



RESEARCH OF TECHNOLOGICAL PROPERTIES OF THE STYRENE-BUTADIENE RUBBER BY THE METHOD OF MATHEMATICAL MODELING
INVESTIGACIÓN DE LAS PROPIEDADES TECNOLÓGICAS DEL CAUCHO DE ESTIRENO-BUTADIENO POR EL MÉTODO DE MODELADO MATEMÁTICO

Vladimir Anatolyevich Mikhailov,
Kazan Federal University. Russia

Olga Anatolievna Medvedeva,
Kazan Federal University. Russia
E-mail: (OAMedvedeva@kpfu.ru),
Tel.: (+7-937-614-18-54)

Sofya Ilshatovna Mustafina,
Bashkir State University. Russia

Tatiana Anatolyevna Mikhailova ,
Bashkir State University. Russia

Svetlana Anatolyevna Mustafina,
Bashkir State University. Russia

Konstantin Alexandrovich Kolyazov,
Moscow State University of Technology and Management. Russia

Fecha de recibido: 2019-12-22

Fecha de aceptado para publicación: 2019-12-29

Fecha de publicación: 2019-12-30

Abstract

On the basis of production experiments and analysis of literary sources, the influence of molecular weight on the resulting copolymers on one of the important technological parameters of synthetic rubber - Mooney viscosity was established. In this paper a dependence is obtained that relates the Mooney viscosity and the molecular weight characteristics of the resulting product – the number-average and weight-average molecular weight. Molecular weight characteristics were determined by the modeling of the copolymerization process on the basis of Monte Carlo method. In this paper, we obtained a dependence linking the molecular weight characteristics of the resulting styrene-butadiene copolymer and the Mooney viscosity of the rubber specimen. For the derivation, the logarithmic regression dependence was used, which was applied to the results of modeling the process of styrene-butadiene copolymerization carried out in accordance with the conduct of this process in an industrial environment. The deviation of the data obtained as a result of applying the derived dependence to the simulation results from the production was no more than 8%.

Keywords: copolymerization, styrene-butadiene rubber, Mooney viscosity, modeling, Monte Carlo method.



Resumen

Sobre la base de experimentos de producción y análisis de fuentes literarias, se estableció la influencia del peso molecular sobre los copolímeros resultantes en uno de los parámetros tecnológicos importantes del caucho sintético: la viscosidad de Mooney. En este trabajo se obtiene una dependencia que relaciona la viscosidad de Mooney y las características de peso molecular del producto resultante: el peso molecular promedio en número y promedio en peso. Las características del peso molecular se determinaron mediante el modelado del proceso de copolimerización sobre la base del método de Monte Carlo. En este artículo, obtuvimos una dependencia que vincula las características de peso molecular del copolímero de estireno-butadieno resultante y la viscosidad de Mooney de la muestra de caucho. Para la derivación, se utilizó la dependencia de regresión logarítmica, que se aplicó a los resultados del modelado del proceso de copolimerización de estireno-butadieno realizado de acuerdo con la conducción de este proceso en un entorno industrial. La desviación de los datos obtenidos como resultado de aplicar la dependencia derivada a los resultados de la simulación de la producción no fue más del 8%.

Palabras clave: copolimerización, caucho de estireno-butadieno, viscosidad Mooney, modelado, método Monte Carlo.

Introduction

Modern chemical industrial production is a complex chemical-technological system, which consists of a large number of devices and technological connections between them. When developing or upgrading a chemical-technological system, the task arises of creating highly efficient chemical production, which is to obtain products of a given quality in the required amount in the most economically viable way.

At present, in the domestic industry, technological processes proceeding through the mechanism of polymerization and copolymerization are widespread. In particular, such processes underlie the production of synthetic rubber and can occur in periodic and continuous mode. The periodic process is carried out for a certain period of time in one device and ends with the exhaustion of reagents. The continuous process is carried out with a constant flow of new reactants into the reactor and a constant withdrawal of interaction products from it, which ensures the continuation of reactions, which are characterized by a certain average residence time in the reactor.

Conducting field experiments to determine the quality characteristics of the resulting product under these conditions is costly and difficult to implement. Replacing real production experiments with computational ones opens up possibilities for solving a number of problems in the modernization of the industrial production of synthetic rubber. Synthetic copolymers of butadiene with styrene are among the most common synthetic rubber general purpose.

