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RESEARCH ARTICLE

Natural and synthetic isoprene rubbers obtained using Ziegler–Natta catalysts

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Abstract

Objectives. To compare the properties of rubber compounds and rubbers based on natural rubber RSS1 and synthetic isoprene rubbers obtained using Ti, Nd, Gd catalysts, both when used individually in the formulation of rubber compounds and when synthetic analogues partially replace natural rubber.

Methods. Rubber compounds were prepared using a laboratory roll and a 100 cm^3 rubber mixer. For rubber compounds, the following factors were determined: Mooney viscosity, cohesive strength, and vulcanization characteristics. For rubbers, the following factors were determined: physical and mechanical parameters, Shore A hardness, rebound resilience, and volume loss upon abrasion.

Results. Based on the results of the rubber compound tests, the study showed that compounds based on all the synthetic polyisoprenes studied are significantly inferior to compounds based on natural rubber in terms of cohesive strength. The partial replacement of natural rubber with synthetic rubber (regardless of the type of catalytic system) leads to a significant decrease in the cohesive strength of the blends. Despite the differences observed in the properties of the rubber compounds, the results of the rubbers based on individual rubbers do not manifest significant differences.

Conclusions. The study demonstrated the influence of defects (oligomers, gel, low molecular weight fractions, branches, and 3,4-units) in the structure of synthetic polyisoprenes on the cohesive strength index of rubber compounds based on them, in which the number of 3,4-units plays a decisive role. The study also showed the potential of studying synthetic polyisoprenes as analogues of natural rubber in formulations of rubber compounds in the aims of resolving the problem of import substitution in the tire and rubber goods industry.

Keywords

natural rubber, synthetic isoprene rubber, carbon black, rubber compound, Mooney viscosity, cohesive strength, rubber

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НАУЧНАЯ СТАТЬЯ

Натуральный и синтетические изопреновые каучуки, полученные с использованием катализаторов Циглера–Натта

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Аннотация

Цели. Сравнение свойств резиновых смесей и резин на основе натурального каучука RSS1 и синтетических изопреновых каучуков, полученных с использованием Ti, Nd, Gd катализаторов, как при индивидуальном использовании в рецептуре резиновых смесей, так и при частичной замене натурального каучука синтетическими аналогами.

Методы. Резиновые смеси изготавливали с использованием лабораторных вальцев и резиносмесителя объемом 100 см^3. Для резиновых смесей определяли вязкость по Муни, когезионную прочность и вулканизационные характеристики, для резин — физико-механические показатели, твердость по Шору А, эластичность по упругому отскоку и потерю объема при истирании.

Результаты. На основании результатов испытаний резиновых смесей показано, что смеси на основе всех исследованных синтетических полиизопренов значительно уступают по когезионной прочности смеси на основе натурального каучука, при этом частичная замена натурального каучука синтетическим (независимо от типа каталитической системы) приводит к существенному снижению когезионной прочности смесей. Несмотря на выявленные различия в свойствах резиновых смесей, показатели резин на основе индивидуальных каучуков не имеют значительных различий.

Выводы. Показано влияние «дефектов» структуры (олигомеры, гель, низкомолекулярные фракции, разветвления, 3,4-звенья) синтетических полиизопренов на показатель когезионной прочности резиновых смесей на их основе, из которых решающую роль играет количество 3,4-звеньев. Показана перспективность исследования синтетических полиизопренов в качестве аналога натурального каучука в рецептурах резиновых смесей для решения проблемы импортозамещения в промышленности шин и резинотехнических изделий.

Ключевые слова

натуральный каучук, синтетический изопреновый каучук, технический углерод, резиновая смесь, вязкость по Муни, когезионная прочность, резина

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INTRODUCTION

In 2020, the Moscow Institute of High Chemical Technologies marked the 120th anniversary of its foundation [1]. In 2022, another anniversary was marked: one of the oldest departments of this Institute—the F.F. Koshelev Chemistry and Technology of Elastomer Processing—celebrated its 90th anniversary. The study of the "synthesis of rubbers–structure–properties–application" chain in rubbers has always been one of the traditional directions of scientific research of the department. An invaluable contribution to this field was made by the works of such outstanding staff members as F.F. Koshelev, A.E. Kornev, I.T. Gridunov, and A.M. Bukanov. The department is currently continuing its work on the study of rubbers of both general [2–6] and special purpose [7–11].

One of the main rubbers in the production of tires and rubber products is polyisoprene. Due to the features of its structure [12], synthetic isoprene rubber (IR) is significantly inferior to natural rubber (NR) in a number of properties. This is especially important for the tire industry since rubber compounds based on it have low cohesive strength, and rubbers are characterized by a higher level of hysteresis losses and low tear

resistance [13]. The molecular colloidal structure of polyisoprene has a decisive influence on its ability to crystallize. Detailed study has shown that even a small proportion of structural inhomogeneities significantly reduces the ability of rubber to crystallize. The half-life of polyisoprene crystallization increases by almost an order of magnitude as the content of *cis*-1,4 units decreases from 98 to 95% [14].

