

UDC 678.4:661.183:66.094:504.054

L.O. Sokolova^a, *V.I. Ovcharov*^a, *T.V. Hridnieva*^a, *O.A. Tertishniy*^b, *V.O. Tyshchenko*^c**ELASTOMERIC COMPOSITIONS WITH RICE HUSK-BASED BIO-INGREDIENTS**^a Ukrainian State University of Science and Technologies, Dnipro, Ukraine^b Dnipro State Agrarian and Economic University, Dnipro, Ukraine^c Zaporizhzhia National University, Zaporizhzhia, Ukraine

In the context of the global growth of green chemistry and the circular economy, the use of crushed rice husk (CRH) as a bio-ingredient in elastomeric compositions offers an environmentally sustainable alternative. It has been found that modification of the husk with surfactants, in particular the cationic quaternary ammonium salt (QAS-4) synthesized from sugar-industry biowaste, significantly improves the interaction between the husk and the rubber matrix, increases the degree of crosslinking, and enhances the physical and mechanical properties of the rubbers, such as tear and heat resistance. Experimental results showed that compositions with CRH modified with QAS-4 demonstrate advantages in processability, including preservation of the rubber compound's plasticity and acceleration of sulfur vulcanization, as well as improved performance characteristics of industrial rubbers compared with traditional fillers. The use of CRH, especially in a modified form, is a promising direction for creating environmentally friendly and cost-effective elastomeric compositions.

Keywords: elastomer composition, bio-ingredient, rice husk, quaternary ammonium salt, properties of rubber compounds and rubbers, renewable bioresource, environmental safety.

DOI: 10.32434/0321-4095-2026-164-1-30-41

Introduction

The use of rice husks as an ingredient of elastomeric compositions is a promising area, primarily in the context of reducing the anthropogenic impact on the ecosystem. Unlike traditional mineral fillers (white soot and carbon black), which are produced using energy-intensive processes with significant carbon dioxide (CO₂) emissions, rice husk is a renewable resource with a low carbon footprint. In addition, the production of carbon black and white soot has been identified as emitting sulfur dioxide (SO₂), nitrogen oxides (NO_x), polycyclic aromatic hydrocarbons, and

solid particles [1].

Recent studies confirm the reduced dependence on petrochemical products and contribution to the circular economy while using bio-waste in polymeric materials [2].

Before its partial occupation, Ukraine was one of the largest rice producers in Europe, so rice husks were a local resource available for processing. In times of war, when the supply of traditional fillers (e.g., white soot, most of which is imported) is difficult, the development of alternatives based on domestic raw materials becomes strategically important. A

© L.O. Sokolova, V.I. Ovcharov, T.V. Hridnieva, O.A. Tertishniy, V.O. Tyshchenko, 2026



This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

L.O. Sokolova, V.I. Ovcharov, T.V. Hridnieva, O.A. Tertishniy, V.O. Tyshchenko

significant number of studies [3] show that ingredients derived from rice husks can replace up to 30–50% of synthetic analogues without losing the quality of the materials. This is especially relevant for the Ukrainian industry, which needs cheap and affordable solutions.

The modification of mineral fillers with surfactants significantly improves their dispersion characteristics in the elastomeric matrix, which contributes to the formation of a more homogeneous structure of the composite and provides an improvement in its performance properties [4]. This effect is primarily due to the enhancement of interfacial interactions and the formation of additional bonds between the elastomer and filler, which contribute to a more homogeneous structure of composite materials [5]. For example, the use of a carbon-silica filler made of rice husk modified with titanium-containing compounds in elastomeric compositions based on butadiene-butadiene rubber has led to an increase in the physical and mechanical properties and heat resistance of rubbers to the level of compositions with carbon black [6].

Thus, the use of rice husks in elastomeric compositions is environmentally friendly, economically feasible, and strategically important for Ukraine, especially in wartime. It reduces dependence on imported materials, reduces production costs, and contributes to a sustainable economy.

This study was aimed to investigate the effect of rice husk bio-ingredients on the formation of a general set of properties of elastomeric compositions of model and industrial types based on butadiene-methylstyrene rubber.