Materials and methods

One of the key technological indicators of rubber and rubber compounds is Mooney viscosity. This indicator characterizes the processability of the elastomer at the stages of



manufacturing rubber products. For rubbers, Mooney viscosity limits delimit membership in one or another quality group. Determination of Mooney viscosity of a rubber specimen in practice is carried out on the basis of rotational viscosimetry using a Mooney shear rotary viscometer.

The method consists in measuring the torque at a circular shear flow of material at a constant speed in a thin annular layer (Averko-Antonovich et al., 2002). The Mooney viscosity of the test material is characterized by the degree of resistance to rotation of a cylindrical metal rotor in the mass of an elastomeric material placed in a test chamber. The characteristics of the viscometer, the temperature of the test and the methods for determining Mooney viscosity are specified in the standard of the International Organization for Standardization ISO 289-1: 2015.

In relation to rubbers obtained by the method of emulsion polymerization, it is necessary to measure the Mooney viscosity of both the final product (commercial rubber) and latex polymer, which led to the development of various rapid methods for determining this indicator. One of them is the search for a fairly accurate and reproducible correlation between characteristics of one polymer and Mooney viscosity (Smith, 1956), which is an urgent task.

In the article by the authors Kramer O. and Good W.R. (Kramer et al., 1972) investigated the correlation of Mooney viscosity and the average molecular weight characteristics of the resulting copolymer — the average number of M_n and the weight-average M_w of molecular weights. The correlation coefficient of the considered quantities according to the article was equal to 0.93, which, according to the Cheddock scale, characterizes the relationship between the quantities as very high.

According to the article, using the least squares method, various types of regression dependencies were constructed, for which the coefficient of determination R^2 and the average relative deviation from the article data δ were calculated (table 1, figure 1), where y

– is the Mooney viscosity, $x = \sqrt{M_n M_w} \cdot 10^{-5}$.

Table 1. Characteristics of regression dependencies

Functional relation	Equation	$\delta, \%$	R^2
Linear	$y(x) = 82.8097 \cdot x - 49.9899$	11.93	0.9268
Cubic	$y(x) = -20.3170 \cdot x^3 - 87.8676 \cdot x^2 - 22.1264 \cdot x - 7.3484$	11.17	0.9278
Power	$y(x) = 30.8549 \cdot x^{2.0665}$	12.81	0.9387
Exponential	$y(x) = 6.5666 \cdot \exp(1.5493 \cdot x)$	16.67	0.8912
Logarithmic	$y(x) = 106.6866 \cdot \ln(x) - 33.6866$	12.45	0.9106