Another significant element is the location of the raw material base. NR is a scarce imported product, and synthetic polyisoprene is produced by factories located in Russia: *Nizhnekamskneftekhim*, *Tolyattikauchuk*, and *Syntez-Kauchuk*. The pricing of natural and synthetic polyisoprenes substitutes is characterized by cross demand, raising the important question of creating a full-fledged synthetic analog of NR.

Over the past 60 years, several ways have been identified to resolve this problem: the search for alternative raw materials in the production of NR [15], the introduction of protein components into synthetic polyisoprene [16, 17], the chemical modification of IR at the stages of rubber synthesis [18], or the introduction of active functional compounds in the production of rubber compounds. All of these methods have their advantages and disadvantages. However, so far none of them have been implemented on an industrial scale, with the exception of the industrial production of titanium IR (Ti–IR) (with a capacity of up to 60000 t) modified with *para*-nitrosodiphenylamine, in the 1970s at the *Kuibyshev Synthetic Rubber Plant* [13, 19].

The development of synthetic polyisoprene production technology should not be forgotten. The search for new catalytic systems and improved synthesis of IRs have always been aimed at reproducing the properties of standard NR due to its unique characteristics: the highest possible content of *cis*-1,4 bonds, the presence of solid phase branching, high linearity of the chains, absence of side groups and branching.

The production of stereoregular synthetic IR commenced in 1964. It was based on a titanium catalytic system at the *Kuibyshev Synthetic Rubber Plant* (Tolyatti) and at the *Volga Synthetic Rubber Plant* [13, 20], then at the *Sterlitamak Synthetic Rubber Plant*, *Nizhnekamskneftekhim*, and *Yaroslavl Synthetic Rubber Plant*. Almost 60 years have passed, during which time a lot of work has been carried out aimed at eliminating the disadvantages of Ti–IR and bringing its properties closer to NR. A large number of studies have been conducted at these industrial production facilities, resulting in the transition to a low-temperature catalyst (*Nizhnekamskneftekhim*), the introduction of modified (three-component) catalytic systems, catalytic complexes. These studies also led to an increase in the quality of rubber, uniformity, stereoregularity, and a decrease in the content of gel and oligomers.

Since 2000, there has been a decrease in the production of Ti–IR in the world due to the establishment of production facilities for synthetic polyisoprene using catalytic systems based on rare earth metals. Neodymium (Nd) IR has a number of undoubted advantages: the absence of gel, oligomers, and a slightly higher molecular weight [21].

Although Russia is a pioneer in the field of research and implementation of new catalytic systems in the production of synthetic rubbers (the work of the Research Institute of Synthetic Rubber devoted to the study of lanthanide catalytic systems dates back to the 1970s and 1980s), there is a low level of Nd–IR production. However, in China, three-quarters of the IR produced is based on the Nd catalyst. This difference is quite understandable given that China is currently the main producer and importer of Nd oxide in the world—the main component in the production of a catalyst.

Among the currently known catalysts based on rare earth elements, the synthesis of polyisoprene on gadolinium (Gd) catalysts appears to be most attractive due to its lower cost relative to the Nd catalyst, low costs for the implementation of the process, and the high quality of the rubber obtained [22].

MATERIALS AND METHODS

Gd–IR and Nd–IR (*Sintez-Kauchuk*, Sterlitamak, Russia) obtained using rare-earth catalysts were selected as the objects of research (Table 1). Comparison objects were RSS1 NR (*PT. Pinago Utama Tbk*, Indonesia) and Ti–IR (*Sintez-Kauchuk*, Sterlitamak, Russia).

The rubber mixtures used to establish cohesive strength and Mooney viscosity contained only elastomeric base and carbon black. The study also examined not only rubber compounds based on individual rubbers, but also blended combinations of RSS1 with other investigated polyisoprenes, the content of which was varied from 10 to 90 pts. wt. in 10 pts. wt. increments.

Before mixing, all rubbers were decrystallized in the SNOL 60/300 drying cabinet (*SNOL-TERM*, Tver, Russia) at a temperature of 70°C for 1 h. Rubber plasticization was carried out on an LB 250 100/100 laboratory roll (*L.B. Krasin Kostroma Plant of Polymer Engineering*, Kostroma, Russia) at a temperature of 100°C for 2 min. After plasticization, the rubber was loaded into a Benbury-type rubber mixer (*Rubber Industry Research Institute*, Sergiev Posad, Russia) with a chamber volume of 100 cm^3. Carbon black N330 (*YATU named after V.Yu. Orlov,* Yaroslavl, Russia) (35 pts. wt. per 100 pts. wt. of rubber) was then added and mixed at 100°C. The rubber mixture was discharged after 2.5 min and then homogenized on the LB 250 100/100 roll.

