SYNTHESIS AND PROCESSING OF POLYMERS AND POLYMERIC COMPOSITES

СИНТЕЗ И ПЕРЕРАБОТКА ПОЛИМЕРОВ И КОМПОЗИТОВ НА ИХ ОСНОВЕ

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RESEARCH ARTICLE

Influence of various factors on surface properties of elastomeric materials based on nitrile butadiene rubbers

Olga A. Dulina✉, Evgeniya V. Eskova, Alina D. Tarasenko, Svetlana V. Kotova

MIREA – Russian Technological University (M.V. Lomonosov Institute of Fine Chemical Technologies), Moscow, 119571 Russia
✉Corresponding author, e-mail: doa1503991@yandex.ru

Abstract

Objectives. *The influence of the technological additive content and accelerated aging conditions on the surface energy and elastic-strength properties of nitrile butadiene rubbers with an average acrylic acid nitrile content and rubbers based on them were studied in the paper.*
Methods. *The free surface energy of the samples was determined under the standard conditions and in the accelerated aging conditions with the use of the Owens, Wendt, Rabel, and Kaelble method.*
Results. *It was shown that the elastomeric materials surface energy is influenced by surfactants such as rosin and stearic acid, which are typical ingredients of rubber compounds. It was also found that the thermal aging effect on the physical and mechanical properties of rubbers based on nitrile butadiene rubbers depends on the method of rubber isolation from latex and on the nature of the surfactant components in the samples.*
Conclusions. *The analysis of the results obtained shows that the change in the vulcanizates physical and mechanical properties, depending on the technological additive content and the temperature effect, occurs along with a change in the critical surface tension.*

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Keywords: *nitrile butadiene rubber, free surface energy, surface tension, surfactant, surface properties, physical and mechanical properties of polymers, thermal aging*

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НАУЧНАЯ СТАТЬЯ

Влияние различных факторов на поверхностные свойства эластомерных материалов на основе бутадиен-нитрильных каучуков

О.А. Дулина✉, Е.В. Еськова, А.Д. Тарасенко, С.В. Котова

МИРЭА – Российский технологический университет (Институт тонких химических технологий им. М.В. Ломоносова), Москва, 119571 Россия
✉Автор для переписки, e-mail: doa1503991@yandex.ru

Аннотация

Цели. *Изучение влияния содержания технологических добавок и условий ускоренного старения на поверхностную энергию, упруго-прочностные и адгезионные характеристики резин на основе бутадиен-нитрильных каучуков со средним содержанием нитрила акриловой кислоты.*
Методы. *С помощью метода Оуэнса–Вендта–Рабеля–Каелбле была определена свободная поверхностная энергия образцов в стандартных условиях и условиях ускоренного старения.*
Результаты. *Было показано, что на поверхностную энергию эластомерных материалов оказывают влияние поверхностно-активные вещества, такие как канифоль и стеариновая кислота, являющиеся типичными ингредиентами резиновых смесей, а также было установлено, что влияние условий ускоренного старения на физико-механические свойства резин на основе бутадиен-нитрильных каучуков зависит от способа выделения каучука из латекса и природы поверхностно-активных компонентов, входящих в состав образцов. Предполагается, что это происходит за счет миграции на поверхность образцов низкомолекулярных компонентов и поверхностно-активных веществ.*
Выводы. *Анализ полученных результатов показывает, что изменение физико-механических свойств вулканизатов в зависимости от содержания технологической добавки и воздействия температуры происходит наряду с изменением критического поверхностного натяжения.*

Ключевые слова: *бутадиен-нитрильный каучук, свободная поверхностная энергия, поверхностное натяжение, поверхностно-активное вещество, поверхностные свойства, физико-механические свойства полимеров, термостарение*

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INTRODUCTION

Nitrile-butadiene rubbers (NBR) are widely used in the production of rubber products operating, inter alia, in aggressive environments and at the elevated temperatures. They are used in almost all industries [1].

Rubber is the multicomponent composite material with a multiphase structure, in which the polymer is in a highly elastic state with high segmental mobility. Therefore, the surface properties of rubber-based products are determined by the nature of polymers, the conditions for their preparation and surface formation, as well as by the composition of the polymer material containing a considerable amount of powdered dispersed fillers and various low molecular weight additives that can migrate into the surface layers and affect the surface free energy (SFE) [1–3]. All this, together with aggressive factors that have a significant impact on the state of product material and of its surface, entails a change in the surface properties and, as a result, in the product operational characteristics.