Experimental

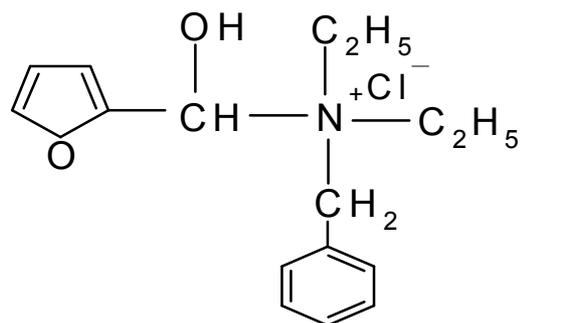
Materials

The rice husk was crushed using an impact mill with a production capacity of 300 kg/h and an energy intensity of 250 kWh/t of the finished product [7]. Before milling, the rice husk was pretreated, including washing and drying [8].

The crushed rice husk (CRH) was a fine powder (flour) of beige color with the following characteristics: silicon (IV) oxide content of 20–23 wt.%, moisture content of 4–6 wt.%, pH of the aqueous suspension of 6.9–7.2; particle size from 45 to 100 μm, and bulk density of 300 kg/m³.

To ensure the effective interaction of the crushed rice husk with the rubber matrix, it was modified with various surface-active substances (surfactants):

1) cationic quaternary ammonium salt synthesized on the basis of furfural, which was obtained from sugar industry bio-waste by acid hydrolysis (designated as QAS-4):



2) nonionic oxyethylated alcohol (OA);

3) ampholyte alkyphenol (A).

The modification of pre-dried (at 100°C for 3 hours to a constant weight) crushed rice husk was performed in a laboratory ball mill MShL-1 with a drum of 5 L by volume at a rotation speed of 200 rpm. The loading was carried out as 2 g (2 wt.%) of surfactant per 100 g of dry CRH. The first stage of homogenization with dispersion took place within 30 minutes. To improve the adsorption of surfactants on the CRH surface, heat treatment was carried out in a drying oven after the first stage of homogenization. The mixture was heated to 80°C for 60 min. The second stage of homogenization with dispersion lasted 30 minutes.

Differential thermal analysis of modified and unmodified CRH (Table 1) showed that all samples lose weight (5.2%) up to a temperature of 156°C in an identical manner, which is associated with the release of adsorption moisture and demonstrates the thermal stability of surfactants used for modification. When the temperature increases to 400°C, along with the degradation of the organic components of the CRH itself (lignin and cellulose) [9], desorption and decomposition of surfactants occur in the samples of modified CRH. The difference in the final weight loss of modified and unmodified CRH was used to determine the surfactant content in the modified forms. The sample of CRH modified with QAS-4 has the maximum content of surfactant used in the processing.

Bio-ingredients from rice husk were studied as part of elastomeric compositions based on butadiene-methylstyrene rubber. SKMS-30 ARK rubber was used for the model rubber compounds, while SKMS-30 ARKM-15 rubber is used for industrial rubber compounds (for the manufacture of molded rubber goods).

The model rubber compounds were manufactured using well-known methods on rollers; the industrial masterbatch was obtained in a laboratory rubber mixer. The mineral additives under study were identically introduced on laboratory rollers. To determine the

Table 1

Results of differential thermal analysis of the studied crushed rice husks

Sample	Weight loss (20–800°C), %	Temperature at which decomposition of organic components begins, °C	Surfactants content in modified CRH form, %
CRH	18.2	221	–
CRH/QAS-4	23.4	195	5.2
CRH/OA	22.1	241	3.9
CRH/A	22.9	226	4.7

physical and mechanical properties of rubbers, vulcanization of elastomeric compositions was carried out in a hydraulic press at the optimum of vulcanization.

Research methods

Differential thermal studies of crushed rice husks and their modified forms were performed on the Q-1500D derivatograph of the F. Paulik, J. Paulik, L. Erdey system of the MOM company under conditions of uniform heating to a temperature of 1000°C with a temperature rise rate (air) of 10°C/min.

The technological characteristics of rubber compounds and the properties of rubber were determined in accordance with current standards and relevant methods [10].

The methodology of the study included: 1) studying unmodified and modified CRH in model elastomeric compositions; and 2) studying modified CRH in industrial elastomeric compositions.

Results and discussion

Elastomeric compositions of the model type

Research on the types and contents of mineral additives

At the first stage, we investigated compositions with the CRH concentration of 10.0 phr and 20.0 phr and compared them with the samples containing the same concentration of known mineral fillers (kaolin, chalk, white soot BS-120).

