Тонкие химические технологии = Fine Chemical Technologies.
2025;20(1):37–46

ISSN 2410-6593 (Print)
ISSN 2686-7575 (Online)

УДК 544.02
https://doi.org/10.32362/2410-6593-2025-20-1-37-46
EDN NZKCWQ

RESEARCH ARTICLE

The influence of halogen-containing modifier on the thermo-oxidative stability of styrene–butadiene–styrene triblock copolymers

Irina S. Almatova[1], Ksenia V. Sukhareva[1,2,]✉, Lyudmila R. Lyusova[3], Svetlana G. Karpova[2], Tatyana V. Monakhova[2], Natalya O. Belyaeva[1]

[1] *Plekhanov Russian University of Economics, Moscow, 117997 Russia*

[2] *N.M. Emanuel Institute of Biochemical Physics, Russian Academy of Sciences, Moscow, 119991 Russia*

[3] *MIREA – Russian Technological University, Moscow, 119454 Russia*

✉ *Автор для переписки, e-mail: Sukhareva.KV@rea.ru*

Abstract

Objectives. Elastomeric materials based on styrene–butadiene–styrene (SBS) triblock copolymers occupy approximately three-quarters of the global thermoplastic elastomer market; in the Russian elastomer market, their share exceeds 80%. Their primary applications include the production of shoe sole materials, anticorrosion coatings, waterproofing, and roofing mastics. The predominant form of degradation of such rubber products, which occurs in the presence of heat and oxygen, is known as thermal-oxidative aging. However, the creation of new functional materials based on modified styrene–butadiene block copolymers will enable the development of materials with enhanced resistance to thermal-oxidative degradation. Chlorinated paraffins, comprising a constituent mixture of polychlorinated *n*-alkanes, can be applied as halogen-containing modifiers for thermoplastic elastomers to enhance their strength and thermal properties. The aim of the present study is to create climate-resistant elastomeric composite materials based on modified SBS triblock copolymers and investigate the influence of a low molecular weight polychlorinated *n*-alkane modifier (chlorinated paraffin) on their thermal-oxidative stability.

Methods. Composite materials based on the SBS triblock copolymers with various amounts of chlorinated paraffin were prepared using the solution blending method. Fourier-transform infrared spectroscopy (FTIR) was used to analyze the impact of the amount of added modifier on the kinetics of thermal-oxidative degradation. The molecular mobility of the elastomers following thermal-oxidation was studied using the paramagnetic probe method to determine the correlation time that characterizes the rotational mobility of the probe in the elastomer matrix. The strength characteristics of the modified elastomer were investigated using a universal testing machine. The kinetics of the thermal-oxidative process were studied using the manometric solid-phase oxidation method.

Results. The results show that oxidation of SBS thermoplastic elastomers occurs mainly in the butadiene blocks. The degradation of unmodified elastomers is caused by chemical bond breakage reactions in the macromolecules. However, due to the sensitivity of double bonds in the polybutadiene segment of SBS, this thermoplastic elastomer is susceptible to light, ozone, and heat.

Conclusions. The multifunctional effect of the halogen-containing modifier on the elastomer leads to increased thermal-oxidative stability of the SBS triblock copolymer thermoplastic elastomer.

Keywords

thermal oxidation, styrene–butadiene–styrene triblock copolymer, modification, polychlorinated *n*-alkanes (chlorinated paraffin), solid-phase oxidation, electron paramagnetic resonance, FTIR spectroscopy

Submitted: 05.06.2024
Revised: 28.10.2024
Accepted: 24.12.2024

For citation

Almatova I.S., Sukhareva K.V., Lyusova L.R., Karpova S.G., Monakhova T.V., Belyaeva N.O. The influence of halogen-containing modifier on the thermo-oxidative stability of styrene–butadiene–styrene triblock copolymers. *Tonk. Khim. Tekhnol. = Fine Chem. Technol.* 2025;20(1):37–46. https://doi.org/10.32362/2410-6593-2025-20-1-37-46

НАУЧНАЯ СТАТЬЯ

Влияние галогеносодержащих модификаторов на термоокислительную стабильность стирол–бутадиен–стирольных триблок-сополимеров

И.С. Алматова[1], К.В. Сухарева[1,2]✉, Л.Р. Люсова[3], С.Г. Карпова[2], Т.В. Монахова[2], Н.О. Беляева[1]

[1] *Российский экономический университет им. Г.В. Плеханова, Москва, 117997 Россия*

[2] *Институт биохимической физики им. Н.М. Эмануэля, Российская академия наук, Москва, 119334 Россия*

[3] *МИРЭА – Российский технологический университет, Москва, 119454 Россия*

✉ *Corresponding author, e-mail: Sukhareva.KV@rea.ru*

Аннотация

Цели. Эластомерные материалы на основе триблок-сополимеров стирола–бутадиена–стирола (СБС) занимают примерно три четверти мирового рынка термопластичных эластомеров, а их доля превышает 80% на российском рынке эластомеров. К сферам их применения относятся производства обувных подошв, антикоррозионных покрытий, гидроизоляционных и кровельных мастик. Резиновые изделия подвержены в разной степени повреждению в результате нагрева и воздействия кислорода. Старение эластомерных изделий в присутствии тепла и кислорода известное как термоокислительное старение, является преобладающим методом старения данных материалов. Создание новых функциональных материалов на основе модифицированных блок-сополимеров стирола и бутадиена позволит разработать материалы с повышенной устойчивостью к термоокислительной деструкции. Хлорированные парафины представляют собой сложную смесь полихлорированных *н*-алканов и могут быть применены в качестве галогенсодержащих модификаторов термопластичных эластомеров для повышения их прочностных и термических свойств. Цель работы — создать климатически стойкие эластомерные композиционные материалы на основе модифицированных триблок-сополимеров СБС и исследовать влияние модификатора низкомолекулярного полихлорированного *н*-алкана (хлорпарафина) на термоокислительную стабильность триблок-сополимера СБС.

Методы. Методом растворного смешения получены композиционные материалы на основе триблок-сополимера СБС с различным количеством хлорпарафина. Инфракрасная спектроскопия с преобразованием Фурье была использована для анализа влияния количества добавленного модификатора на кинетику термоокислительной деструкции. Молекулярную подвижность эластомеров после термоокисления изучали методом парамагнитного зонда, определяя время корреляции, характеризующее вращательную подвижность зонда в матрице эластомера. Прочностные характеристики модифицированного эластомера исследовали на универсальной испытательной машине. Кинетику термоокислительного процесса изучали методом манометрического твердофазного окисления.