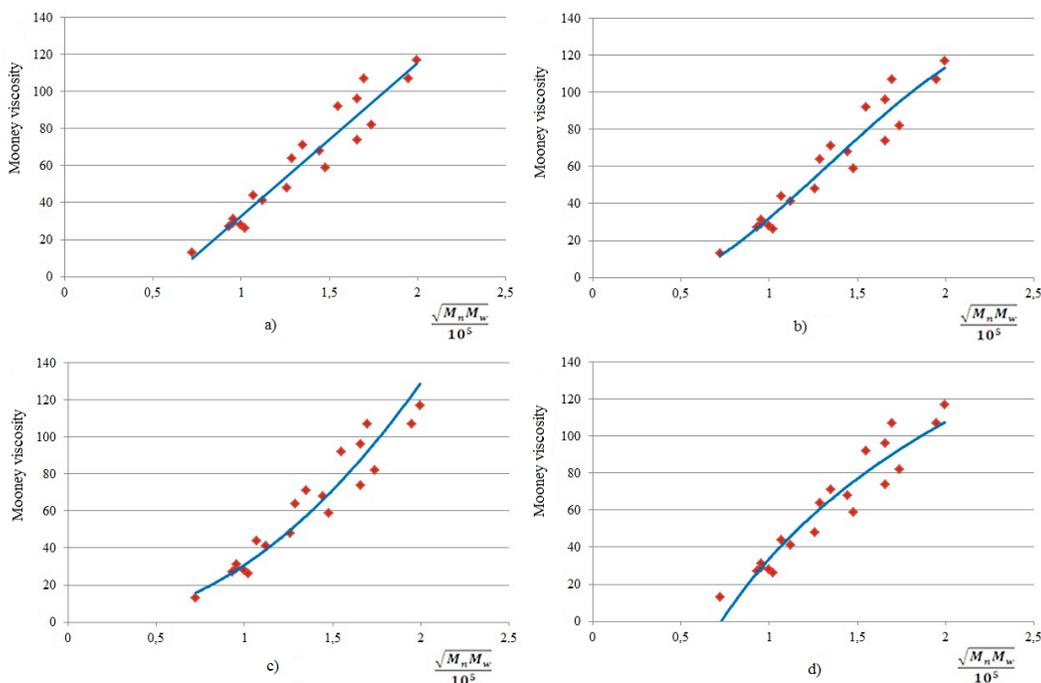


Figure 1. The dependence of the Mooney viscosity on the geometric mean number-average and weight-average molecular weights of the product: a) linear, b) cubic, c) power, d) logarithmic (line – regression dependence, points – experimental data)

As part of the industrial production of styrene-butadiene synthetic rubber, a series of experiments were carried out in a single batch reactor to study the Mooney viscosity depending on the dosage of the chain transfer agent (tert-dodecyl mercaptan) (Table 2) for the conversion of monomers equal to 70%. The experiments were carried out with the following compounding: the dosage of butadiene is 70 parts by weight, the dosage of styrene is 30 parts by weight, the dosage of initiator (pinane hydroperoxide) is 0.06 parts by weight, the water content to monomers is 210:100, the working volume of the reactor is 10.8 m^3 .

Table 2. The results of the experiment in the apparatus of periodic action

Dosage regulator, parts by weight	Mooney viscosity
0.1	138
0.12	135
0.14	128
0.15	125
0.16	110
0.175	80
0.2	55
0.21	55



However, carrying out field experiments to calculate the characteristics of the resulting product in industrial or laboratory conditions is associated with high costs of available resources. Due to the widespread using of computer technologies, the direction of computer modeling is actively developing, which occupies an intermediate position between analytical methods for studying phenomena or processes and field experiments.

Results and discussion

Previously, an approach to modeling polymerization processes based on the Monte Carlo method was described in (Mikhailova et al., 2016). The main idea of the approach is to simulate the processes occurring in each macromolecule of polymers at the level of particles. This allows you to exhaustively describe the detailed structure of macromolecules in terms of several probabilistic parameters. In this case, the model took into account that the process can proceed in a batch or continuous mode in one reactor or in a cascade of series-connected reactors (Mustafina et al., 2015, Mikhailova et al., 2016, Medvedeva et al., 2018). The using of the Monte Carlo method to simulate the process allows simulating the technology of the copolymerization process in dynamics, which allows you to observe the process and the characteristics of the resulting product in "real time".

As a result, based on the constructed mathematical model for the same monomer conversion and dosing options of the regulator, calculations of average molecular characteristics were carried out, which were converted into conventional Mooney viscosity values according to the presented in table. 1 regression dependencies (Figure 2). For each dependence, the mean relative deviation from the experimental data was calculated: linear - 13.35%, cubic - 12.69%, power - 16.58%, exponential - 31.72%, logarithmic - 15.54%.