In connection with the foregoing, it is advisable to find a way of assessing the state of the surface subjected to aggressive action in order to identify changes in its properties during operation.

In the works of Tarasenko and Dulina [4, 5], the effect of low molecular weight rubber compound additives on the surface properties was studied. It was found that the elastomer compositions surface properties significantly depend on the rubber compound ingredients solubility and on their adsorption properties. It was found that the effect of surfactants on the surface energy of rubber compounds is different and depends on their nature. Sulfur, as a partially soluble component, does not affect the samples surface energy in small amounts, and if it is present in the system in amounts greater than the solubility limit, it significantly reduces the SFE.

The aim of this work was to study the stearic acid and rosin content effect on the surface energy and elastic-strength properties of rubber samples based on NBRs, with an average content of acrylic acid nitrile, among other things, under the accelerated aging conditions of rubbers.

EXPERIMENTAL

The objects of study were NBR samples with an average acrylic acid nitrile content. The samples were obtained by two different methods of isolation from latex [6]. Besides, rubbers based on them were studied.

SKN-26 SM rubber (*Voronezh branch of Scientific-Research Institute of Synthetic Rubber*, Voronezh, Russia) was obtained using an alkyl sulfonate emulsifier. The latter is almost completely washed out in the process of isolation from the latex. BNKS-28 AMN rubber (*Krasnoyarsk Synthetic Rubber plant, SIBUR Holding*, Krasnoyarsk, Russia) was obtained using fatty acids, followed by neutralization at the phase boundary to obtain the emulsifier—the potassium or sodium salt of the fatty acid. The rubber was isolated from the latex with the calcium or magnesium chloride solution. As a result, the emulsifier and coagulator interaction products remained in the polymer—slightly soluble salts of fatty acids.

Rubber samples were obtained using the following formulation: for 100 mass fractions of the unvulcanized rubber, zinc oxide (*Empils-Zink*, Rostov-on-Don, Russia)—5 mass fractions, sulfur (*Rosneft*, Moscow, Russia)—2 mass fractions, carbon black P-514 (*Omsktekhuglerod*, Omsk, Russia)—50 mass fractions, and accelerator CBS (*VitaHim*, Dzerzhinsk, Russia)—1.2 mass fractions. The vulcanization time corresponded to the optimum vulcanization for this type of rubber compound.

To determine the critical surface tension, which is a criterion for estimating the SFE of rubber samples, the Owens, Wendt, Rabel, and Kaelble (OWRK) method was chosen. It is based on determining the contact angles of material surface wetting by liquids with different surface tension [7–9]. The OWRK method is more preferable, because the Zisman method, which is widely used to assess the surface state, does not take into account the surface energy polar component contribution. Studies [10] have shown that the surface energy values obtained by the Zisman method practically reproduce the SFE dispersion component values calculated by the OWRK method.

The obtained contact angles values are used to calculate the SFE using a mathematical model, according to which the SFE is the sum of the dispersion and polar components [11–14].

For determining the SFE, unvulcanized rubber samples were obtained by pressing between fluoroplast films. Rubber samples were pressed plates.

Since this work considers the SFE as the comparative characteristic for the series of samples under study, standard requirements were imposed on wetting liquids: physicochemical characteristics stability during storage and high surface tension and its dispersion and polar components values. These values should provide sufficiently large and reliably measured contact angles. As a result, water and nonvolatile alcohols—propylene glycol, ethylene glycol, and glycerin—were chosen as wetting liquids.

The contact angles were determined by the sessile drop method using an LK-1 goniometer (*OpenScience*, Russia). The device makes it possible to obtain an image of a drop lying on a substrate using a digital video camera, export the image to a computer, and determine the contact angle by the tangent method.

The elastomeric material surface was cleaned with an inert solvent, ethanol. After that, a drop was applied to the cleaned surface of the sample using a microsyringe. The contact angles were measured after an hour of rest of the samples. This was necessary for the formation of an equilibrium surface layer after surface treatment with the cleaning solvent [15].

The main physical and mechanical properties of the studied rubbers were determined in accordance with the current state standards (GOST 263-75[1], GOST 27110-86[2], GOST 270-75[3], GOST 262-93[4], GOST 6768-75[5]).