The Mooney viscosity of rubber compounds was determined in accordance with DIN 53523 (Parts 2, 3, and 4) using a MV 3000 Basic Mooney viscometer

Table 1. Specifications of polyisoprenes *Sintez-Kauchuk*

Parameters	Gd–IR	Nd–IR	Ti–IR
Mooney viscosity ML 1+4 (100°C)	73.0	75.0	71.0
Loss on drying, %	0.13	0.27	0.39
Content of 3,4-units, %	1.0	2.1	0.8
Glass transition temperature, °C	−56.6	−56.8	−59.4
Molecular weight characteristics			
Number average molecular weight $M_n \cdot 10^{-3}$	361	327	288
Weight average molecular weight $M_w \cdot 10^{-3}$	1603	1592	1125
Average molecular weight $M_z \cdot 10^{-3}$	3635	2540	2539
Polydispersity coefficient M_w/M_n	4.4	4.9	3.9
Branching factor g_f	0.947	0.945	0.954
Fractional composition			
>1000000	48.5	49.0	38.5
500000–1000000	20.5	20.0	22.5
100000–500000	24.0	24.0	31.0
<100000	7.0	7.0	8.0

(*MonTech*, Buchen, Germany). The cohesive strength was determined according to the ASTM D 6746-15 "Standard Method for determining the cohesive Strength and Stress Relaxation of Crude Rubber or Non-vulcanized Rubber Compounds" using a AI-3000-U universal testing machine (*GOTECH Testing Machines Inc*. and *UGNLAB Testing Equipment,* Taichung, Taiwan).

In order to determine the physical, mechanical, and operational properties of rubbers based on individual rubbers, rubber mixtures of the following composition (per 100.0 pts. wt. of rubber) were made: stearic acid (*VitaHim*, Dzerzhinsk, Russia)—2.0 pts. wt., zinc oxide (*Empils-zinc*, Rostov-on-Don, Russia)—5.0 pts. wt., zinc oxide (*Empils-zinc*, Rostov-on-Don, Russia)—5.0 pts. wt., Sulfenamide C (*VitaHim*, Dzerzhinsk, Russia)—0.7 pts. wt., carbon black N330 (*YATU named after V.Yu. Orlov*, Yaroslavl, Russia)—35.0 pts. wt., sulfur (*VitaHim*, Dzerzhinsk, Russia)—2.25 pts. wt.

The procedure of decrystallization of rubbers prior to mixing was similar to that previously described. The plasticization of rubber and the manufacture of rubber mixtures were carried out on the LB 320 160/160 roll (*Metallist*, Russia) according to ASTM D3184-11—for NR, and according to GOST 14925-79[1]—for synthetic polyisoprenes.

The vulcanization characteristics of rubber compounds were determined at 150°C using an MDR3000 rotor-free rheometer (*MonTech*, Buchen, Germany) according to ISO 6502 (ASTM D 5289, DIN 53529).

The rubber samples were vulcanized in a hydraulic vulcanization press with electric heating of the plates at a temperature of 150°C during the optimal vulcanization time.

[1] GOST 14925-79. State Standard of the USSR. Synthetic *cis*-isoprene rubber. Technical conditions. Moscow: Izdatel'stvo standartov; 1988.

The physico-mechanical properties of rubbers were determined on the AI-3000-U universal testing machine according to GOST 270-75[2]. The elasticity by elastic rebound was established using the GT-7042-RDA (*GOTECH Testing Machines Inc*. and *UGNLAB Testing Equipment*, Taichung, Taiwan) apparatus according to DIN 53512 (ISO 4662). Shore A hardness was determined using the HT3000 device (*MonTech*, Buchen, Germany) according to ASTM D 2240 (DIN 53505). Rubber abrasion resistance when sliding on a renewable surface was established using the ABR3000 device (*MonTech*, Buchen, Germany) according to DIN 53516 (ISO 4649:2002 (E)).

RESULTS AND DISCUSSION

Figure 1 shows the test results of rubber compounds based on individual rubbers.

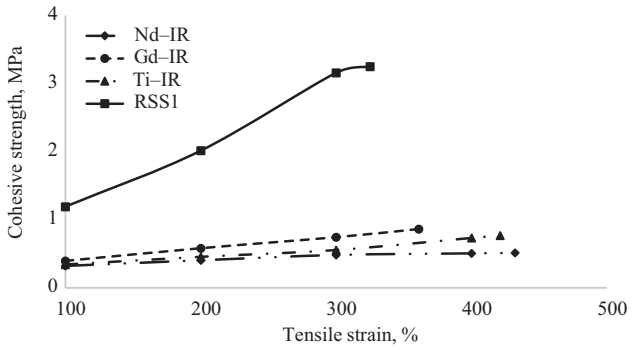

Fig. 1. Cohesive strength of rubber compounds based on RSS1 and synthetic polyisoprenes

The results obtained correlate well with the data available in literature. The significant tendency of NR to crystallization explains the high cohesive strength of the RSS1-based rubber compound. This significantly exceeds the values of this indicator for mixtures based on all the considered synthetic polyisoprenes. It should also be noted that there are practically no differences in the indicators of cohesive strength between rubbers obtained on the basis of Ti and Nd catalysts. The slightly higher values for Gd–IR can generally be attributed to the measurement error of the device.