Результаты. Результаты показывают, что окисление термопластичных эластомеров СБС происходит преимущественно в бутадиеновых блоках. Деструкция немодифицированных эластомеров вызвана реакциями разрыва химических связей в макромолекулах. Из-за чувствительности двойных связей в полибутадиеновом сегменте СБС данный термопластичный эластомер чувствителен к воздействию света, озона и тепла.

Выводы. Галогенсодержащий модификатор оказывает многофункциональное воздействие на эластомер, повышая термоокислительную стабильность триблок-сополимера термопластичного эластомера СБС.

Ключевые слова

термическое окисление, стирол–бутадиен–стирольный триблок-сополимер, модификация, полихлорированные *н*-алканы (хлорпарафин), твердофазное окисление, электронный парамагнитный резонанс, ИК-Фурье спектроскопия

Поступила: 05.06.2024
Доработана: 28.10.2024
Принята в печать: 24.12.2024

Для цитирования

Almatova I.S., Sukhareva K.V., Lyusova L.R., Karpova S.G., Monakhova T.V., Belyaeva N.O. The influence of halogen-containing modifier on the thermo-oxidative stability of styrene–butadiene–styrene triblock copolymers. *Tonk. Khim. Tekhnol. = Fine Chem. Technol.* 2025;20(1):37–46. https://doi.org/10.32362/2410-6593-2025-20-1-37-46

INTRODUCTION

Significant expanded areas of application for elastomeric composite materials and products based on styrene–butadiene–styrene (SBS) indicates increased attention to this type of material. Thermoplastic elastomers are of great interest due to the possibility of purposeful combination of the physicochemical properties of the original elastomers. SBS triblock copolymer, which shares many characteristics with styrene–butadiene rubber, is the most widely used thermoplastic elastomer worldwide. However, SBS exhibits weak thermal oxidation stability, restricting its processing to temperatures up to 80°C [1, 2]. The unsaturation of the polymer indicates the presence of a double carbon–carbon bond –C=C– in its main chain, making it vulnerable to oxygen in the surrounding environment. The aging of composite elastomeric products as a result of oxidative degradation, leads to a deterioration in their physical and mechanical properties, including fatigue characteristics, which directly affects the lifespan of such products. The production of SBS is continuously expanding and has become an important part of the petrochemical industry. Similar to butadiene rubbers, the double bonds in the polybutadiene segment of SBS are sensitive to light, heat, and oxidation. This susceptibility leads to yellowing, crosslinking, and hardening, which can adversely affect its performance [3]. Elastomers are significantly influenced by environmental factors such as temperature, radiation, oxygen, ozone, ultraviolet radiation, humidity, etc. [4]. Thermal oxidation due to exposure of the material to heat in the presence of air, which has a substantial impact on the lifespan of such products, involves the combined effects of thermal energy and atmospheric oxygen on the elastomer.

While butadiene polymers and copolymers experience both scission and crosslinking during thermal oxidation, scission slightly predominates. Although research on their degradation remains limited, degradation processes in SBS triblock copolymers are known to occur in both the polystyrene and elastomer phases. The elastomer phase is more susceptible to degradation due to its low triglyceride level, which enhances oxygen permeability [5]. Research into the impact of thermo-oxidative aging on SBS structure reveals thermo-oxidative aging to be a critical factor leading to structural damage and performance deterioration in SBS [6–8]. Understanding the type and quantity of oxygen-containing groups in aged SBS under various conditions is essential for reconstructing the SBS molecule. While several studies have qualitatively analyzed the structure and properties of aged SBS, quantitative results are rarely reported. Wang *et al.* used Fourier-transform infrared spectroscopy (FTIR) to study SBS thermal oxidation involving the emergence of polar hydroxyl and carbonyl groups to reveal that the 1,4-polybutadiene portion degrades more easily than the 1,2-polybutadiene portion [9]. Munteanu *et al*. examined the thermo-oxidative behavior of SBS with different structures and detected hydroxyl and carboxyl groups on the molecular chain through FTIR [10]. Singh *et al*., who used dynamic contact angle, FTIR spectrometry, and scanning electron microscopy to investigate changes in SBS following ultraviolet irradiation, propose a photo-oxidation aging mechanism [11]. Prasad *et al*. analyzed SBS aging after dissolution in various solvents using ^{13}C nuclear magnetic resonance to identify epoxides and alcohols as photoproducts [12]. The effects of aging on rubber materials can manifest as increased hardness [13], reduced surface energy, and decreased surface roughness [14].

Over the past 50 years, significant elaborations have been made to increase the oxidative resistance of elastomers by studying the causes and consequences of their degradation when exposed to oxygen and ozone in the air. Resistance to thermo-oxidative degradation is a critical criterion for rubber products used in outdoor applications. The degradation of rubber is well known to result from its reaction with molecular oxygen. This reaction can be mitigated by reducing the number of double bonds or by introducing functional groups that can deactivate these bonds. A described method for modifying SBS with maleic anhydride (MAH) involves an increase in the induction temperature and oxidation time of SBS-g-MAH compared to pure SBS due to the reduction of double bonds and α–H in the polybutadiene segment. This suggests that the thermo-oxidative stability of SBS-g-MAH is superior to that of SBS in polymer-modified asphalt applications.

Previously, the enhancement of flame resistance in highly flammable SBS was investigated through chemical modification with phosphorus-containing substances [15]. It was found that phosphorus-modified SBS undergoes charring, which correlates with the reduced flammability of the modified elastomer. The resistance of polymer composites to ultraviolet radiation is typically improved by introducing antioxidants [16] and ultraviolet absorber/ultraviolet stabilizers into the polymer matrix [17]. However, due to the tendency of such additives to migrate to the polymer surface, only short-term protection is provided. Currently, chemical modification of elastomers with organic halogen-containing (primarily chlorine-containing) compounds is widely researched and implemented. Chlorinated rubbers are used to produce elastomeric materials offering a wide range of desirable properties, including heat-, flame-, gasoline-, oil-, and ozone resistance, as well as resistance to aggressive environments, nonflammability, high strength, and gas impermeability [18]. The introduction of polar groups can also be used to enhance resistance to oil, ozone, flame, and solvents [19]. In order to increase the physical properties of rubbers to satisfy the growing demand for materials offering specific properties for extreme conditions, chemical modification of polymers becomes a crucial factor [20]. The halogenation of thermoplastic elastomers represents a convenient means to increase their compatibility with polar polymers, providing versatile curing possibilities that enhance adhesion, resistance to aging, and chemical resistance.