RESULTS AND DISCUSSION

In order to study the influence on the NBRs surface properties of non-rubber components, the content and nature of which is determined by the rubber obtaining method, the critical surface tension was determined by the OWRK method. The results presented in Table 1 indicate that the rubbers production characteristics affect their surface properties.

Table 1. Surface properties of nitrile butadiene rubbers obtained by different methods of isolation from latex

Rubber brand	SFE*, mJ/m^2
SKN-26 SM	28
BNKS-28 AMN	22.4

*Surface free energy determined by the OWRK method.

SKN-26 SM rubber obtained with the use of an alkyl sulfonate emulsifier, which is almost completely washed out in the process of isolation from the latex, has a more polar surface. BNKS-28 AMN rubber has a lower SFE. This rubber contains a residual emulsifier—sparingly soluble salts of fatty acids capable of migrating to the surface and reducing the samples surface tension.

The critical surface tension of samples obtained based on unvulcanized rubbers was determined at certain time intervals (0, 1, 3, and 24 h) after cleaning the surface. As can be seen from Table 2, the dependence obtained for the unvulcanized rubbers is also preserved for the rubber samples based on them. The surfaces of the rubber samples based on “pure” SKN-26 SM unvulcanized rubber have higher polarity. An increase in the time elapsed after surface cleaning slightly decreases the critical surface tension of all the types of samples. This is explained by the system tendency to a minimum of SFE, mainly due to the release of its lowering components to the surface.

Similar studies were carried out for rubber samples, in which the content of anionic surfactants—stearic acid and rosin—was varied (Table 2).

An analysis of the presented results makes it possible to conclude that in case of rubber based on “pure” SKN-26 SM unvulcanized rubber, an increase in the stearic acid and rosin content decreases the SFE, probably, due to surfactant migration to the samples surface, and the stearic acid effect being more significant.

In case of rubbers based on BNKS-28 AMN, the introduction of surfactants also decreases the SFE, but a greater effect is manifested upon the introduction of rosin. It is possible that resin acids that are part of rosin interact with divalent metal salts remaining in the system after coagulation, thus forming divalent metals salts of the resin acids with more pronounced surface-active properties.

In all the cases, these tendencies in the corresponding samples are preserved for 24 h after the moment of purification. However, the effect from the introduced surfactants becomes less significant.

To expand the understanding of the stearic acid and rosin role in the NBR-based elastomeric

[1] GOST 263-75. USSR State Standard. Rubber. Method for determination of Shore A hardness. Moscow: Izd. Standartov; 1989 (in Russ.).

[2] GOST 27110-86. USSR State Standard. Rubber. Method for determination of rebound elasticity on the Shob type machine. Moscow: Izd. Standartov; 1987 (in Russ.).

[3] GOST 270-75. Interstate Standard. Rubber. Method of the determination elastic and tensile stress-strain properties. Moscow: Standartinform; 2008 (in Russ.).

[4] GOST 262-93. Interstate Standard. Rubber, vulcanized. Determination of tear strength (trouser, angle and crescent test pieces). Moscow: IPK Izd. Standartov; 2002 (in Russ.).

[5] GOST 6768-75. USSR State Standard. Rubber and rubberized fabric. Method for determination of bond strength at ply separation. Moscow: Izd. Standartov; 1998 (in Russ.).

Table 2. Surface free energy of rubber samples based on nitrile butadiene rubber containing surfactants in accelerated aging conditions

