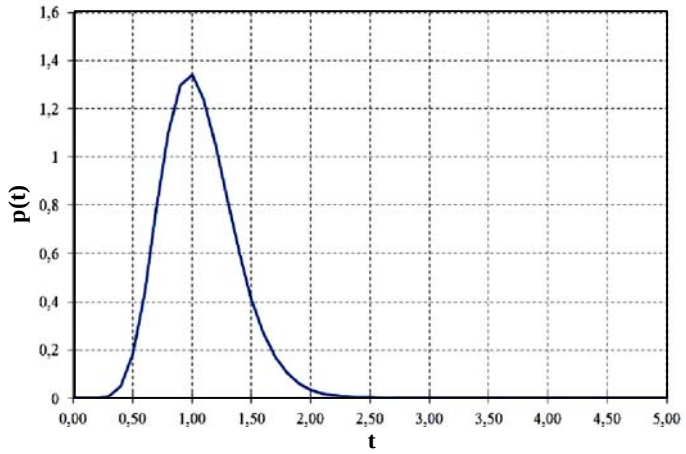

Fig. 1: Residence time distribution in the cascade of 12 reactors

After that, it is necessary to generate random number $r_p \in [0,1]$ and choose the value of the serial number f, to the inequality:

$$\sum_{i=1}^{f-1} p((f-1)\cdot dt) < r_p < \sum_{i=1}^{f} p(f\cdot dt) \qquad \ldots(3)$$

Consequently, as a result of the simulation to the selected particle corresponds the residence time $f \cdot dt$. Then the process for which corresponds average residence time of the reaction mixture 1.125 hrs, such time interval is the interval from 0 to 5 hrs in 0.1 hrs.

Algorithm of modeling of continuous styrene-butadiene copolymerization process can be represented as a sequence of steps, taking into consideration that every hour in the first reactor is added the portion of the reaction mixture, corresponding to the recipe of rubber's production.

(1). We define the volume and characteristics of the feed portion of the reaction mixture, beforehand calculating the number of molecules of each component of the mixture: butadiene M^1, styrene M^2, initiator I and chain transfer agent S. It is also necessary to set technological parameters of process: reactor volume – V, count of reactors – m, volumetric flow rate C_f and serial numbers of polymerizers, in which are supplied chain transfer agent.

(2). Transform the experimental rate constant of elementary reactions to stochastic rate constants according to the following equations:

$\widetilde{k} = k$ for first order reactions;

$\widetilde{k} = \frac{k}{V \cdot N_A}$ for bimolecular reactions between different species (N_A is the Avogadro's number).

(3). Then calculate the reaction rate for every reaction R_i of kinetic scheme for the reactor with a serial number j according to the equation:

$$R_i = \widetilde{k}_i \cdot X_A \cdot X_B$$

where $\widetilde{k}_i$ - is the rate constant of the i-th reaction in which reagents A and B participate; X_A, X_B are the numbers of reagent's molecules.

The total reaction rate is then calculated as the summation of the individual reaction rates:

$$R_{sum} = R_1 + R_2 + \ldots + R_n$$

where n - is the number of elementary reactions forming kinetic scheme of the copolymerization process.

(4). Then the probability of any reaction taking place at a given time is calculated by the following equation:

$$p_i = \frac{R_i}{R_{sum}}, \quad i = 1..n$$

It is apparent that $p_1 + p_2 + \ldots + p_n = 1$.

(5). Generate a random number r_p uniformly distributed between 0 and 1 and pick up such value of serial number f of the reaction in kinetic scheme that the inequality took place:

$$\sum_{i=1}^{f-1} p_i < r < \sum_{i=1}^{f} p_i .$$

Consequently, reaction under an index f has to result from an imitating choice $(f = \overline{1,n})$.

(6). Calculate the time of modeling of selected reaction Δt_j according to the formula (1) and for each formed or terminated particle as a result of step 5, calculate the time of escaping from the current reactor t_{ex}:

$$t_{ex} = t + t_{dm}$$

here t – current time of modeling process from the beginning, t_{dm} – the residence time of the molecules in the current reactor, calculated according to the distribution (2).

(7). Repeat the procedure from step 3 to step 6 for each reactor of the cascade $(j = \overline{1,m})$.