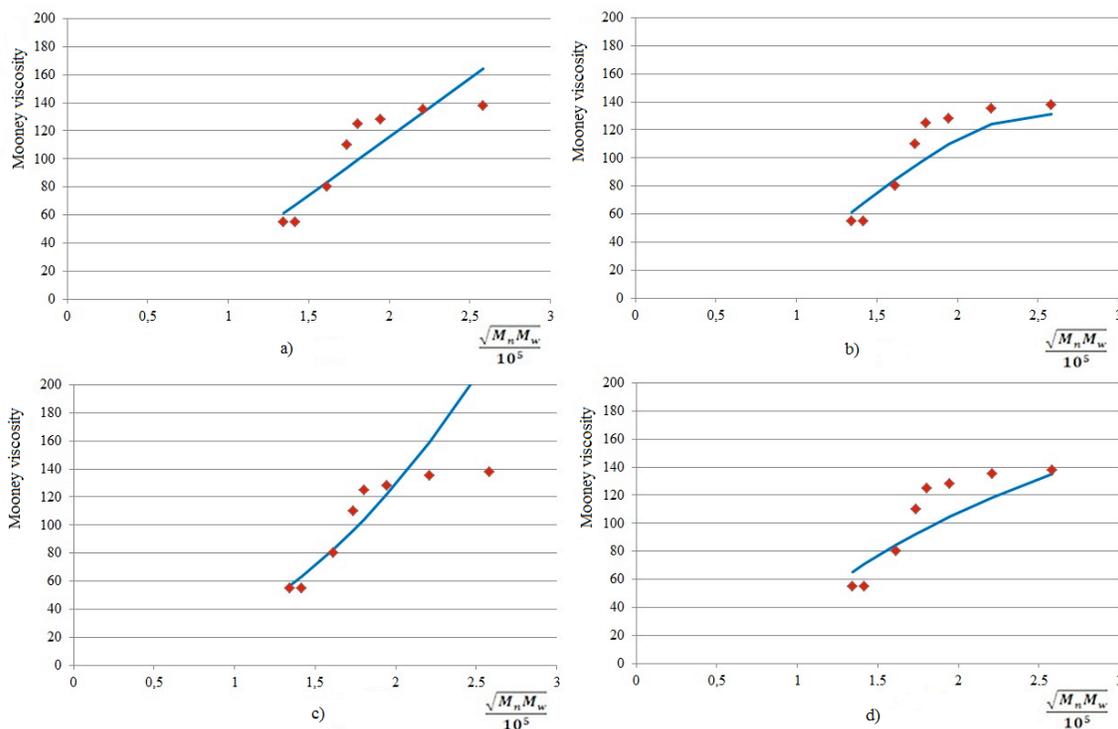


Figure 2. The dependence of the Mooney viscosity on the geometric mean number-average and weight-average molecular weights of the product obtained in the batch reactor: a)



linear, b) cubic, c) power, d) logarithmic (line - regression dependence, points - experimental data)

According to the results of the calculations, the best agreement with the experimental data was shown by linear, logarithmic and cubic dependences. Consider their behavior when $\sqrt{M_n M_w} \cdot 10^{-5} > 0$ (Figure 3).

The most adequate approximation to the experimental data gives a logarithmic dependence, since a linear relationship with increasing molecular weight demonstrates too rapid growth of viscosity. While cubic, despite the smallest values of the average relative deviation, shows a further decrease in Mooney viscosity with increasing molecular weight of the product, which is impossible.

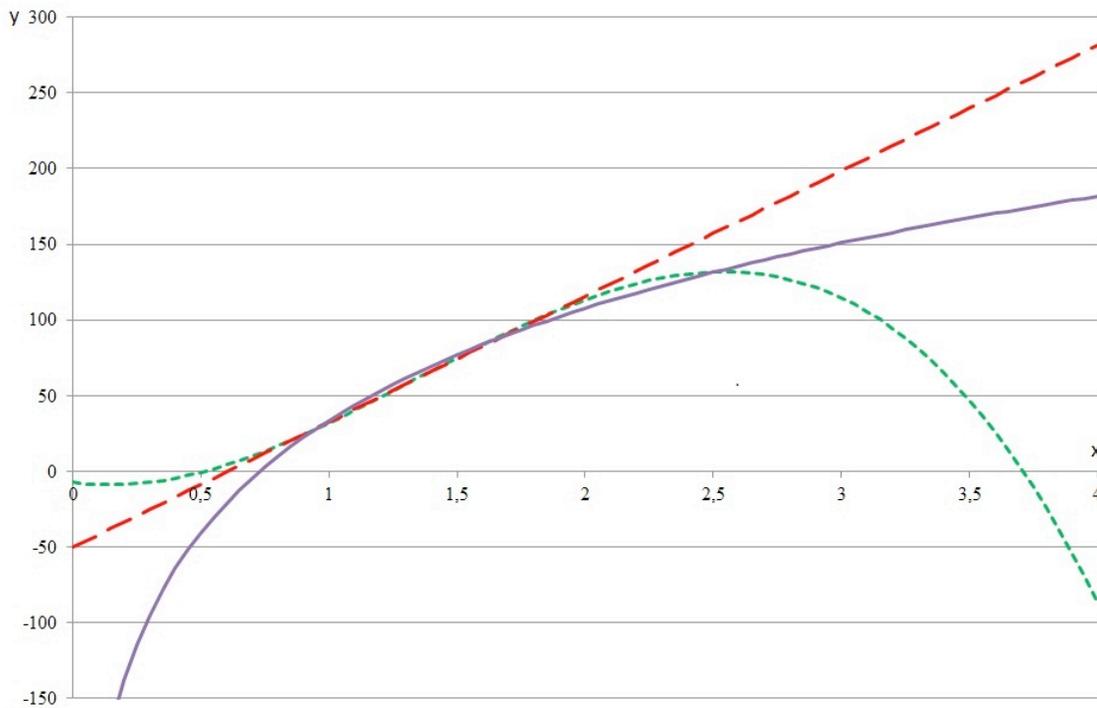


Figure 3. The dependence of the Mooney viscosity on the geometric mean number-average and mass-average molecular weights of the product: a) linear, b) cubic, c) power, d) logarithmic (line - regression dependence, points - experimental data)