Samples composition	SFE,* mJ/m²				Temperature duration, h
	Time after surface cleaning, h				
	0	1	3	24	
SKN-26 SM	38.4	37.0	36.3	34.8	0
	34.3	31.1	30.5	30.0	6
	36.7	34.0	33.8	33.3	12
	43.4	41.5	40.9	40.1	18
SKN-26 SM + 1 mass fract. of rosin	33.8	31.1	30.8	28.2	0
	36.5	35.8	34.1	33.4	6
	34.6	31.7	30.8	27.3	12
	38.6	33.7	32.1	29.6	18
SKN-26 SM + 2 mass fract. of rosin	32.3	29.9	29.1	28.3	0
	31.1	28.8	27.3	27.1	6
	32.3	27.2	26.8	26.6	12
	31.8	25.3	24.6	23.2	18
SKN-26 SM + 1 mass fract. of stearic acid	31.3	30.5	28.2	25.1	0
	29.5	27.6	25.6	23.1	6
	29.2	26.3	25.2	23.3	12
	27.4	25.8	24.7	22.9	18
SKN-26 SM + 2 mass fract. of stearic acid	27.3	26.2	24.7	21.4	0
	22.1	21.9	21.0	18.0	6
	20.4	20.6	20.1	17.2	12
	21.1	19.5	19.1	17.0	18
BNKS-28 AMN	34.4	33.9	32.4	30.2	0
	28.5	25.1	24.8	23.5	6
	34.7	34.1	32.8	30.4	12
	34.5	34.2	32.4	29.9	18
BNKS-28 AMN + 1 mass fract. of rosin	30.2	29.3	28.5	26.9	0
	32.0	31.2	29.8	27.6	6
	35.6	34.0	32.4	29.4	12
	36.8	35.1	33.3	32.1	18

Table 2. Continued

Samples composition	SFE,* mJ/m²				Temperature duration, h
	Time after surface cleaning, h				
	0	1	3	24	
BNKS-28 AMN + 2 mass fract. of rosin	31.9	30.2	27.8	24.4	0
	32.4	31.5	30.9	30.5	6
	34.8	33.2	31.6	29.7	12
	40.9	40.3	39.4	38.4	18
BNKS-28 AMN + 1 mass fract. of stearic acid	31.8	31.0	30.6	30.4	0
	25.5	25.0	24.5	23.9	6
	29.8	29.7	29.5	28.0	12
	28.1	27.6	25.9	24.6	18
BNKS-28 AMN + 2 mass fract. of stearic acid	31.5	31.3	30.8	29.4	0
	25.0	24.6	23.9	23.5	6
	31.5	30.9	30.2	29.6	12
	30.3	28.6	27.1	24.4	18

*Surface free energy determined by the OWRK method.

materials properties formation, we studied the accelerated aging conditions effect on the surface energy of NBR-based rubber samples without surfactants and containing 1 or 2 mass fractions of rosin or stearic acid. The samples were subjected to accelerated aging[6] at 100°C for 6, 12, and 18 h (Table 2).

In case of all the rubber samples, the dependence of the critical surface tension is nonlinear and passes through an extremum. This trend is basically preserved 24 h after cleaning the surface.

An analysis of the critical surface tension dependence on the thermal aging time for rubber samples based on SKN-26 SM indicates that in case of samples containing surfactants (rosin or stearic acid), the increase of the thermal aging time slightly decreases the SFE, while for a sample without a surfactant, SFE grows.

For rubber samples based on BNKS-28 AMN, the effect of thermal aging on surface properties is the least pronounced in most cases.

These results can be explained by the complex physicochemical processes occurring in the elastomeric material under the action of elevated temperature. Under such conditions, oxidation actively takes place. It is accompanied by the formation of polar groups, free radicals, and intermediate products, in particular, oxidation inhibitors. When heated, rubbers can form substances incompatible with unvulcanized rubber, and these substances can migrate to the surface. The complex of changes occurring in the polymer upon heating results in the change in the structure of the polymer matrix and significantly affects the surface properties. Just like for samples not exposed to temperature, the critical surface tension decreases as a result of the system tendency to the equilibrium state as the time elapsed after cleaning increases.

The above research results show that NBRs differing in the methods of production and in the technological additives content have various

[6] GOST ISO 188-2013. Interstate Standard. Vulcanized rubber and thermoplastics. Accelerated ageing and heat resistance tests. Moscow: Standartinform; 2014 (in Russ.).

surface properties. So, it was logical to assume that the factors affecting the surface properties also affect the physical and mechanical properties of vulcanizates.

As the analysis of the literature data [6, 7, 11, 17] shows, the emulsifier–coagulating agent systems used in the NBR synthesis affect the complex of rubber compounds and rubbers properties. In this work, a comparative assessment for the effect of rosin and stearic acid content on the physicomechanical, technical, and adhesive properties of elastomeric materials was carried out. Tables 3 and 4 present test results for vulcanizates based on two NBR grades: BNKS-28 AMN and SKN-26 SM. They have similar molecular weights and differ in the concentration of nonrubber impurities remaining in the rubbers commercially produced by emulsion polymerization. Considering that NBR-based rubbers are recommended for rubber products operating at elevated temperatures, vulcanizates subjected to the procedure of accelerated thermal-oxidative aging were studied (Table 4). In addition, the accelerated aging conditions have a significant effect on the polymer material structure, as a result of which both its surface and bulk properties change.