MATERIALS AND METHODS

A radial SBS (SBS R 3000A grade) triblock copolymer supplied by *Sibur*, Russia, having a styrene/butadiene ratio of 30 : 70 and melt mass-flow rate <1 g/10 min (200°C, 5 kg), was used as the polymer matrix. SBS R 3000A is widely used for modifying bitumen, plastics, rubber products, and protective coatings.

Industrial chlorinated paraffins (CPs) are constituent mixtures of polychlorinated *n*-alkanes that vary in chain length and degree of chlorination. Technical CP mixtures (CP-66T) obtained from *Kaustik*, Volgograd, Russia, which contain 69.5 ± 0.1 wt % chlorine, appear as a yellow-tinged, partly clotted powder. CPs produced by chlorinating alkane mixtures are used in complex products having thousands of homologs and congeners. CP-66T, which typically has one chlorine that can be changed to almost every carbon atom, is classified as a long-chain chlorinated paraffin. The mean carbon formula of CP ($C_{30}H_{38}Cl_{24}$) reveals the approximate average number of chlorine and hydrogen atoms per carbon atom; accordingly, 1 g of CP contains 0.695 g of chlorine.

SBS/CP composites were prepared by incorporating various amounts (2, 5, 10, 15, and 20 g per 100 g of resin (phr)) of chlorinated paraffin using the solution blending compounding method according to the formulation in the table. After casting the SBS/CP solutions into glass Petri dishes, the solvent was evaporated at room temperature of 22 ± 2°C until a constant weight was obtained.

Table. Formulation of chlorinated paraffin and thermoplastic elastomer solutions, mass parts per 100 mass parts of SBS (phr) and wt %

Copolymer	SBS	CP	Toluene	Total
SBS-0, phr	100	0	695	795
wt %	12.58	0	87.42	100
SBS-2, phr	100	2	695	797
wt %	12.55	0.25	87.20	100
SBS-5, phr	100	5	695	800
wt %	12.50	0.62	86.88	100
SBS-10, phr	100	10	695	805
wt %	12.42	1.24	86.34	100
SBS-15, phr	100	15	695	810
wt %	12.35	1.85	85.80	100
SBS-20, phr	100	20	695	815
wt %	12.27	2.45	85.28	100

A sample of 0.5 g dried SBS/CP was dissolved in a beaker including 50 mL of toluene at room temperature 22 ± 2°C over a period of 3 days. The solution concentration was adjusted to contain 1% solution (w/v). The sample for measurement of the Fourier-transform infrared spectroscopy (FTIR) spectroscopy was prepared as follows. A transparent thin film of raw SBS and SBS/CP was made on a transparent KBr window with dimension of 20 × 20 × 3 mm (width × length × thickness) by coating from 1% solution. The solution (0.2 mL) was dropped and coated thinly on a KBr window using a glass capillary. A sample coating on a KBr window was maintained to evaporate toluene in a dark at room temperature for 5 days. Thermal oxidation was performed on transparent thin films of the original SBS and modified SBS samples, applied to a KBr optical window, and then thermostated for 120 h at a temperature of 70°C.

The chemical composition of the samples was analyzed using FTIR with a Lumos FTIR microscope (*Bruker*, Germany). Spectra were recorded at a temperature of 22 ± 2°C in the wavenumber range of 4600–650 cm^{-1}. The spectra were processed using Bruker OPUS software. Transmission FTIR can be used to study rubber oxidation due to its high sensitivity to carbonyl groups.

Electron paramagnetic resonance (ESR) spectra were obtained using a EMX spectrometer (*Bruker*, Germany) with 100 kHz magnetic field modulation. The experiment was conducted at 22°C at a modulation amplitude of <0.5 G, microwave power of 2.1 mW, sweep width of 100 G, and 1,024 recorded points. 2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO) chosen as a spin probe had a radical concentration not exceeding $1 \cdot 10^{-3}$ $mol{\cdot}dm^{-3}$. TEMPO introduced into the sample at 30°C was initially in the vapor phase. ESR spectral data were obtained without saturation, verified by the signal intensity dependence on the microwave field power. The probe rotation correlation time τ_c was determined using the equation involving the width of the low-field spectral component (ΔH_{+1}) and intensities of high/low-field components ($I_{\pm 1}$):

$$\tau_c = \Delta H_{+1} \times [(I_{+1}/I_{-1})^{0.5-1}] \times 6.65 \times 10^{-10}\ \text{(s)}.$$

Data were mathematically processed using WINESR and SIMFONIA (*Bruker*, Germany) software.

The influence of the amount of chlorinated paraffin introduced into the SBS thermoplastic elastomer matrix on the kinetics of thermo-oxidation of the samples was studied using the manometric solid-phase oxidation method for determining the resistance of elastomers to the impact of oxygen at elevated temperatures. Since the oxidation reaction is always accompanied by the absorption of oxygen from the surrounding medium of the oxidizing substance, the oxidation process can be recorded by measuring the amount of oxygen absorbed by the elastomer. In this case, the oxidation rate was determined by the amount of captured oxygen using a manometric device. Rubber oxidation was conducted in the temperature range of 120°C ± 2°C and $p(O_2)$ = 500 torr. Solid KOH was used to absorb volatile oxidation products. The experiment was carried out for 400 min. The sample weight was 0.1 ± 0.001 g.

The tests for determining the elastic-strength properties were conducted on a Tinius Olsen universal testing machine (USA) designed for axial tensile testing in accordance with GOST 270-75[1]. Samples were prepared in the form of rectangular blades with dimensions of 100 × 10 mm; the length of the working section was 60 mm. The blade breakage speed was 50 mm/min. Each data point was confirmed by five measurements.

RESULTS AND DISCUSSION

Figure 1 present the FTIR spectra of the received SBS (SBS-0) and SBS/CP blends with different chlorinated paraffin amount (SBS-2, SBS-5, SBS-10, SBS-15, SBS-20).

The FTIR spectra of SBS triblock copolymers with different chlorinated paraffin contents clearly show the following absorption bands: 699 cm^{-1} (styrene block vibrations), 730 cm^{-1} (*cis*-1,4-polybutadiene vibrations), 910 cm^{-1} (vinyl bonds vibrations), and 965 cm^{-1} (*trans*-1,4-polybutadiene vibrations). The absorption intensity at 699 cm^{-1}, which remained constant during sample oxidation, was used as an internal standard for quantitative calculations of the degree of oxidation. The kinetics of carbonyl group accumulation, represented as the ratio of the optical absorption bands at 1731 cm^{-1} and 699 cm^{-1} over the thermostation time, is indicated in Fig. 2.