Thus, the dependence of the Mooney viscosity on the averaged molecular characteristics of the styrene-butadiene copolymer is:

$$\eta_{Mooney} = 106.6866 \cdot \ln(\sqrt{M_n M_w} \cdot 10^{-5}) - 33.6866, \quad (1)$$

where $\sqrt{M_n M_w} \cdot 10^{-5} > 0.7292$.

The obtained dependence was tested on the results of a production experiment for the styrene-butadiene copolymerization, carried out in a cascade of continuous stirred tank reactors under the following conditions and recipe of production: the load on the battery



according to monomers is 3.5 tonnes per hour, the dosage of butadiene is 70 parts by weight, the dosage of styrene – 30 parts by weight, initiator dosage (pinane hydroperoxide) – 0.054 parts by weight, regulator dosage (tert-dodecyl mercaptan) – 0.125 parts by weight. (the first point is the first reactor), 0.027 parts by weight (the second point is the third reactor), 0.027 parts by weight (the third point is the sixth reactor), the content water: monomers is 220:100, the working volume of the reactor is 10.8 m³, the number of reactors is 11, the volumetric flow rate is 9.5982 m³ per hour, the residence time of the reaction mixture in one reactor is 1.125 hours. Data of experiments are presented in table 3.

A computational experiment based on Monte Carlo simulation was conducted for the presented recipe. To take into account the condition that the process is carried out in industry continuously, the residence time distribution of particles was used (a modified algorithm is described in paper (Medvedeva et al., 2018)). The values of the averaged molecular characteristics were obtained as a result of the simulation, for which the values of the characteristic viscosity and Mooney viscosity by applying the dependence (1).

Table 3. The results of an experiment in a cascade of continuous stirred tank reactors of with a three-point feed mode of the chain transfer agent

Reactor Number	Conversion of monomers, %	Intrinsic viscosity, dl/g	Mooney viscosity
1	5.5	0.73	-
2	14.1	-	-
3	23.7	0.86	-
4	29.6	1.28	-
5	32.0	1.28	-
6	41.8	-	-
7	51.3	1.66	38
8	55.8	1.70	-
9	64.0	2.24	79
10	69.0	2.31	-
11	70.4	2.42	87

In figures 4-5 show the obtained dependences of the intrinsic viscosity values on the reactor number and monomer conversion based on the results of 15 and 30 hours of the process.

The behavior of the intrinsic viscosity curve is associated with a change in the concentration of the chain transfer agent (figure 6). More than half of the charge of the chain transfer agent portion is consumed in the first and second reactors, which significantly slows down the increase in viscosity. Additionally, the chain transfer agent is fed to the second point in the third reactor, and to the third point in the sixth reactor, which corresponds to the slow nature of the change in the Mooney viscosity – from 37% in the third reactor to 11% in the seventh reactor. But in the remaining reactors of the cascade, the chain transfer agent particles are contained in a significantly smaller amount, which does



not interfere with the further increase in molecular weight, and, accordingly, the intrinsic viscosity of the copolymer

Figure 7 shows the obtained dependence of the calculated Mooney viscosity values on the number of the reactor in the cascade. The deviation of the calculated data from the experimental ones amounted to 8%.