(8). Change the total time of modeling, increasing it on the minimum time of reaction's modeling among all polymerizers:

$$t = t + \min_{j=1,m} \Delta t_j .$$

(9). Transfer to the next reactor all molecules than the time of escaping smaller the total time of process course for each reactor in the cascade. After that, go back to step 3.

(10). Continuing the reasoning and repeating the steps from 3 to 9, build the complete process simulation scheme.

The developed model makes it possible to study the characteristics of styrene-butadiene copolymer. The information on the state of the resulting product may be obtained as the output from each reactor and in achieving the required conversion values.

RESULTS AND DISCUSSION

On the basis of the developed algorithm, the software package was created in the integrated development programming environment Visual Studio in the C# and Visual C++ languages. It allows to carry out computing experiments of simulation of styrene-butadiene copolymerization process in the cascade of continuous stirred tank reactor. The software package makes it possible to solve the direct problem of determining the molecular weight and viscosity characteristics of the resulting product and investigate compositional heterogeneity of formed copolymer.

During the computational experiment was investigated styrene-butadiene copolymerization process with the following parameters of the process and the production's recipe of portion of the reaction mixture[7]:

- The load on the cascade by monomers: 3.0 t/h (butadiene – 70 w.p., styrene – 30 w.p.);
- Dosage of initiator (pinane hydroperoxide): 0.048 w.p.;
- Dosage of chain-transfer agent (tertiary dodecyl mercaptan): 0.26 w.p. – 1st point (1 polymerizer), 0.02 w.p. – 2nd point (7 polymerizer);
- Ratio water/monomers = 220.8 / 100;
- Working volume of polymerizer V = 10.8 m^3;
- Count of polymerizers: 12;
- Volumetric flow rate C_f = 10.1432 m^3/h.
- Residence time of the reaction mixture in polymerizer $\theta = V / C_f$ = 1.065 h.

Table 1: Data of production experiment

Number of reactor	Conversion of monomers (%)	Intrinsic viscosity, (dl/g)	Content of bound styrene (%)
4	42.0	1.13	20.8
5	60.5	1.23	21.5
9	76.6	1.52	23.3
12	82.0	1.74	24.7

Fig. 2-4 shows the behavior of conversion's curve and dependencies of the intrinsic viscosity on reactor's serial number and conversion of monomers. The results were obtained on the basis of the simulation 15 and 30 hrs of the process and are consistent with the experimental data.

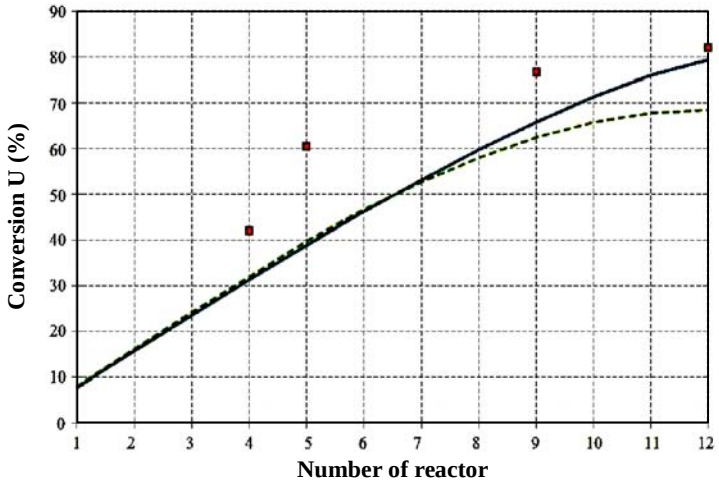

Fig. 2: The dependence of the calculated (lines) and experimental (points) conversion's values from reactor's number in the cascade: the dotted line – 15 hrs, the solid line – 30 hrs conducting of the process

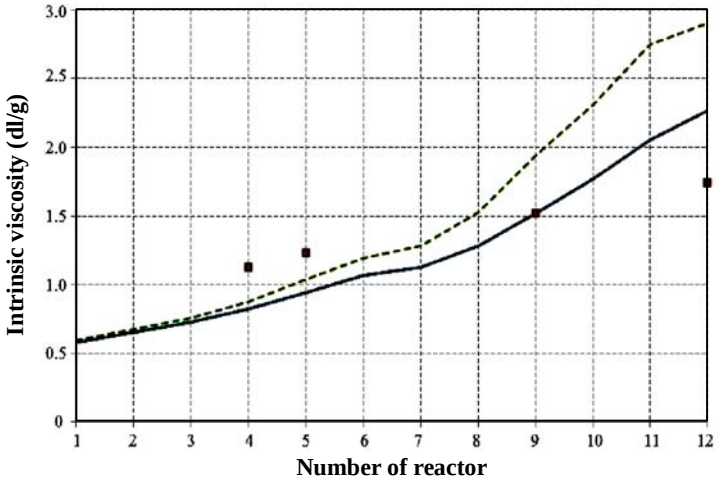

Fig. 3: The dependence of the calculated (lines) and experimental (points) intrinsic viscosity's values from reactor's number in the cascade: the dotted line – 15 hrs, the solid line – 30 hrs conducting of the process