Transmission FTIR was successfully used to study the oxidation of rubber due to the high sensitivity of the carbonyl groups. The kinetics of oxidation of the original SBS sample and SBS with various amounts of chlorinated paraffin were studied using FTIR spectroscopy (transmission mode) (Fig. 3).

Thermal oxidation of unsaturated elastomers follows an autocatalytic free radical chain reaction. Consequently, the progression of oxidation can be tracked by the enhance in oxygen-containing functional groups, such as carbonyls (C=O). Here, the absorption intensity of the carbonyl stretching vibration at 1731 cm^{-1} is used as an indicator of the degree of oxidation [21].

The ESR spectra of radical probes in SBS-0, SBS-2, and SBS-20 samples before and after 120 h of thermo-oxidation are indicated in Fig. 4, while the correlation time dependencies for the samples over the oxidation period are exposed in Fig. 5.

According to molecular dynamics data, the introduction of more than 10% chlorinated paraffin

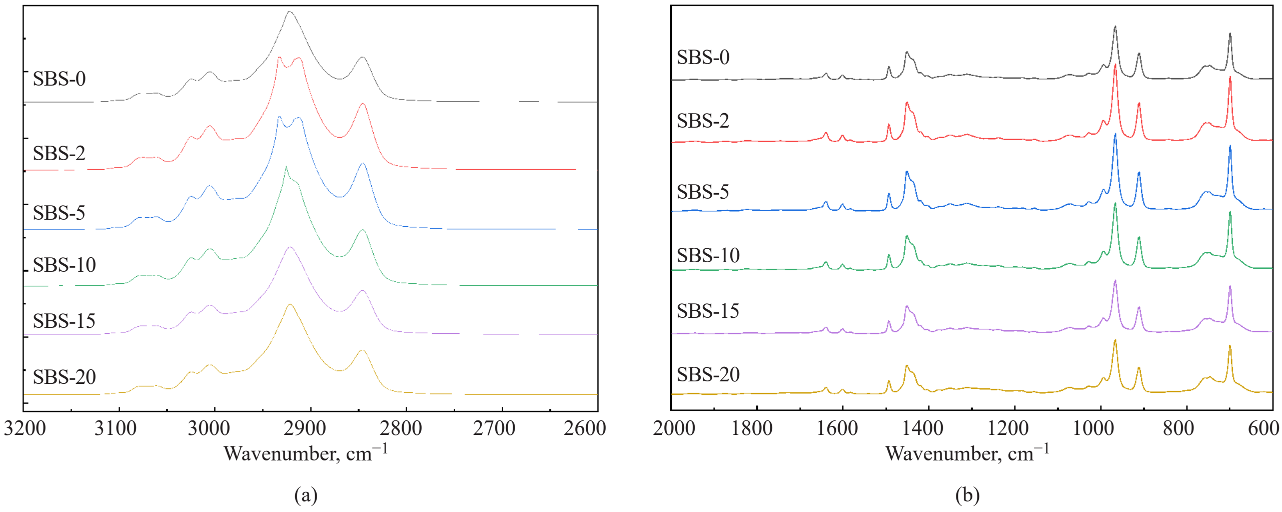

Fig. 1. FTIR spectra of SBS-0, SBS-2, SBS-5, SBS-10, SBS-15, and SBS-20: (a) in the wavelength range 3200–2600 cm^{-1}, (b) in the wavelength range 2000–600 cm^{-1}

---

[1] GOST 270-75. Interstate Standard. Rubber. Method of the determination elastic and tensile stress-strain properties. Moscow: IPK Izdatelstvo standartov; 1978 (in Russ.).