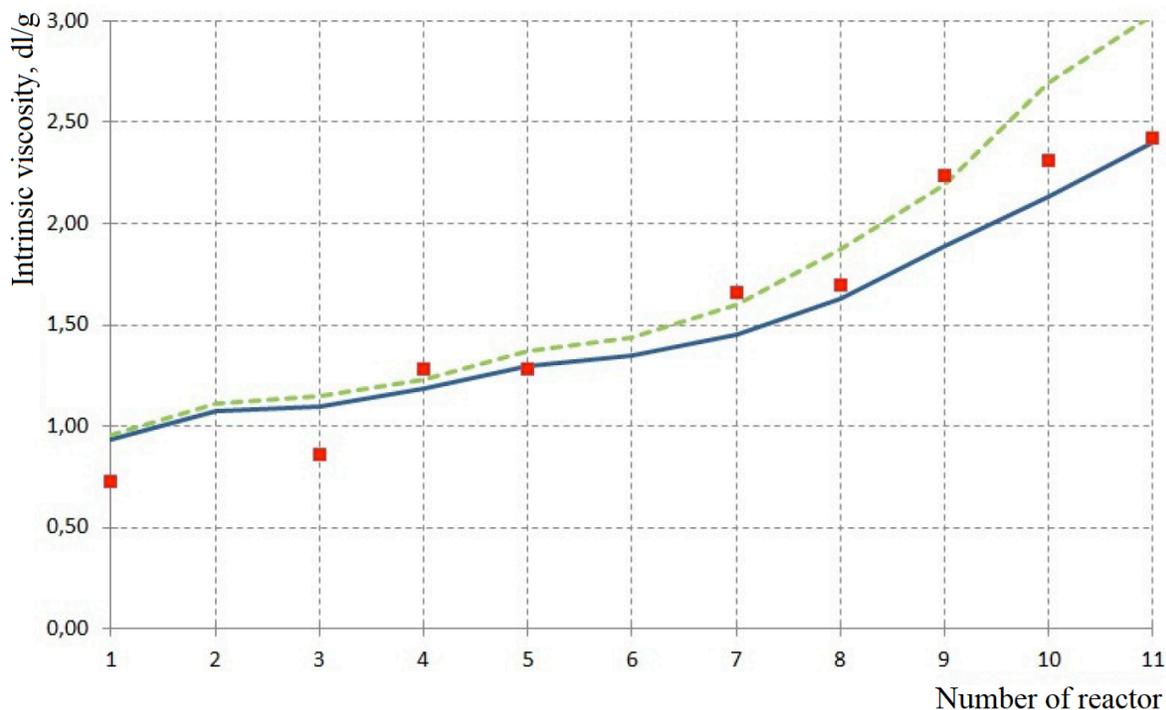


Figure 4. The dependence of the calculated and experimental values of the intrinsic viscosity on the number of the reactor in the cascade (dashed line – simulation results for 15 hours of the process, solid line – simulation results of 30 hours of the process, points – data from the production experiment)

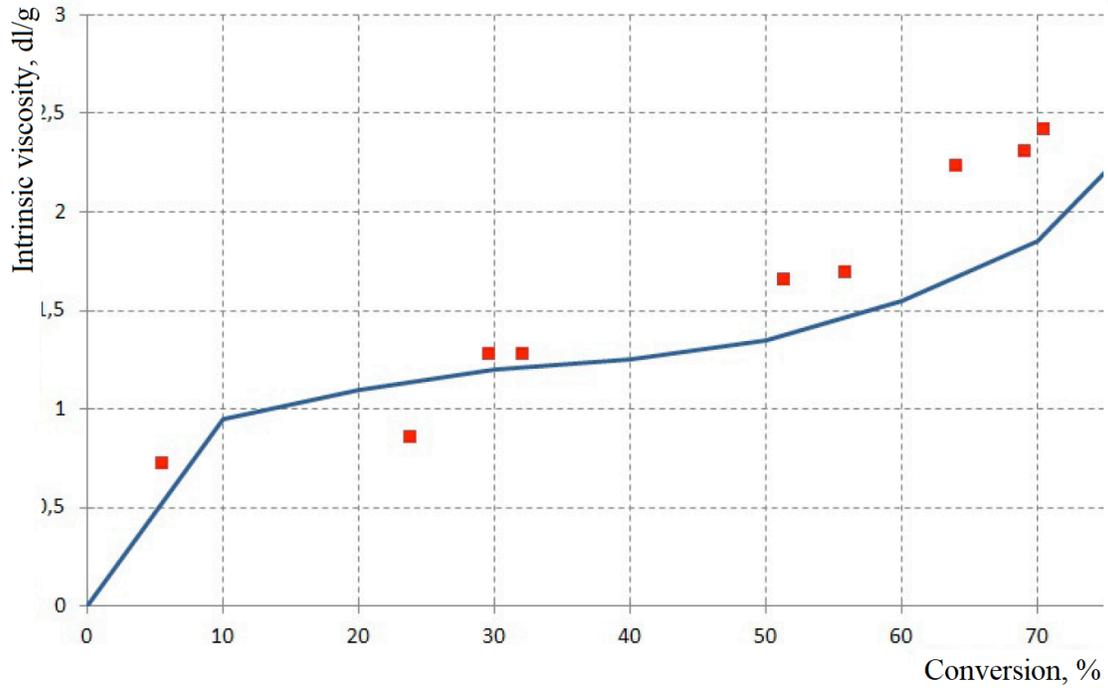


Figure 5. The dependence of the calculated and experimental values of the intrinsic viscosity on the conversion of monomers (dashed line – simulation results for 15 hours of the process, solid line – simulation results of 30 hours of the process, points – data from the production experiment)