Due to their frequent use in real rubber formulations, mixed compositions of synthetic polyisoprenes with RSS1 NR were also considered. The graphical dependencies of cohesive strength and Mooney viscosity are shown in Figs. 2–4.

A significant variation in both the Mooney viscosity and cohesive strength is most probably related to the method of manufacturing mixtures. The rolling process has a significant effect on the molecular weight of rubbers.

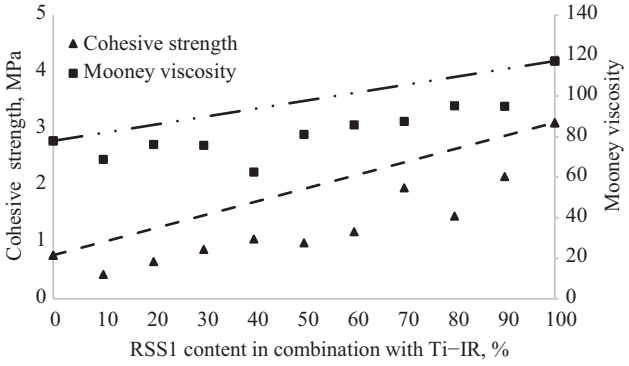

Fig. 2. Dependence of cohesive strength and Mooney viscosity of rubber mixtures based on combination of Ti–IR and RSS1 rubbers on RSS1 content

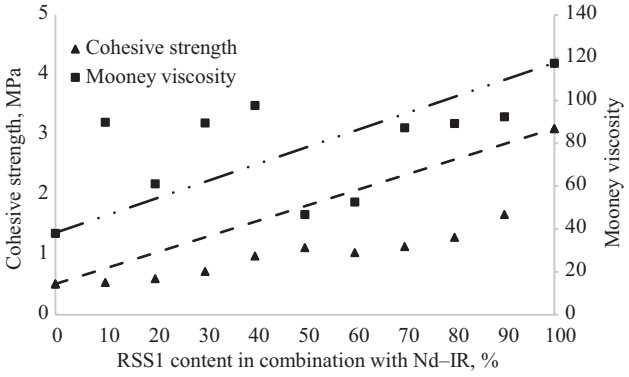

Fig. 3. Dependence of cohesive strength and Mooney viscosity of rubber mixtures based on combination of Nd–IR and RSS1 rubbers on RSS1 content

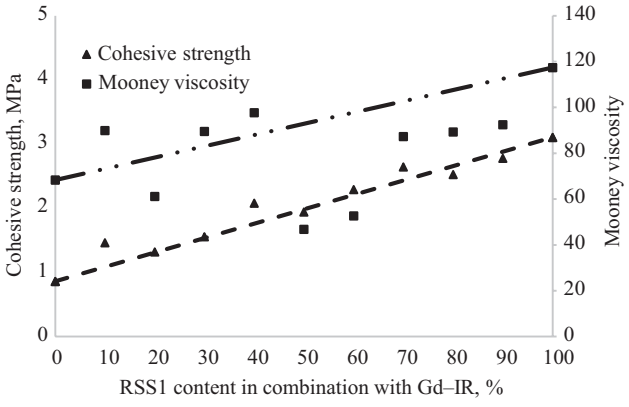

Fig. 4. Dependence of cohesive strength and Mooney viscosity of rubber mixtures based on combination of Gd–IR and RSS1 rubbers on RSS1 content

[2] GOST 270-75. Interstate Standard. Rubber. Method for determining elastic-strength properties under tension. Moscow: Standartinform; 2008.

This weight decreases due to the predominant process of mechanical destruction. A decrease in molecular weight leads to a decrease in the considered indicators [23]. It is also important to note the significant deviation of the experimental values of the indicators from the straight line, based on the principle of additivity for mixed compositions. The replacement of even 10% NR results in a significant decrease in cohesive strength. A slightly different picture is observed in mixtures with Gd–IR. In this case the deviations from the straight line, built on the principle of additivity, as significantly smaller.

For both individual rubbers and mixed compositions, a decrease in the cohesive strength of rubber compounds is associated with defects in the structure of synthetic polyisoprenes (oligomers, gel, low molecular weight fractions, branching, 3,4-links). The use of Nd-catalytic systems in comparison with Ti-catalysts has made it possible to completely remove gel, *trans*-1,4-links, and head-to-head and tail-to-tail type connections from rubber. However, the content of 3,4-links increased. Synthetic polyisoprene, obtained on the basis of the Gd-catalytic system, does not contain gel, and the content of 3,4-links is lower when compared to Nd-rubber. The results obtained confirm that the content of 3,4-links plays an important role in reducing the tendency of IRs to crystallization.