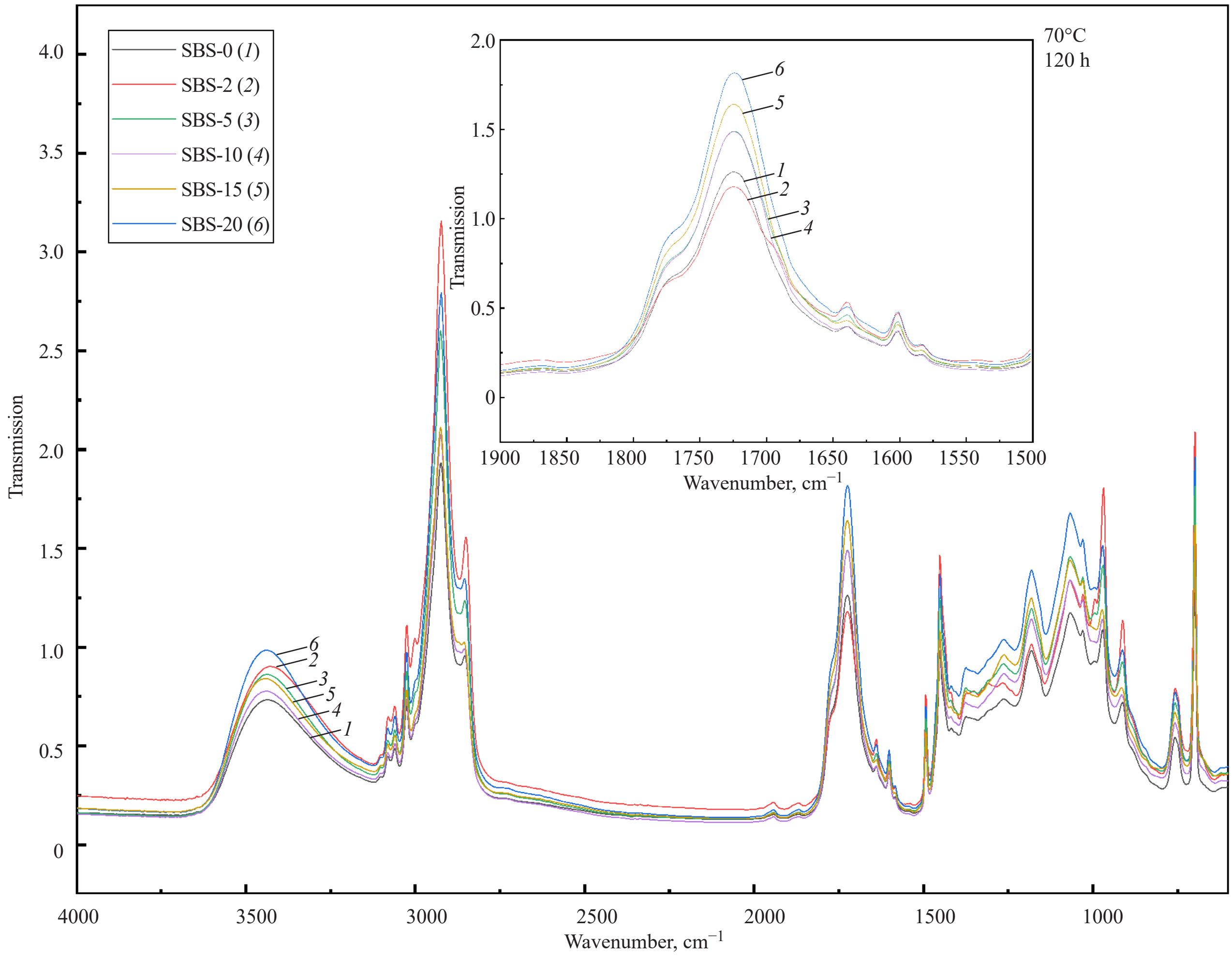

Fig. 2. FTIR spectra of SBS-0, SBS-2, SBS-5, SBS-10, SBS-15, and SBS-20 after 120 h of thermo-oxidation (70°C) in the wavelength range 4000–600 cm^{-1}

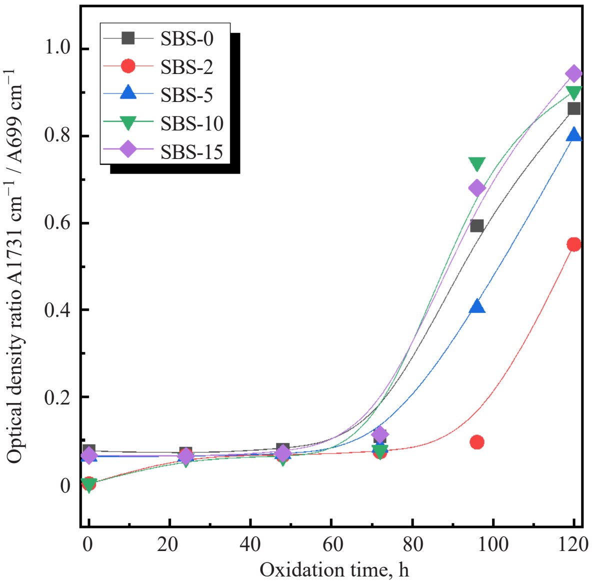

Fig. 3. Dependence of ratio between integrated absorbance values of bands at 1731 cm^{-1} and 699 cm^{-1} on the oxidation time

into the SBS matrix increases the correlation time of the radical probe, thereby reducing the segmental mobility of the elastomer chains. This indicates that chlorinated paraffins do not act as plasticizers in the mixture, since plasticizers typically increase the molecular mobility of elastomers. The unified approach presented in the literature suggests that lower molecular mobility in elastomers due to reduced intermolecular interactions results in higher thermal and thermo-oxidative stability. This approach is valid only for SBS-2 and SBS-5 samples, where the initial correlation time of the radical probe increases compared to the original SBS; according to FTIR spectroscopy, this indicates reduced molecular mobility and enhanced thermo-oxidative stability. The introduction of more than 5% chlorinated paraffin significantly increases the initial correlation time, including an extreme rise after 96 h of oxidation, which indicates further reduced molecular mobility during active oxidation. SBS-0, SBS-2, and SBS-5 samples do not exhibit a sharp increase in correlation

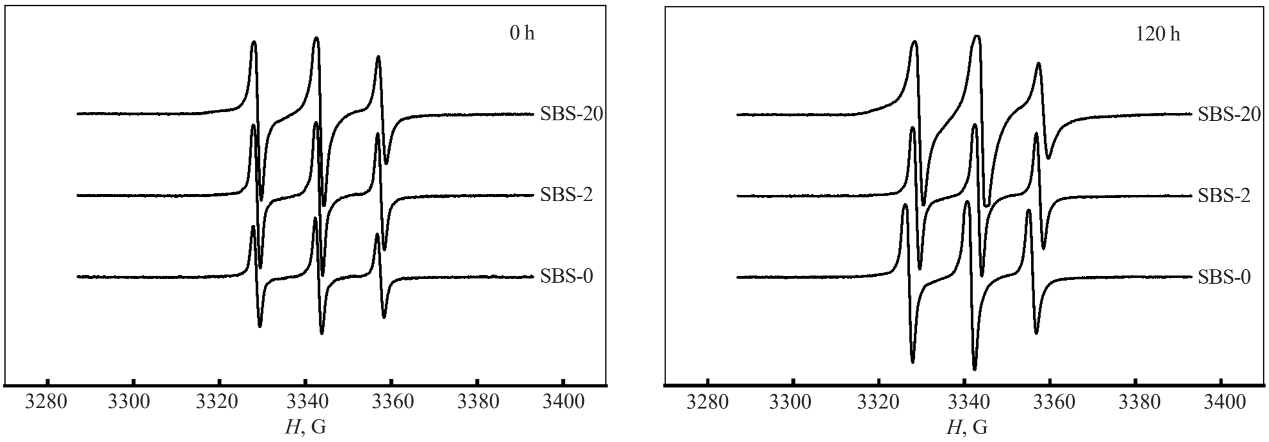

Fig. 4. ESR spectra of the spin probe incorporated in SBS-0, SBS-2, and SBS-20 before and after 120 h of thermal oxidation

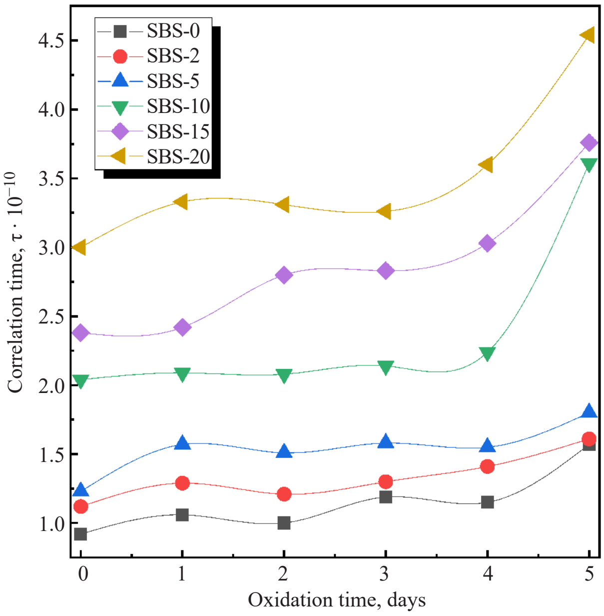

Fig. 5. Dependence of the rotational correlation times of TEMPO spin probe in SBS-0, SBS-2, SBS-5, SBS-10, SBS-15, and SBS-20 on the oxidation time