The data presented in Table 3 indicate that as the content of rosin and stearic acid increases to 2 mass fractions (per 100 mass fractions of rubber), the strength indicators level comparable to the base composition is preserved. In case of vulcanizates based on BNKS-28 AMN, an increase in their concentration resulted in the most significant changes in terms of relative and residual elongation and tear resistance; in case of rubbers based on SKN-26 SM—in terms of relative elongation. This is consistent with the data of [16]. An analysis of the indicators of vulcanizates subjected to the accelerated aging procedure demonstrates the preservation of the trends in changes in the elastic-strength properties identified for the original rubbers upon the introduction of rosin and stearic acid. At the same time, after aging, an increase in the relative tensile strength and hardness of the vulcanizates is observed. In this case, the relative and permanent elongation, elasticity and tear resistance decrease, which indicates the predominance of structuring processes in elastomeric materials under the action of elevated temperatures in the air.

The adhesive properties of rubbers were evaluated by the adhesive joints delamination method, in which the substrates—vulcanizates based on BNKS-28 AMN and SKN-26 SM—were glued together using a cold curing adhesive composition based on chloroprene rubber. According to the data obtained (Table 3),

Table 3. Influence of the kind and content of technological additives on the physical, mechanical, and operational characteristics of rubbers based on nitrile butadiene rubber

Indicators	Additives content				
	Without additives	Rosin		Stearic acid	
		1	2	1	2
BNKS-28 AMN					
Tensile strength, MPa	19.2 ± 2.1	18.3 ± 2.1	18.9 ± 1.9	18.6 ± 1.6	18.1 ± 1.8
Elongation at break, %	335 ± 30	345 ± 30	410 ± 38	315 ± 25	310 ± 24
Residual elongation, %	8.0 ± 0.9	9.0 ± 1.0	14.0 ± 1.5	9.0 ± 0.8	12.0 ± 1.1
Tear resistance, kN/m	23.0 ± 2.2	28.0 ± 2.9	30.0 ± 3.1	31.0 ± 2.7	24.0 ± 2.4
Rebound elasticity, %	19.0 ± 2.0	20.0 ± 2.0	21.0 ± 2.2	19.0 ± 1.8	19.0 ± 1.8
Shore hardness, A	62.0 ± 5.0	59.0 ± 5.0	60.0 ± 5.2	61.0 ± 5.1	60.0 ± 5.0
Adhesion strength, kN/m	2.0 ± 0.22	2.5 ± 0.23	2.8 ± 0.25	1.8 ± 0.16	1.7 ± 0.20

Table 3. Continued

Indicators	Additives content				
	Without additives	Rosin		Stearic acid	
		1	2	1	2
SKN-26 SM					
Tensile strength, MPa	19.4 ± 2.4	19.4 ± 2.4	20.0 ± 2.7	18.9 ± 2.7	18.7 ± 2.7
Elongation at break, %	300 ± 28	340 ± 33	380 ± 36	275 ± 25	285 ± 21
Residual elongation, %	8.0 ± 0.9	8.0 ± 1.0	8.0 ± 1.1	8.0 ± 0.7	8.0 ± 0.7
Tear resistance, kN/m	25.0 ± 2.8	23.0 ± 2.8	24.0 ± 2.9	23.0 ± 3.2	23.0 ± 3.0
Rebound elasticity, %	15.0 ± 1.4	14.0 ± 1.4	14.0 ± 1.4	17.0 ± 2.0	16.0 ± 1.8
Shore hardness, A	63.0 ± 4.4	62 ± 5.0	61.0 ± 5.1	62 ± 5.0	64 ± 5.8
Adhesion strength, kN/m	2.5 ± 0.20	3.2 ± 0.26	3.1 ± 0.29	2.2 ± 0.20	2.2 ± 0.21

Table 4. Influence of the kind and content of technological additives on the physical, mechanical and operational characteristics of rubbers based on nitrile butadiene rubber subjected to accelerated aging