The study of the plasticity of rubber compounds (Fig. 1) showed that, in contrast to the introduction of 20.0 phr of the active filler of white soot BS-120, which leads to a 1.8-fold decrease in the indicator value, the use of CRH allows maintaining the processing efficiency without significant reduction of the plasticity (1.13-fold decrease), approaching the indicators of rubber compounds with semi-active filler (kaolin) and inert filler (chalk) (1.1-fold decrease).

The analysis of the kinetic curves (Fig. 2) showed that all mineral additives, except chalk, reduce the induction period. An increase in concentration to 20.0 phr is accompanied by a decrease in the duration of the induction period. According to the slope of the

kinetic curve in the main period, the vulcanization rate of the compositions with CRH is close to the compositions with kaolin, inferior to BS-120, and exceeds the compositions with chalk.

With an increase in concentration to 20.0 phr, the relative degree of crosslinking of compositions with CRH increases to 18.7 dN·m, approaching the values of kaolin, which is 19.3 dN·m, and BS-120, which is 19.8 dN·m (Fig. 2). Probably, CRH provides a moderate increase in this indicator due to the physical filling of the elastomeric matrix with fibrous particles, while BS-120 gives a much higher result due to chemical interaction with the matrix.

Changes in the relative degree of crosslinking affect the formation of a set of physical and mechanical properties of rubbers. The study of the conditional stress at a given elongation (Fig. 3) showed that CRH also occupies an intermediate position. For example, the introduction of 20.0 phr CRH (as well as kaolin) increases the conditional stress at 300% elongation by more than 2 times compared to rubber without additives, but without reaching the level of rubber with 20.0 phr of BS-120. The reason is the lack of CRH chemical adhesion to rubber and its predominantly mechanical effect. White soot, due to its high specific surface area and active groups, forms a dense network that dramatically increases the

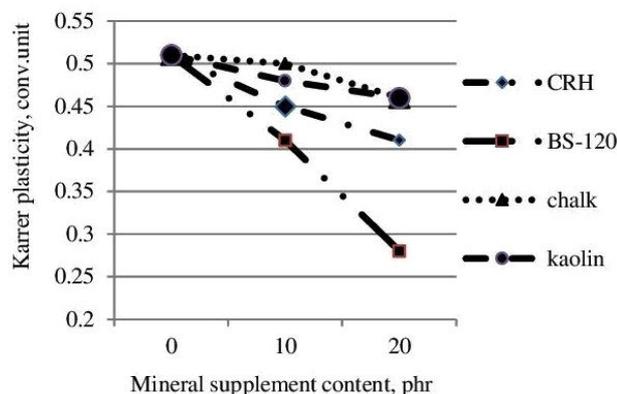


Fig. 1. Plasticity of model elastomeric compositions with different types and contents of mineral additives

resistance to deformation, while the inert filler (chalk) only nominally changes the properties.

The conditional tensile strength (Fig. 4a) and the heat resistance coefficient (Fig. 4b) diagrams show that CRH demonstrates a moderate effect on these parameters, occupying an intermediate position between active white soot BS-120 and other mineral fillers (kaolin and chalk). In terms of conditional tensile strength under normal conditions and after thermal aging, CRH is inferior to BS-120, which, due to its high specific surface area and chemical interaction with the elastomeric matrix, provides the highest values, but surpasses chalk, which has a minimal effect due to the lack of an active surface, approaching kaolin under normal conditions and exceeding it after aging.

In terms of heat resistance, CRH performs better than BS-120, demonstrating a higher coefficient of strength retention after thermal exposure, which is likely due to its lower tendency to thermal oxidation than white soot due to the absence of catalytically active surface groups [5]. White soot, despite its high initial strength, shows a significant reduction of heat resistance due to the destruction of chemical bonds when heated.

The results of the analysis of the relative elongation at break (Fig. 4c) and the corresponding heat resistance coefficient (Fig. 4d) confirmed the known mechanism of BS-120 effect on deformation

properties, which consists in the formation of a composite framework with a high density of interfacial interactions, which significantly limits the segmental mobility of polymer chains [11]. In contrast, the fibrous morphology of CRH provides a less pronounced restriction of macromolecular mobility [12], while maintaining increased values of relative elongation at break. In the context of thermo-oxidative stability, CRH shows significant advantages, which are manifested in the maximum values of the preservation coefficient of properties after thermal exposure.