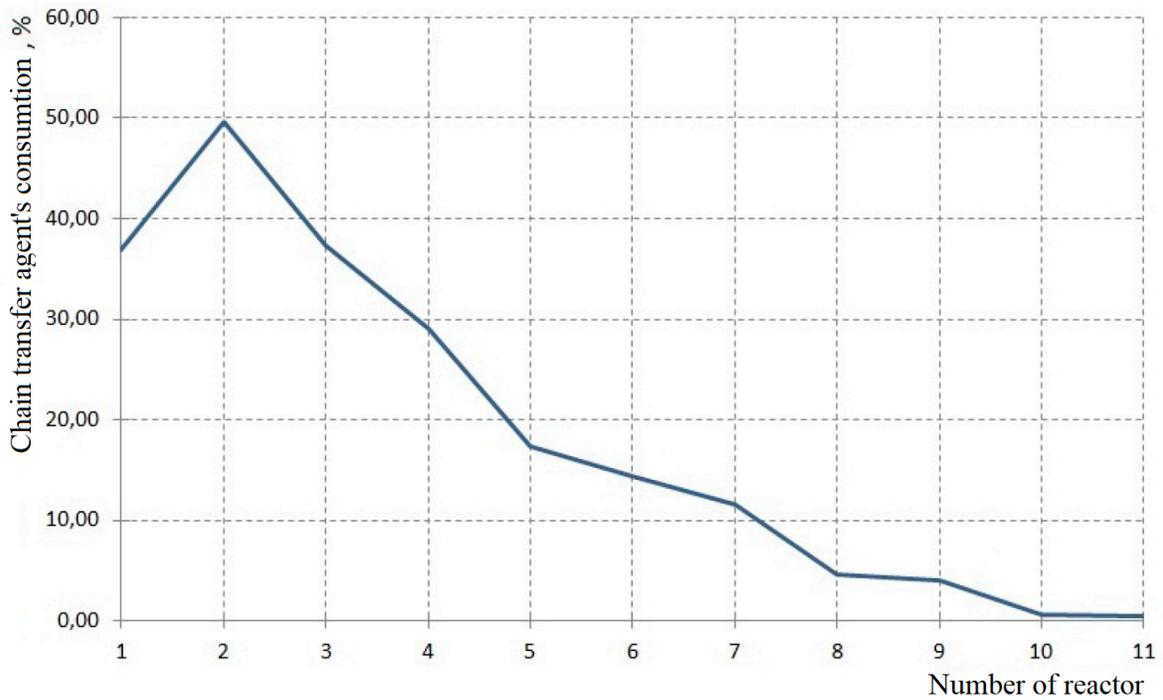


Figure 6. The dependence of the calculated values of the concentration of the chain transfer agent from the number of the reactor