Indicators	Additives content				
	Without additive	Rosin		Stearic acid	
		1	2	1	2
BNKS-28 AMN					
Tensile strength, MPa	21.1 ± 2.0	18.9 ± 1.8	19.5 ± 1.9	20.7 ± 1.9	20.1 ± 2.0
Elongation at break, %	320 ± 33	330 ± 33	390 ± 38	300 ± 31	290 ± 30
Residual elongation, %	7.0 ± 0.7	8.0 ± 0.8	12.0 ± 1.3	8.0 ± 0.7	10.0 ± 0.9
Tear resistance, MPa	21.0 ± 2.2	25.0 ± 2.7	27.0 ± 2.8	28.0 ± 2.6	22.0 ± 2.0
Rebound elasticity, %	17.0 ± 1.7	18.0 ± 1.9	19.0 ± 1.9	17.0 ± 1.7	18.0 ± 1.7
Shore hardness, A	64.0 ± 6.5	60.0 ± 6.2	61.0 ± 6.2	64.0 ± 6.3	63.0 ± 6.0

Table 4. Continued

Indicators	Additives content				
	Without additive	Rosin		Stearic acid	
		1	2	1	2
SKN-26 SM					
Tensile strength, MPa	21.8 ± 1.7	20.0 ± 1.9	20.6 ± 1.9	21.0 ± 1.9	20.8 ± 1.8
Relative extension, %	290 ± 23	320 ± 29	360 ± 31	260 ± 23	270 ± 25
Elongation at break, %	7.0 ± 0.6	8.0 ± 0.7	8.0 ± 0.7	7.0 ± 0.6	7.0 ± 0.6
Tear resistance, MPa	24.0 ± 1.9	21.0 ± 1.9	22.0 ± 2.0	21.0 ± 1.5	21.0 ± 1.6
Rebound elasticity, %	14.0 ± 1.1	13.0 ± 1.1	13.0 ± 1.2	16.0 ± 1.5	15.0 ± 1.3
Shore hardness, A	66.0 ± 5.3	63.0 ± 5.5	62.0 ± 5.4	65.0 ± 4.8	67.0 ± 4.9

vulcanizates based on paraffin rubber demonstrated a lower level of adhesive properties in the entire range of rosin and stearic acid content. The positive effect of rosin on the delamination resistance index of samples of adhesive joints was predictable, given the ability of rosin to increase the elastomeric materials adhesiveness and gummosity [2]. At the same time, the introduction of stearic acid deteriorated a little the adhesive properties of the studied rubbers. The noted regularities in the change in adhesive strength upon increasing the concentration of technological additives and depending on the grade of NBR used in the elastomeric substrates can be explained by the migration of these components to the rubber surface and by the effects of intermolecular interaction of the nitrile groups of rubber with molecules of the introduced acid and fatty acid salts already contained in NBR. This decreases the share of “free” nitrile groups and the polarity of the substrate surface (Table 1), and, consequentially, this decreases the intensity of physicochemical interactions at the polychloroprene–NBR rubber interface of the adhesive film.

Traditionally, higher carboxylic acids and their derivatives having a biphilic nature are used in the composition of elastomeric compositions as ingredients of polyfunctional action. Fatty acids and their salts acting as dispersants and mollifiers/plasticizers improve the compositions processability and the distribution quality of rubber compound ingredients, positively affecting the vulcanizates properties complex [2]. Being activators of diene rubbers vulcanization with sulfur-containing vulcanizing systems, they affect the o vulcanization kinetics and the vulcanization network structure, and they have a significant effect on the complex of technical properties of rubbers [2, 3, 5]. However, it is known [17] that the activators action mechanisms of the sulfur-containing vulcanizing system in NBRs fundamentally differ from those known for unsaturated nonpolar rubbers. Analysis of the data (Tables 3 and 4) indicates a significant role of nonrubber impurities—fatty acid salts in NBRs—in the formation of a set of properties of elastomeric materials. This role is determined by the conditions of their industrial synthesis. This analysis requires additional deeper study using modern physicochemical research methods.