The introduction of CRH (20.0 phr) allows to increase the tear resistance of rubbers by 1.7 times (Table 2), which is the highest value among the studied natural mineral additives, but does not reach the value of rubber containing BS-120. According to da Costa [13], the hardness and modulus of rubbers usually increase with increasing concentrations of solid fillers. When filled with CRH, rubbers become more rigid, as demonstrated by the Shore hardness index. It is associated with a partial restriction of the polymer chain mobility. However, the restriction is less intense than in the case of BS-120, since CRH fibers do not form a rigid interfacial network and retain the segmental mobility of elastomer macromolecules. This statement is also illustrated by a slight decrease in rebound elasticity and relative elongation at break (Fig. 4c).

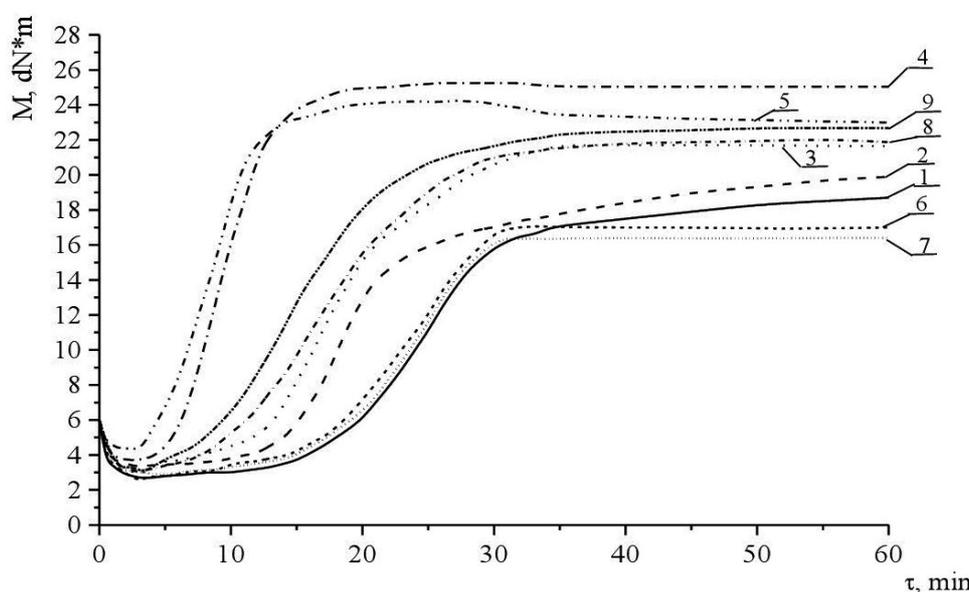


Fig. 2. Kinetic curves of sulfur vulcanization ($T=155^{\circ}\text{C}$) of model elastomeric compositions with 10.0 phr and 20.0 phr contents of mineral additives and relative degree of crosslinking of rubbers (indicated in parentheses with asterisk *):
 1 – without additives (16.0 dN·m)*; 2 – CRH 10.0 phr (16.8 dN·m)*; 3 – CRH 20.0 phr (18.7 dN·m)*;
 4 – BS-120 10.0 phr (21.5 dN·m)*; 5 – BS-120 20.0 phr (19.8 dN·m)*; 6 – chalk 10.0 phr (16.4 dN·m)*;
 7 – chalk 20.0 phr (13.4 dN·m)*; 8 – kaolin 10.0 phr (19.1 dN·m)*; 9 – kaolin 20.0 phr (19.3 dN·m)*

Thus, the introduction of crushed rice husk into model elastomeric compositions based on SKMS-30 ARK demonstrates several positive effects, in particular, the preservation of the technological processability of the mixtures even at high concentrations (up to 20 phr), which significantly distinguishes it from active fillers such as white soot. It has been found that CRH has a moderate effect on the sulfur vulcanization process, accelerating it compared to compositions without additives, but without causing sharp changes in kinetics, which makes it stable and predictable in use. The compositions with CRH are characterized by higher tear resistance compared to other mineral additives, which is

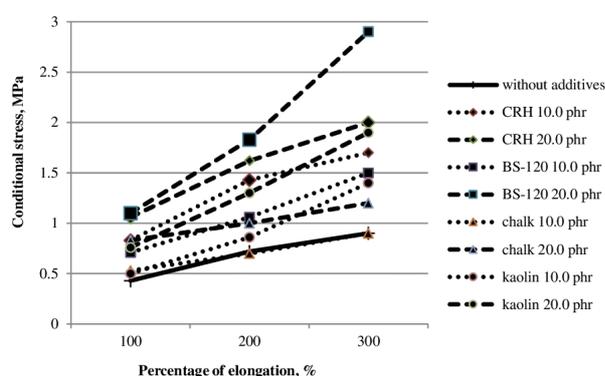


Fig. 3. The influence of the type and content of mineral additives on the conditional stress at a given elongation of model elastomeric compositions