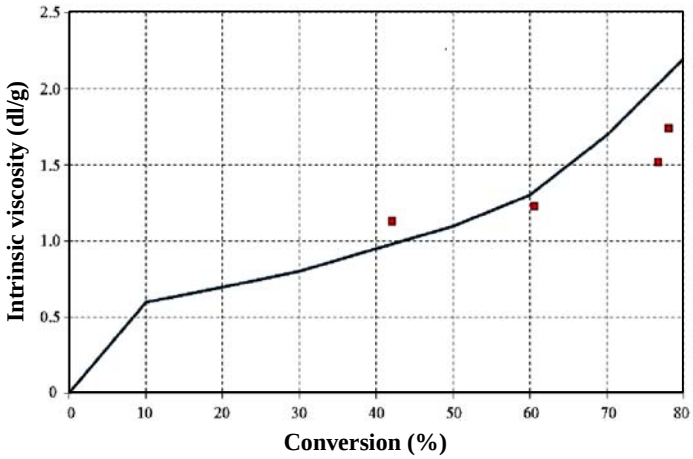

Fig. 4: The dependence of the calculated (lines) and experimental (points) intrinsic viscosity's values from conversion of monomers

The behavior of the curve of intrinsic viscosity is associated with the consumption of chain transfer agent (Fig. 5). The main part of chain transfer agent (more than half portion) is consumed in the first and second reactors, than significantly slows the growth of intrinsic viscosity. Further addition of chain transfer agent in the second point in the 7^{th} reactor promotes repeated slowing of the rapid growth of the product's characteristics. In the future, chain transfer agent is completely consumed, then corresponds to a sharp increase of molecular weight and thus, the intrinsic viscosity of the copolymer.

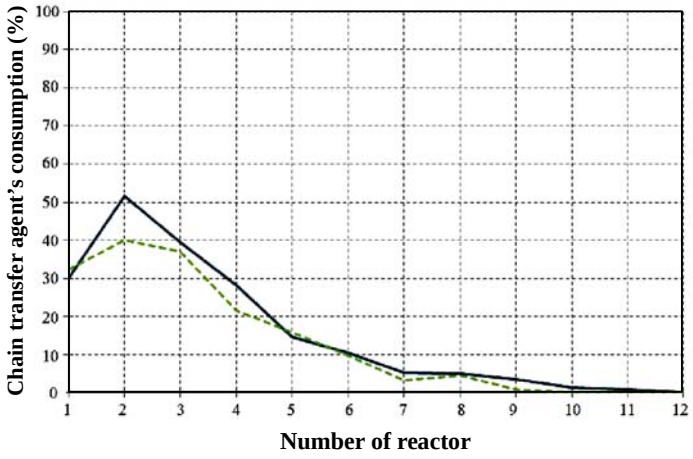

Fig. 5: Changing chain transfer agent's concentration in the reactors: the dotted line – 15 hrs, the solid line – 30 hrs conducting of the process

The nature of changes of the molecular weight of formed styrene-butadiene copolymer displays the dependence the polydispersity index from polymerizer's serial number in the cascade (Fig. 6). Following the results of modeling of 30 hrs of conducting process the value of polydispersity index changes from 2 units in the first reactor to 5.5 units in the last reactor of the cascade that corresponds to standard measures of styrene-butadiene rubber. The point of inflection of the curve characterizing dependence of polydispersity index from serial number of reactor are associated with the fractional addition of the chain transfer agent.