CONCLUSIONS

The method for evaluating the surface properties of elastomeric materials based on NBRs makes it possible to purposefully control the strength and adhesion properties of vulcanizates, their resistance to aging by introducing technologically active additives. Comparison of the obtained results showed that the change in the physical and mechanical properties of vulcanizates, depending on the content of technological additives and the effect of temperature, is accompanied by a change in the critical surface tension. This, as expected, is caused by migration of the low molecular weight additive to the surface, which leads to a cumulative change in both surface and bulk properties of elastomeric materials. During operation, especially under the temperature influence, the migration of components increases and changes the surface state. This can be monitored by the change in the surface energy. The accumulation of the certain amount of statistical data concerning the effect of accelerated aging on the properties of vulcanizates based on various rubbers and concerning the change in critical surface tension will make it possible to judge not only the change in surface properties, but also the rubber product physical and mechanical characteristics and, thus, to control its condition under operation.

Authors' contributions

O.A. Dulina – development of the research concept, formulation and discussion of the experiment results;

E.V. Eskova – analysis and processing the data obtained, discussion of the experiment results;

A.D. Tarasenko – study of surface properties of the samples, data collection and processing, and formatting the text of the article;

S.V. Kotova – study of the physical and mechanical properties of samples, discussion of the experiment results.

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About the authors:

Olga A. Dulina, Cand. Sci. (Chem.), Associate Professor, Department of Nanoscale Systems and Surface Phenomena, M.V. Lomonosov Institute of Fine Chemical Technologies, MIREA – Russian Technological University (86, Vernadskogo pr., Moscow, 119571, Russia). E-mail: doa1503991@yandex.ru. https://orcid.org/0000-0002-2990-4447

Evgeniya V. Eskova, Senior Lecturer, Department of Nanoscale Systems and Surface Phenomena, M.V. Lomonosov Institute of Fine Chemical Technologies, MIREA – Russian Technological University (86, Vernadskogo pr., Moscow, 119571, Russia). E-mail: eskovae@rambler.ru. https://orcid.org/0000-0003-2536-1884

Alina D. Tarasenko, Assistant, Department of Nanoscale Systems and Surface Phenomena, M.V. Lomonosov Institute of Fine Chemical Technologies, MIREA – Russian Technological University (86, Vernadskogo pr., Moscow, 119571, Russia). E-mail: ad_abramova@mail.ru. https://orcid.org/0000-0002-5457-0506

Svetlana V. Kotova, Cand. Sci. (Eng.), Associate Professor, F.F. Koshelev Department of Chemistry and Technology of Elastomers Processing, M.V. Lomonosov Institute of Fine Chemical Technologies, MIREA - Russian Technological University (86, Vernadskogo pr., Moscow 119571, Russia). E-mail: s.v.kotova@mail.ru. https://orcid.org/0000-0002-7076-4669

Об авторах:

Дулина Ольга Анатольевна, к.х.н., доцент кафедры наноразмерных систем и поверхностных явлений им. С.С. Воюцкого Института тонких химических технологий им. М.В. Ломоносова ФГБОУ ВО «МИРЭА – Российский технологический университет» (119571, Россия, Москва, пр-т Вернадского, д. 86). E-mail: doa1503991@yandex.ru. https://orcid.org/0000-0002-2990-4447

Еськова Евгения Владимировна, старший преподаватель кафедры наноразмерных систем и поверхностных явлений им. С.С. Воюцкого Института тонких химических технологий им. М.В. Ломоносова ФГБОУ ВО «МИРЭА – Российский технологический университет» (119571, Россия, Москва, пр-т Вернадского, д. 86). E-mail: eskovae@rambler.ru. https://orcid.org/0000-0003-2536-1884

Тарасенко Алина Дмитриевна, ассистент кафедры наноразмерных систем и поверхностных явлений им. С.С. Воюцкого Института тонких химических технологий им. М.В. Ломоносова ФГБОУ ВО «МИРЭА – Российский технологический университет» (119571, Россия, Москва. пр-т Вернадского, д. 86). E-mail: ad_abramova@mail.ru. https://orcid.org/0000-0002-5457-0506

Котова Светлана Владимировна, к.т.н., доцент кафедры Химии и технологии переработки эластомеров им. Ф.Ф. Кошелева Института тонких химических технологий им. М.В. Ломоносова ФГБОУ ВО «МИРЭА – Российский технологический университет» (119571, Россия, Москва. пр-т Вернадского, д. 86). E-mail: s.v.kotova@mail.ru. https://orcid.org/0000-0002-7076-4669

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