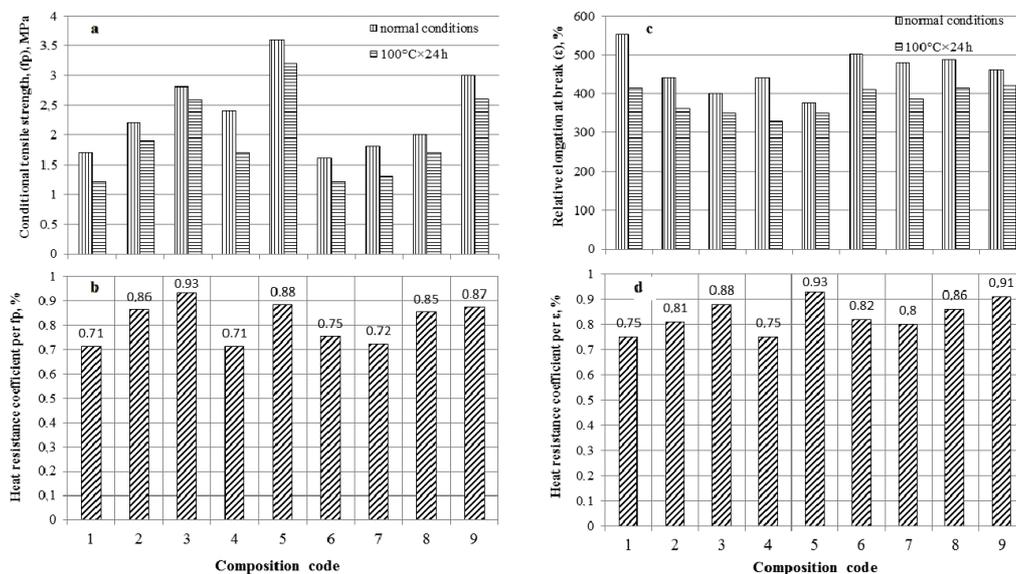


Fig. 4. The influence of the type and content of mineral additives on the conditional tensile strength (a), relative elongation at break (c), and thermal stability coefficients according to the data indicators (b, d) respectively for model elastomeric compositions: 1 – without additives; 2 – CRH 10.0 phr; 3 – CRH 20.0 phr; 4 – BS-120 10.0 phr; 5 – BS-120 20.0 phr; 6 – chalk 10.0 phr; 7 – chalk 20.0 phr; 8 – kaolin 10.0 phr; 9 – kaolin 20.0 phr

explained by the fibrous structure of CRH, which provides additional strength without significant limitation of the polymer chain mobility. In addition, CRH provides an increase in heat resistance of rubbers, which is manifested in an increase of the preservation coefficients of strength and deformation properties after thermal exposure.

Research into the type of surface treatment of the selected mineral additive

To verify the reliability of the results obtained and further improve the properties of elastomeric compositions with CRH, we investigated methods of modifying the CRH surface to improve its adhesion to the rubber matrix and increase its strength characteristics.

We studied CRH modified forms as part of model elastomeric compositions (dosage of 5.0 phr and 10.0 phr) and compared them with unmodified CRH and BS-120.

The treatment of CRH with surfactants significantly affected the technological characteristics of rubber compounds. This was confirmed by the increase in the plasticity of the composites (Fig. 5), which improves their deformation properties and facilitates the processing process. The modification with quaternary ammonium salt, QAS-4, gives the best results. For example, the introduction of 10.0 phr of CRH/QAS-4 increases the plasticity by more than 11% compared to the composition with 10.0 phr of unmodified CRH.

Increasing the dosage to 10.0 phr of modified CRH intensifies the crosslinking process, shortening the induction period, accelerating vulcanization in the main period (reducing the angle of inclination of the kinetic curve), and increasing the maximum torsional moment (especially CRH/QAS-4) (Fig. 6).

The change in the maximum torsional moment affected the relative degree of crosslinking of the elastomeric compositions (Fig. 7), which became higher in compositions with 10.0 phr of all modified forms of CRH.