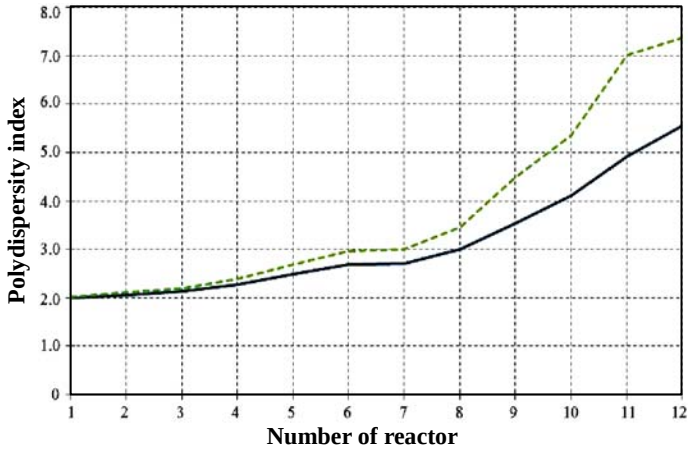

Fig. 6: Changing polydispersity index of the formed copolymer depending on the number of reactor: the dotted line – 15 hrs, the solid line – 30 hrs conducting of the process

Changing the weight composition of the formed styrene-butadiene copolymer is displayed in Fig. 7: butadiene content varies from 80% in the first reactor to 72% to the last reactor of the cascade, styrene - from 20% to 28%, respectively.

Fig. 8 displays a differential curve of the molecular weight distribution (MWD), which shows the ratio of macromolecules of different molecular weights in a sample of the copolymer. In the simulation of copolymerization process by the Monte Carlo method for constructing MWD, it is necessary to make numerical fractionating by weight of macromolecules of formed copolymer and calculate the weight fraction of each copolymer fraction. MWD of styrene-butadiene copolymer with an increase of volume of the reaction mixture reproduces the behavior of the Schulz-Flory model distribution, that takes into account chain termination a result of the interaction with chain transfer agent.

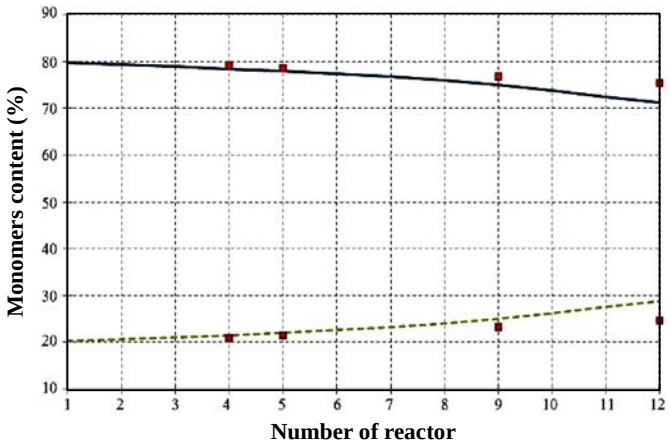

Fig. 7: Dependence of weight content of butadiene (solid line) and styrene (dotted line) from number of the reactor (points - experimental data)

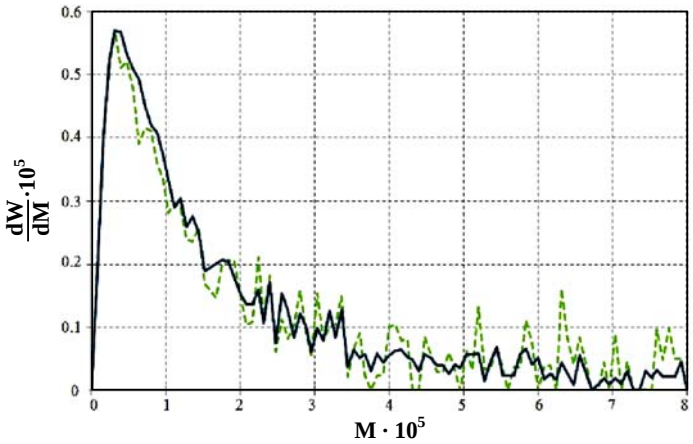

Fig. 8: Differential curve of the molecular weight distribution of the styrene-butadiene copolymer

CONCLUSION

Thus, the proposed simulation algorithm based on Monte Carlo method, adequately describes the continuous process of styrene-butadiene copolymerization, which takes place in the cascade of continuous stirred tank reactors. For realization of the simulation process is taken into account the residence time distribution of the particles in the system. Obtained information as a result of simulation provides an opportunity to explore molecular weight and viscosity characteristics of the formed copolymerization product in the dynamics at constant loading of reaction mixture.

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