In order to study the effect of the type of rubber on the properties of rubbers, we selected standard formulations of rubber mixtures. The vulcanization characteristics are shown in Fig. 5 and in Table 2.

In practice, the results obtained do not differ from each other for all polyisoprenes. The slightly higher vulcanization rate of Ti–IR is probably due to the presence of oligomers and gel in the rubber.

The results of the physico-mechanical and certain operational properties of rubbers also indicate the absence of any significant differences between the rubbers under consideration (Fig. 6 and 7).

The values of these indicators are decisively influenced by the presence of an active filler in the formulation of rubber compounds.

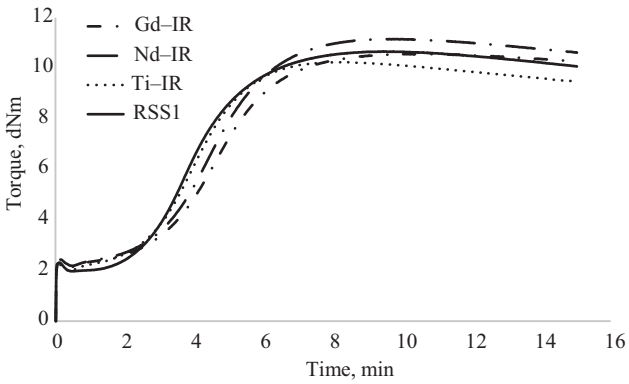

Fig. 5. Vulcanization properties of rubber compounds based on various polyisoprenes

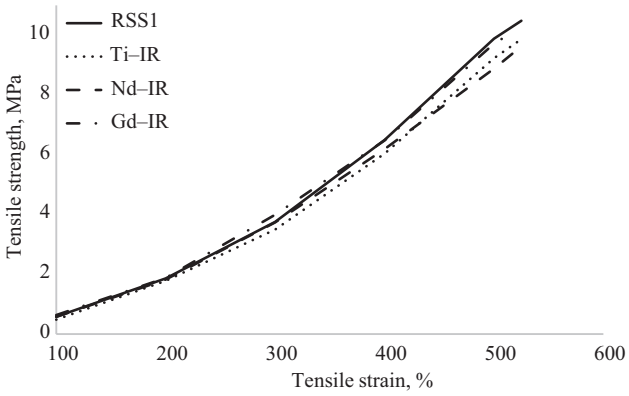

Fig. 6. Dependence of conditional stress on the relative elongation of rubber

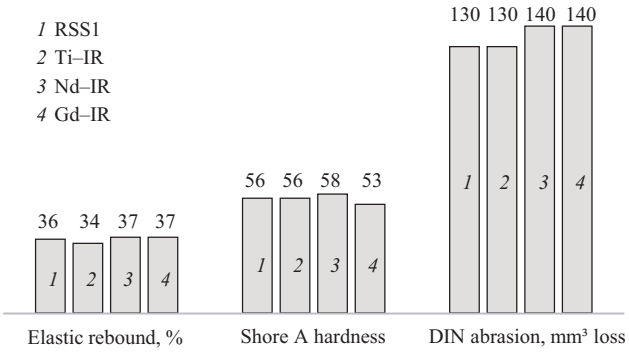

Fig. 7. Performance properties of rubbers based on various polyisoprenes

Table 2. Vulcanization characteristics of rubber compounds (test temperature 150°C)

Mixture	S'_{min}	S'_{max}	$S'_{max} - S'_{min}$	Scorch time	t_{C90}
RSS1	1.97	10.66	8.69	2.51	6.11
Ti–IR	1.99	10.24	8.25	2.4	5.69
Nd–IR	2.18	11.15	8.97	2.66	6.56
Gd–IR	2.13	10.57	8.44	2.76	6.71

Note: S'_{min} is the minimum torque, S'_{max} is the maximum torque, $S'_{max} - S'_{min}$ is the difference between the maximum and minimum torques, and t_{C90} is the optimal vulcanization time.

CONCLUSIONS

Unfortunately, due to the lack of dynamic test results, the work performed on comparing polyisoprenes is incomplete. Thus is does not allow us to draw comprehensive conclusions about the effect of the type of catalyst used in the synthesis of synthetic polyisoprene on the properties of rubber compounds and rubbers.

However, the study suggests the possible potential of using gadolinium in the production of IR both from an economic point of view, and also from the point of view of creating a more perfect microstructure. This is because the low tendency to crystallization and the high hysteresis losses of synthetic rubbers currently produced by the industry, in comparison with NRs, significantly limit their use in the tire industry. The volume of experimental data so far obtained forms the basis for further research in this area. This is especially important in the current situation, which requires methods of import substitution of expensive and often inaccessible foreign raw materials to be developed.