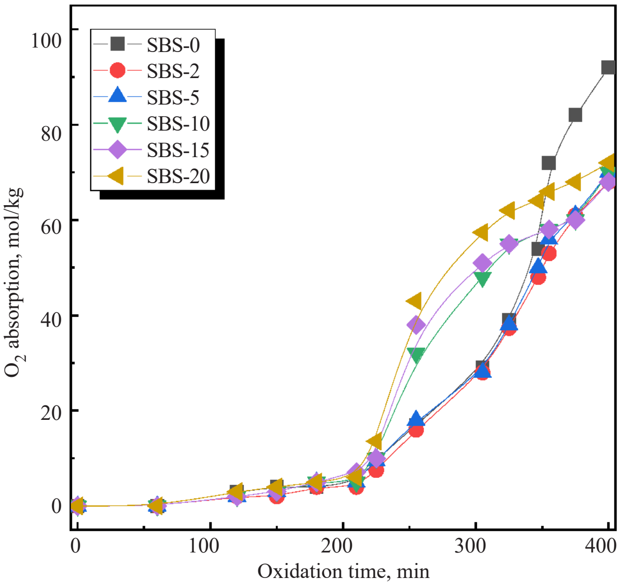

Fig. 6. Oxygen absorption kinetic curves for as-received SBS (SBS-0) and SBS with different chlorinated paraffins amounts (SBS-2, SBS-5, SBS-10, SBS-15, and SBS-20) at temperature 120°C and oxygen pressure 500 torr

time after 96 h of thermo-oxidation. Correlation time is defined as the time required for a molecule to rotate by one radian. The EPR spectrum of the nitroxide radical provides information about the nature of its microenvironment. Introducing nitroxide radicals into the studied systems allows the aggregation parameters and dynamics of these processes to be examined using ESR. Kinetic curves of oxygen absorption by the original SBS thermoplastic elastomer and SBS samples with different chlorinated paraffin contents at 120°C are shown in Fig. 6.

According to analysis of the oxygen absorption time dependence for modified SBS samples with different amounts of the modifier and the received SBS sample, all samples exhibit high hermos-oxidative stability during the initial oxidation stage (up to 200 min) at a low initial oxidation rate. The induction time for oxidation is the same for all samples. A sharp acceleration in the oxidation process observed in samples with 10, 15, and 20 wt % chlorinated paraffin after 200 min is due to a rapid increase in oxygen absorption by the elastomers. During this oxidation stage, the oxygen absorption rate can be reduced by introducing 2 wt % of chlorinated paraffin to enhance hermos-oxidative stability. Various studies suggest that low-molecular-weight additives that transfer free valence during co-oxidation with the elastomer can be used to inhibit oxidation.

In SBS samples with 10, 15, and 20% chlorinated paraffin, a heterogeneous system forms in which modifier molecule aggregates act as inclusion phases to offer a more developed surface than tightly packed polymer chains. Aggregation of modifier molecules at concentrations above 5 wt % is due to the accumulation of unreacted modifier to form clusters. The consequent creation of micropores offering a more developed surface allows higher oxygen diffusion compared to a homogeneous system based on SBS and SBS with low modifier concentrations. The observed reduction in the autocatalytic oxidation stage rate in SBS-2 and SBS-5 samples may result from decreased conformational mobility of thermoplastic elastomer chains in the presence of low-chlorinated paraffin additives and the absence of aggregate formation. The introduction of 2 wt % chlorinated paraffin reduces the initial oxidation and autocatalysis rates, serving to inhibit oxidation and increase the activation energy of autocatalysis in the elastomer mixture.

The dependence of physicomechanical properties on the amount of modifier introduced is shown in Fig. 7.

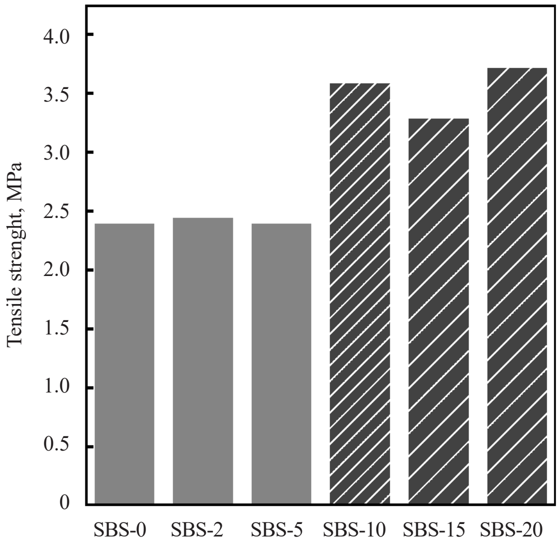

Fig. 7. Mechanical properties of the initial samples SBS-0, SBS-2, SBS-5, SBS-10, SBS-15, and SBS-20

Analysis of the strength characteristics of the original SBS-0 and samples with different modifier amounts revealed the following trend: the introduction of up to 5 wt % chlorinated paraffin into SBS maintains the strength characteristics at the level of the original SBS-0. Small amounts of low-molecular-weight halogen-containing modifiers do not significantly affect the elastomer strength properties. SBS-10, SBS-15, and SBS-20 form a distinct group with higher strength characteristics compared to SBS-0, SBS-2, and SBS-5 samples. This trend aligns with ESR spectroscopy data, indicating that reduced polymer molecule flexibility, or molecular mobility, results in a stiffer polymer with higher modulus of elasticity and strength.