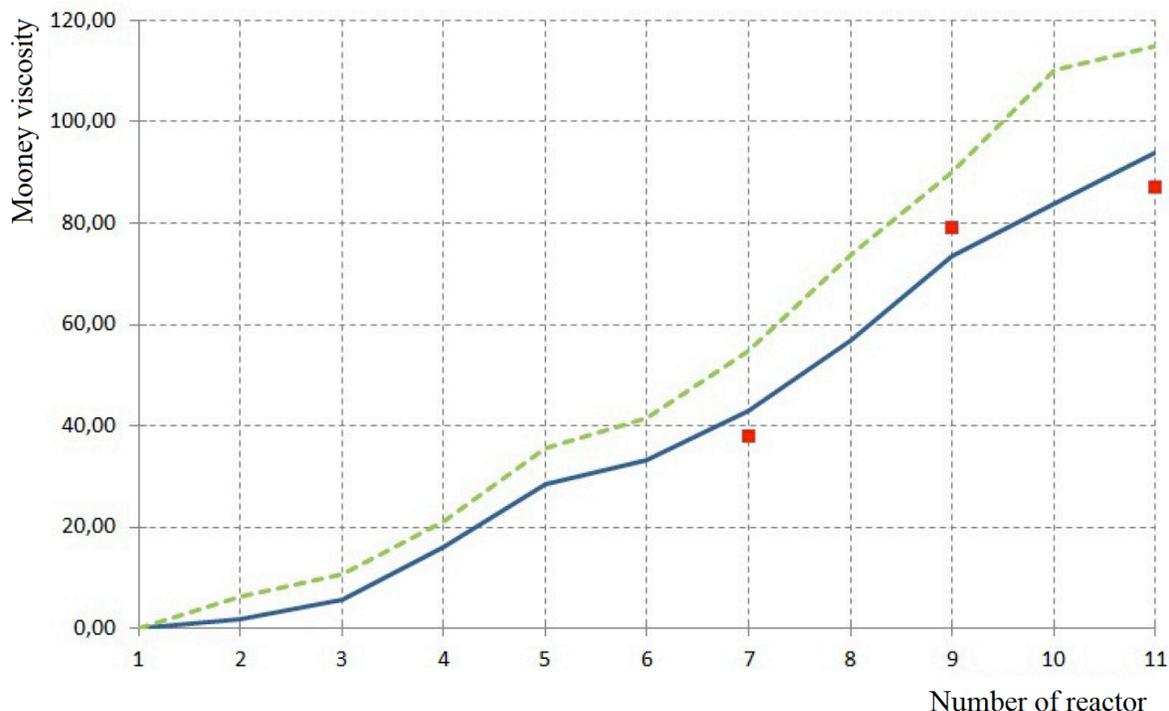


Figure 7. The dependence of the Mooney viscosity of the styrene-butadiene copolymer on the number of the reactor in the cascade (dashed line – simulation results for 15 hours of the process, solid line – simulation results of 30 hours of the process, points – data from the production experiment)

Conclusion

In this paper, we obtained a dependence linking the molecular weight characteristics of the resulting styrene-butadiene copolymer and the Mooney viscosity of the rubber specimen. For the derivation, the logarithmic regression dependence (1) was used, which was applied to the results of modeling the process of styrene-butadiene copolymerization carried out in accordance with the conduct of this process in an industrial environment. The deviation of the data obtained as a result of applying the derived dependence to the simulation results from the production was no more than 8%.

Acknowledgements

The work is performed according to the Russian Government Program of Competitive Growth of Kazan Federal University. The reported study was funded by RFBR according to the research project № 17-47-020068.

References

- Averko-Antonovich, I.Yu. & Bikhmullin, R.T. (2002). Methods for studying the structure and properties of polymers. Kazan State Technological University, Kazan.
- Kramer, O. & Good, W.R. (1972). Correlating Mooney Viscosity to Average Molecular Weight. *Journal of Applied Polymer Science*, 16, 2677-2684.
- Medvedeva, O., Mustafina, S., Mikhailov, V., Mikhailova, T. & Mustafina, S. (2018). Application of Monte Carlo Method in the Construction of Copolymerization Process



Modeling Algorithm for the Continuous Mode in the Reactors Cascade. Proceedings of IEEE East-West Design & Test Symposium (EWDTS'2018), 209-212.

- Mikhailova, T.A., Miftakhov, E.N., & Mustafina, S.A. (2016). Simulation of copolymerization processes. In: Kochnev, A.M., Stoyanov, O.V., Zaikov, G.E. and Akhmetkhanov, R.M. (eds) Compositional Analysis of Polymers: An Engineering Approach. Apple Academic Press, Oakville, pp. 265-272.
- Mikhailova, T., Miftakhov, E. & Mustafina, S. (2016). Mathematical Simulation of the Styrene-Butadiene Rubber's Production in the Cascade of Reactors by the Monte-Carlo Method. International Journal of Chemical Sciences, 14(4), 1865-1876.
- Mustafina, S., Mikhailova, T. & Miftakhov, E. (2015). Mathematical Study of the butadiene-styrene copolymerization product by the Monte-Carlo method. International Journal of Chemical Sciences, 13(2), 849-856.
- Smith, B.R. (1956). Measurement of Molecular Weight Distribution of SBR and Prediction of Rubber Processability. Trans. Faraday Soc., 2, 1286-1291.