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Authors' contributions

A.A. Zuev—analyzing the literature on the research topic, performing experimental studies, discussing the results obtained, and writing the text of the article.

V.L. Zolotarev—initiation of the research and development of its concept, scientific advising, and making valuable scientific comments in the text of the article.

I.P. Levenberg—formulation of the problem and formulation of the research task, discussion of the results obtained.

L.A. Kovaleva—search and classification of literary sources, performance of experimental studies, design of the article in accordance with the requirements of the publishing house, and discussion of the obtained results.

I.Sh. Nasyrov—synthesis of polyisoprene prototypes, discussion of the results obtained.

The authors declare no conflicts of interest.

REFERENCES

1. Frolkova A.K. To the true benefit and glory of the Fatherland. *Fine Chem. Technol*. 2020;15(6):7–8 (in Russ.). https://doi.org/10.32362/2410-6593-2020-15-6-7-8
2. Zolotaryov V.L., Levenberg I.P., Kovaleva L.A. Long-benchmenal branches of macromolecules 1,4-*cis*-polybutadiene. *Promyshlennoe proizvodstvo i ispol'zovanie elastomerov = Industrial Production and Use of Elastomers*. 2018;2:19–22 (in Russ.). https://doi.org/10.24411/2071-8268-2018-10203
3. Zolotaryov V.L., Levenberg I.P., Kovaleva L.A., Zuev A.A., Lyusova L.R. *Cis*-1,4-polybutadiene and frost resistance of rubber based on it. *Promyshlennoe proizvodstvo i ispol'zovanie elastomerov = Industrial Production and Use of Elastomers*. 2020;3–4:3–7 (in Russ.). https://doi.org/10.24412/2071-8268-2020-3-4-3-7
4. Zolotaryov V.L., Levenberg I.P., Zuev A.A., Kovaleva L.A., Lyusova L.R., Lipatova A.A. Once again about *cis*-1.4-polyisoprene rubber. *Promyshlennoe proizvodstvo i ispol'zovanie elastomerov = Industrial Production and Use of Elastomers*. 2021;2:3–9 (in Russ.). https://doi.org/10.24412/2071-8268-2021-2-03-09
5. Lyusova L.R., Chernyshov S.V. Study of the possibility of modifying synthetic polyisoprene by combining it with a highly cohesive polymer. *Promyshlennoe proizvodstvo i ispol'zovanie elastomerov = Industrial Production and Use of Elastomers*. 2022;1:40–44 (in Russ.). https://doi.org/10.24412/2071-8268-2022-1-40-44
6. Chernyshov S.V., Lyusova L.R., Makhmudova S.R., Zolotaryov V.L. The effect of 1,2-polybutadiene on the properties of elastomeric materials made of synthetic polyisoprene. *Kauchuk i rezina*. 2023;82(2):66–70 (in Russ.). https://doi.org/10.47664/0022-9466-2023-82-2-66-70

СПИСОК ЛИТЕРАТУРЫ

1. Фролкова А.К. К истинной пользе и славе Отечества. *Тонкие химические технологии*. 2020;15(6):7–8. https://doi.org/10.32362/2410-6593-2020-15-6-7-8
2. Золотарев В.Л., Левенберг И.П., Ковалева Л.А. Длинноцепочечные разветвления макромолекул 1,4-*цис*-полибутадиена. *Промышленное производство и использование эластомеров*. 2018;2:19–22. https://doi.org/10.24411/2071-8268-2018-10203
3. Золотарев В.Л., Левенберг И.П., Ковалева Л.А., Зуев А.А., Люсова Л.Р. *Цис*-1,4-полибутадиен и морозостойкость резин на его основе. *Промышленное производство и использование эластомеров*. 2020;3–4:3–7. https://doi.org/10.24412/2071-8268-2020-3-4-3-7
4. Золотарев В.Л., Левенберг И.П., Зуев А.А., Ковалева Л.А., Люсова Л.Р., Липатова А.А. Еще раз о 1,4-*цис*-полиизопренах. *Промышленное производство и использование эластомеров*. 2021;2:3–9. https://doi.org/10.24412/2071-8268-2021-2-03-09
5. Люсова Л.Р., Чернышов С.В. Изучение возможности модификации синтетического полиизопрена путем совмещения с высококогезионным полимером. *Промышленное производство и использование эластомеров*. 2022;1:40–44. https://doi.org/10.24412/2071-8268-2022-1-40-44
6. Чернышов С.В., Люсова Л.Р., Махмудова С.Р., Золотарев В.Л. Влияние 1,2-полибутадиена на свойства эластомерных материалов из синтетического полиизопрена. *Каучук и резина*. 2023;82(2):66–70. https://doi.org/10.47664/0022-9466-2023-82-2-66-70
7. Боброва И.И., Котова С.В., Наумова Ю.А. Исследование влияния стеарата кальция на свойства резиновых смесей и их вулканизатов на основе бутадиен-нитрильных каучуков. *Промышленное производства и использование эластомеров*. 2021;4:3–7. https://doi.org/10.24412/2071-8268-2021-4-3-7