CONCLUSIONS

According to FTIR spectroscopy data, the introduction of 2 and 5 wt % chlorinated paraffin results in uniform distribution of modifier molecules within the elastomer phase, which interact with elastomer macromolecules during swelling. However, higher chlorinated paraffin concentrations hinder uniform distribution due to the aggregation of chlorinated paraffin molecules as reflected in increased radical probe correlation time in samples with over 5% paraffin. The mechanical characteristics are significantly improved in samples with 10 to 20 wt % paraffin. As unreacted chlorinated paraffin accumulates, its particles aggregate due to thermodynamic affinity to form polar-polar interactions within the nonpolar polymer matrix. Consequently, the introduction of more than 5 wt % chlorinated paraffin creates a heterogeneous system with an unstable inclusion phase based on chlorinated paraffin aggregates, which is more diffusively accessible to oxygen during oxidation processes.

Acknowledgments

The work was carried out using the equipment of the Joint Research Center of Plekhanov Russian University of Economics and the Center of Shared Usage “New Materials and Technologies” at the Emanuel Institute of Biochemical Physics.

Authors’ contributions

I.S. Almatova—investigating the composition and properties of mechanoactivated SBS triblock copolymers, analyzing the data and writing the manuscript.

K.V. Sukhareva—supervising the project.

L.R. Lyusova— analysis the results, critical feedback and shaping the research.

S.G. Karpova—contributing to the final version of the manuscript.

T.V. Monakhova—performing the experiments/calculations/simulations, analyzing the data.

N.O. Belyaeva—performing the experiments, contributing to the interpretation of the results.

The authors declare no conflict of interest warranting disclosure in this article.

REFERENCES

1. Li H., Wu H., Wang C., Zheng J. Styrene–butadiene–styrene/graphene nanocomposites with improved thermal oxidation stability. *Polym. Int*. 2024;73(6):446–453. https://doi.org/10.1002/pi.6611
2. Adhikari R., Michler G.H. Influence of molecular architecture on morphology and micromechanical behavior of styrene/butadiene block copolymer systems. *Prog. Polym. Sci*. 2004;29(9):949–986. https://doi.org/10.1016/j.progpolymsci.2004.06.002
3. Xu J., Zhang A., Zhou T., Cao X., Xie Z. A study on thermal oxidation mechanism of styrene–butadiene–styrene block copolymer (SBS). *Polym. Degrad. Stab*. 2007;92(9):1682–1691. https://doi.org/10.1016/j.polymdegradstab.2007.06.008
4. Rezig N., Bellahcene T., Aberkane M., Nait A.M. Thermo-oxidative ageing of a SBR rubber: effects on mechanical and chemical properties. *J. Polym. Res*. 2020;27(10):339. https://doi.org/10.1007/s10965-020-02330-y
5. Allen N.S., Barcelona A., Edge M., Wilkinson A., Merchan C.G., Ruiz Santa Quiteria V. Thermal and photooxidation of high styrene–butadiene copolymer (SBC). *Polym. Degrad. Stab*. 2004;86(1):11–23. https://doi.org/10.1016/j.polymdegradstab.2003.10.010
6. Su T-T., Jiang H., Gong H. Thermal Stabilities and Thermal Degradation Kinetics of a Styrene-Butadiene-Styrene Star Block Copolymer. Polym. Plast. Technol. Eng. 2009;48(5):535–541. https://doi.org/10.1080/03602550902824341
7. Chiantore O., Tripodi S., Sarmoria C., Vallés E. Mechanism and molecular weight model for thermal oxidation of linear ethylene–butene copolymer. *Polymer*. 2001;42(9):3981–3987. https://doi.org/10.1016/S0032-3861(00)00736-9
8. Xu X., Yu J., Xue L., Zhang C., Zha Y., Gu Y. Investigation of Molecular Structure and Thermal Properties of Thermo-Oxidative Aged SBS in Blends and Their Relations. *Materials*. 2017;10(7):768. https://doi.org/10.3390/ma10070768
9. Wang S-M., Chang J-R., Tsiang RC-C. Infrared studies of thermal oxidative degradation of polystyrene-*block* polybutadiene-*block*-polystyrene thermoplastic elastomers. *Polym. Degrad. Stab*. 1996;52(1):51–57. https://doi.org/10.1016/0141-3910(95)00226-X
10. Munteanu S.B., Brebu M., Vasile C. Thermal and thermo-oxidative behaviour of butadiene–styrene copolymers with different architectures. *Polym. Degrad. Stab*. 2005;89(3):501–512. https://doi.org/10.1016/j.polymdegradstab.2005.01.037
11. Singh R.P., Desai S.M., Solanky S.S., Thanki P.N. Photodegradation and stabilization of styrene-butadiene-styrene rubber. *J. Appl. Polym. Sci*. 2000;75(9):1103–1114. https://doi.org/10.1002/(SICI)1097-4628(20000228)75:9<1103::AID-APP3>3.0.CO;2-M
12. Prasad A.V., Singh R.P. Photooxidative degradation of styrenic polymers: ^{13}C-NMR and morphological changes upon irradiation. *J. Appl. Polym. Sci*. 1998;70(4):637–645. https://doi.org/10.1002/(SICI)1097-4628(19981024)70:4<637::AID-APP2>3.0.CO;2-R
13. Li X.G., Zhang Y.L., Yang M.Y. Study on Thermal Oxidative Aging of Nitrile Rubber. *Appl. Mech. Mater*. 2013;299:199–202. http://doi.org/10.4028/www.scientific.net/AMM.299.199
14. Garcia-Garcia D., Crespo-Amorós J.E., Parres F., Samper M.D. Influence of Ultraviolet Radiation Exposure Time on Styrene-Ethylene-Butadiene-Styrene (SEBS) Copolymer. *Polymers*. (Basel). 2020;12(4):862. https://doi.org/10.3390/polym12040862
15. Chernyy S., Ullah S., Jomaas G., Leisted R.R., Mindykowski P.A., Ravnsbæk J.B., *et al*. Modification of poly(styrene-*block*-butadiene-*block*-styrene) [SBS] with phosphorus containing fire retardants. *Eur. Polym. J*. 2015;70:136–146. https://doi.org/10.1016/j.eurpolymj.2015.07.015
16. Li Y., Li L., Zhang Y., Zhao S., Xie L., Yao S. Improving the aging resistance of styrene-butadiene-styrene tri-block copolymer and application in polymer-modified asphalt. *J. Appl. Polym. Sci*. 2010;116(2):754–761. https://doi.org/10.1002/app.31458
17. Ching Y.C., Gunathilake T.U., Ching K.Y., Chuah C.H., Sandu V., Singh R., Liou K.Y. Effects of high temperature and ultraviolet radiation on polymer composites. In: *Durability and Life Prediction in Biocomposites, Fibre-Reinforced Composites and Hybrid Composites*. Elsevier; 2019. P. 407–426. https://doi.org/10.1016/B978-0-08-102290-0.00018-0
18. Sukhareva K.V., Mikhailov I.A., Mamin E.A., Monakhova T.V., Kasparov V.V., Kolesnikov E.A., Popov A.A. Modification of nitrile-butadiene rubber surface by immersion into 1,1,2-trifluoro-1,2,2-trichlor-ethane and its physio-chemical properties. *Polym. Eng. Sci*. 2023;63(9):2891–2904. https://doi.org/10.1002/pen.26413
19. Ramesan M.T., Kumar T.A. Preparation and properties of different functional group containing styrene butadiene rubber. *J. Chil. Chem. Soc*. 2009;54(1):23–27. http://doi.org/10.4067/S0717-97072009000100006
20. Sukhareva K.V., Sukharev N.R., Levina I.I., Offor P.O., Popov A.A. Solvent Swelling-Induced Halogenation of Butyl Rubber Using Polychlorinated N-Alkanes: Structure and Properties. *Polymers*. 2023;15(20):4137. https://doi.org/10.3390/polym15204137
21. Li G-Y., Koenig J.L. A Review of Rubber Oxidation. *Rubber Chemistry and Technology*. 2005;78(2):355–390. https://doi.org/10.5254/1.3547888