7. Bobrova I.I.., Kotova S.V., Naumova Yu.A. Investigation of the calcium stearate influence on the rubber mixtures and their vulcanizates based on nitrile butadiene rubbers properties. *Promyshlennoe proizvodstvo i ispol'zovanie elastomerov = Industrial Production and Use of Elastomers*. 2021;4:3–7 (in Russ.). https://doi.org/10.24412/2071-8268-2021-4-3-7
8. Dulina O.A., Eskova E.V., Tarasenko A.D., Kotova S.V. Influence of various factors on surface properties of elastomeric materials based on nitrile butadiene rubbers. *Tonk. Khim. Tekhnol. = Fine Chem. Technol*. 2022;17(2):152–163 (Russ., Eng.). https://doi.org/10.32362/2410-6593-2022-17-2-152-163
9. Bobrova I.I., Sinelnikova L.N., Kotova S.V., Gamlitsky Yu.A. Adhesive properties of vulcanizates based on various butadiene-nitrile rubber grades investigation. *Kauchuk i rezina*. 2022;81(6):292–297 (in Russ.). https://doi.org/10.47664/0022-9466-2022-81-6-292-297
10. Bobrova I.I., Kotova S.V., Lyusova L.R., Zabuga N.N. Study of adhesion modifiers for rubbers based on nitrile butadiene rubber. *Promyshlennoe proizvodstvo i ispol'zovanie elastomerov = Industrial Production and Use of Elastomers*. 2022;2:18–23 (in Russ.). https://doi.org/10.24412/2071-8268-2022-2-18-23
11. Volkov A.O., Naumova Yu.A., Kozlova A.O., Konovalova K.D., Kovaleva L.A., Dorokhov A.V. The effect of aluminum-doped zinc oxide on the properties of an elastomeric composition based on nitrile rubber. *Izvestiya Kabardino-Balkarskogo gosudarstvennogo universiteta = Proceedings of the Kabardino-Balkarian State University*. 2022;XII(5):49–53 (in Russ.).
12. Tanaka Y., Kawahara S., Tangpakdee J. Structural characterization of natural rubber. *Kautschuk Gummi Kunststoffe*. 1997;50(1):6–11.
13. Zolotaryov V.L. "Titanic" IR. *Promyshlennoe proizvodstvo i ispol'zovanie elastomerov = Industrial Production and Use of Elastomers*. 2009;6:8–12 (in Russ.).
14. Vasil'ev V.A., Nasyrov I.Sh. *Otechestvennye promyshlennye stereoregulyarnye kauchuki. Issledovaniya i razrabotki* (*Domestic Industrial Stereoregular Rubbers. Research and Development*). Ufa: Gilem; 2018. 288 p. (in Russ.). ISBN 978-5-88185-426-3
15. Zolotaryov V.L. Once again about BR sodium butadiene rubber. *Promyshlennoe proizvodstvo i ispol'zovanie elastomerov = Industrial Production and Use of Elastomers*. 2010;4:3–6 (in Russ.).
16. Potapov E.E., Goncharova Yu.E., Imnadze E.G., Lonina N.I. Chemical modification of elastomers as a method for obtaining a synthetic analogue of NK. *Kauchuk i rezina*. 2004;1:48–57 (in Russ.).
17. Rakhmatullina A.P., Chan Kh.T., Potapov E.E. Effect of the amount of protein-lipid complexes acting as a modifier on the characteristics of synthetic polyisoprene vulcanisates. *Kauchuk i rezina*. 2019;78(6):350–355 (in Russ.).
18. Vasil'ev V.A., Khvostik G.M., Smirnov V.P., Morozov Yu.V., Nasyrov I.Sh., Bazhenov Yu.P., Slanevskii A.A. Modification of Isoprene rubber with maleic acid monoesters. *Kauchuk i rezina*. 2010;6:2–6 (in Russ.).
19. Boreyko N.P., Papkov V.N., Komarov E.V. Prerequisites for the development of a state_program to create an artificial analogue of natural rubber. *Kauchuk i rezina*. 2019;78(6):380–383 (in Russ.).
20. Masagutova L.V. Once more on polyisoprene. (Historical aspect). *Kauchuk i rezina*. 2015;2:44–47 (in Russ.).
21. Smirnova L.A., Kovalev N.F., Tsypkina I.M., Kormer V.A. Influence of the molecular characteristics of polyisoprene on the quality of mixing with carbon black and the properties of rubber compounds. *Kauchuk i rezina*. 1991;4:5–7 (in Russ.).
8. Дулина О.А., Еськова Е.В., Тарасенко А.Д., Котова С.В. Влияние различных факторов на поверхностные свойства эластомерных материалов на основе бутадиен-нитрильных каучуков. *Тонкие химические технологии*. 2022;17(2):152–163. https://doi.org/10.32362/2410-6593-2022-17-2-152-163