About the authors

Irina S. Almatova, Postgraduate Student, Basic Department of Chemistry of Innovative Materials and Technologies, Plekhanov Russian University of Economics (36, Stremyannyi per., Moscow, 115054, Russia). E-mail: AlmatovaIS@rea.ru. https://orcid.org/0009-0005-3415-9196

Ksenia V. Sukhareva, Cand. Sci. (Chem.), Senior Researcher, Associate Professor, Higher Engineering School “New Materials and Technologies,” Plekhanov Russian University of Economics (36, Stremyannyi per., Moscow, 115054, Russia). E-mail: Sukhareva.KV@rea.ru. Scopus Author ID 57191042974, RSCI SPIN-code 1883-8039, https://orcid.org/0000-0002-0282-7015

Lyudmila R. Lyusova, Dr. Sci. (Eng.), Professor, Head of the F.F. Koshelev Department of Chemistry and Technology of Processing of Elastomers, M.V. Lomonosov Institute of Fine Chemical Technologies, MIREA – Russian Technological University (78, Vernadskogo pr., Moscow, 119454, Russia). E-mail: lyusova@mirea.ru. Scopus Author ID 6508196636, RSCI SPIN-code 6390-2313, https://orcid.org/0000-0001-9515-6347

Svetlana G. Karpova, Cand. Sci. (Chem.), Senior Researcher, N.M. Emanuel Institute of Biochemical Physics, Russian Academy of Sciences (4, Kosygina ul., Moscow, 119334, Russia). E-mail: karpova@sky.chph.ras.ru. Scopus Author ID 16218970000, RSCI SPIN-code 4449-9506, https://orcid.org/0000-0003-3514-5843

Tatyana V. Monakhova, Cand. Sci. (Chem.), Senior Researcher, N.M. Emanuel Institute of Biochemical Physics, Russian Academy of Sciences (4, Kosygina ul., Moscow, 119334, Russia). E-mail: monakhova-81@mail.ru. https://orcid.org/0000-0002-0731-8412

Natalya O. Belyaeva, Research Assistant, Basic Department of Chemistry of Innovative Materials and Technologies; Student, Higher Engineering School "New Materials and Technologies," Plekhanov Russian University of Economics (36, Stremyannyi per., Moscow, 115054, Russia). E-mail: nataly12022004@yandex.ru. Scopus Author ID 59172652500, RSCI SPIN-code 2652-3760, https://orcid.org/0009-0004-1566-2952

Об авторах

Алматова Ирина Сергеевна, аспирант, базовая кафедра химии инновационных материалов и технологий, ФГБОУ ВО «Российский экономический университет им. Г.В. Плеханова» (115054, Россия, Москва, Стремянный пер., д. 36). E-mail: AlmatovaIS@rea.ru. https://orcid.org/0009-0005-3415-9196

Сухарева Ксения Валерьевна, к.х.н., старший научный сотрудник, доцент, Высшая инженерная школа «Новые материалы и технологии», ФГБОУ ВО «Российский экономический университет им. Г.В. Плеханова» (115054, Россия, Москва, Стремянный пер., д. 36). E-mail: Sukhareva.KV@rea.ru. Scopus Author ID 57191042974, SPIN-код РИНЦ 1883-8039, https://orcid.org/0000-0002-0282-7015

Люсова Людмила Ромуальдовна, д.т.н., профессор, заведующая кафедрой химии и технологии переработки эластомеров им. Ф.Ф. Кошелева, Институт тонких химических технологий им. М.В. Ломоносова, ФГБОУ ВО «МИРЭА – Российский технологический университет» (119454, Россия, Москва, пр-т Вернадского, д. 78). E-mail: lyusova@mirea.ru. Scopus Author ID 6508196636, SPIN-код РИНЦ 6390-2313, https://orcid.org/0000-0001-9515-6347

Карпова Светлана Геннадьевна, к.х.н., старший научный сотрудник, ФГБУН Институт биохимической физики им. Н.М. Эмануэля Российской академии наук (199334, Россия, Москва, ул. Косыгина, д. 4). E-mail: karpova@sky.chph.ras.ru. Scopus Author ID 16218970000, SPIN-код РИНЦ 4449-9506, https://orcid.org/0000-0003-3514-5843

Монахова Татьяна Вадимовна, к.х.н., старший научный сотрудник, ФГБУН Институт биохимической физики им. Н.М. Эмануэля Российской академии наук (199334, Россия, Москва, ул. Косыгина, д. 4). E-mail: monakhova-81@mail.ru. https://orcid.org/0000-0002-0731-8412

Беляева Наталья Олеговна, лаборант-исследователь, базовая кафедра химии инновационных материалов и технологий; студент, Высшая инженерная школа «Новые материалы и технологии», ФГБОУ ВО «Российский экономический университет им. Г.В. Плеханова» (115054, Россия, Москва, Стремянный пер., д. 36). E-mail: nataly12022004@yandex.ru. Scopus Author ID 59172652500, SPIN-код РИНЦ 2652-3760, https://orcid.org/0009-0004-1566-2952

The text was submitted by the authors in English
and edited for English language and spelling by Thomas A. Beavitt