9. Боброва И.И., Синельникова Л.Н., Котова С.В., Гамлицкий Ю.А. Исследование адгезионных свойств резин на основе различных марок бутадиен-нитрильных каучуков. *Каучук и резина*. 2022;81(6):292–297. https://doi.org/10.47664/0022-9466-2022-81-6-292-297
10. Боброва И.И., Котова С.В., Люсова Л.Р., Забуга Н.Н. Исследование модификаторов адгезии для резин на основе бутадиен-нитрильного каучука. *Промышленное производство и использование эластомеров*. 2022;2:18–23. https://doi.org/10.24412/2071-8268-2022-2-18-23
11. Волков А.О., Наумова Ю.А., Козлова А.О., Коновалова К.Д., Ковалева Л.А., Дорохов А.В. Влияние оксида цинка, легированного алюминием, на свойства эластомерной композиции на основе бутадиен-нитрильного каучука. *Известия Кабардино-Балкарского государственного университета*. 2022;XII(5):49–53.
12. Tanaka Y., Kawahara S., Tangpakdee J. Structural characterization of natural rubber. *Kautschuk Gummi Kunststoffe*. 1997;50(1):6–11.
13. Золотарев В.Л. Российскому «титановому» СКИ – 45 лет. *Промышленное производство и использование эластомеров*. 2009;6:8–12.
14. Васильев В.А., Насыров И.Ш. *Отечественные промышленные стереорегулярные каучуки. Исследования и разработки*. Уфа: Гилем; 2018. 288 с. ISBN 978-5-88185-426-3
15. Золотарев В.Л. Еще раз о натрийбутадиеновом каучуке СКБ. *Промышленное производство и использование эластомеров*. 2010;4:3–6.
16. Потапов Е.Э., Гончарова Ю.Э., Имнадзе Е.Г., Лонина Н.И. Химическая модификация эластомеров как способ получения синтетического аналога НК. *Каучук и резина*. 2004;1:48–57.
17. Рахматтулина А.П. Чан Х.Т., Потапов Е.Э. Влияние количества белково-липидных комплексов, действующих в качестве модификатора, на характеристики резин на основе синтетического полиизопрена. *Каучук и резина*. 2019;78(6):350–355.
18. Васильев В.А., Хвостик Г.М., Смирнов В.П., Морозов Ю.В., Насыров И.Ш., Баженов Ю.П., Сланевский А.А. Модификация изопренового каучука моноэфирами малеиновой кислоты. *Каучук и резина*. 2010;6:2–6.
19. Борейко Н.П., Папков В.Н., Комаров Е.В. Предпосылки для разработки государственной программы создания искусственного аналога натурального каучука. *Каучук и резина*. 2019;78(6):380–383.
20. Масагутова Л.В. Еще раз о полиизопрене. (Исторический аспект). *Каучук и резина*. 2015;2:44–47.
21. Смирнова Л.А., Ковалев Н.Ф., Цыпкина И.М., Кормер В.А. Влияние молекулярных характеристик полиизопрена на качество смешения с техническим углеродом и свойства резиновых смесей. *Каучук и резина*. 1991;4:5–7.
22. Насыров И.Ш., Фаизова В.Ю., Жаворонков Д.А., Шурупов О.К., Васильев В.А. Натуральный и синтетический *цис*-полиизопрены. Часть 2. Свойства СКИ мировых производителей и российских торговых марок производства ОАО «Синтез-Каучук». *Промышленное производство и использование эластомеров*. 2020;3–4:45–55.
23. Куперман Ф.Е. *Новые каучуки для шин: приоритетные требования, методы оценки*. М.: Научно-технический центр «НИИШП»; 2005. 329 с. ISBN 5-98746-005-0

22. Nasyrov I.Sh., Faizova V.Yu., Zhavoronkov D.A., Shurupov O.K., Vasiliev V.A. Natural rubber and synthetic *cis*-polyisoprene. Part 2. Properties of polyisoprenes of global manufacturers and Russian brands production of *Sintez-Kauchuk*. *Promyshlennoe proizvodstvo i ispol'vanie elastomerov = Industrial Production and Use of Elastomers*. 2020;3–4:45–55 (in Russ.).
23. Kuperman F.Ye. *Novye kauchuki dlya shin: prioritetnye trebovaniya, metody otsenki* (*New Rubbers for Tires: Priority Requirements, Evaluation Methods*). Moscow: NIIShP; 2005. 329 p. (in Russ.). ISBN 5-98746-005-0

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