The highest value of the relative degree of crosslinking is characteristic of the composition with 10.0 phr of CRH/QAS-4, which exceeds the value of the composition without additives by 1.4 times, the composition with other modified forms and unmodified CRH by more than 1.3 times, and exceeds the composition with 10.0 phr of BS-120.

Increasing the concentration to 10.0 phr significantly intensified the crosslinking process (Fig. 8). The greatest influence on the vulcanization rate is exerted by the CRH modified with ampholytic alkylphenol. In particular, the introduction of 10.0 phr of CRH/A increases the rate (R_v) by

1.9 times compared to the composition without mineral additives and with unmodified CRH, as well as by 1.3 and 1.5 times compared to CRH/QAS-4 and CRH/OA, respectively. Although CRH/A has the maximum effect on the vulcanization rate, CRH/QAS-4 turns out to be optimal for achieving both high rate and high-quality crosslinking, as evidenced by an increase in the relative degree of crosslinking (Fig. 7). Probably, the modification of the crushed rice husk with cationic QAS-4 synthesized on the basis of furfural leads to the formation of a functional surface of the CRH with increased vulcanization activity [14]. In addition, the cationic nature of QAS-4 promotes effective interaction with the anionic centers of the sulfur-based vulcanization system, as demonstrated by the difference in the maximum and minimum torsional moments of the filled ($(M_H - M_L)_{filled}$) and unfilled ($(M_H - M_L)_{unfilled}$) elastomeric compositions, and corresponds to the effect of crosslinking when using an individual additive under study (Fig. 9a).

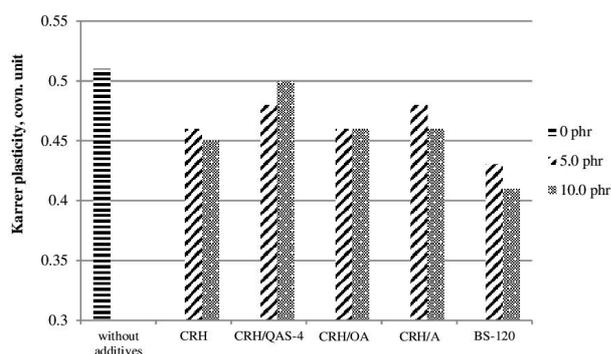


Fig. 5. Plasticity of model rubber compounds in the presence of modified and unmodified CRH

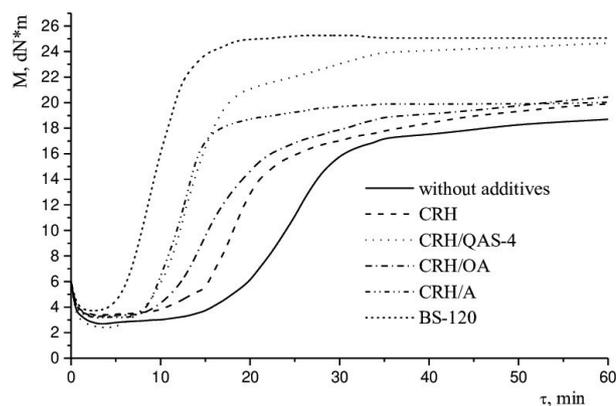


Fig. 6. Kinetic curves of sulfur vulcanization ($T=155^{\circ}\text{C}$) of model elastomeric compositions with 10.0 phr contents of mineral additives

Table 2
Physical-mechanical properties of model elastomeric compositions with different types and contents of mineral additives

Names of ingredients and parameters	Ingredient content (phr), value of parameters									
	without additives	CRH	BS-120	chalk	kaolin	Tear resistance, B, kN·m	Shore hardness A, H, arbitrary units	Rebound elasticity, S, %		
without additives	–	–	–	–	–	–	–	–	–	–
CRH	–	10.0	20.0	–	–	–	–	–	–	–
BS-120	–	–	–	10.0	20.0	–	–	–	–	–
chalk	–	–	–	–	–	10.0	20.0	–	–	–
kaolin	–	–	–	–	–	–	–	10.0	20.0	–
Tear resistance, B, kN·m	6	9	10	8	16	7	6	8	6	–
Shore hardness A, H, arbitrary units	38	40	48	41	62	43	44	42	50	–
Rebound elasticity, S, %	56	51	47	50	38	52	49	48	41	–

The greatest influence on the crosslinking effect is exerted by CRH/QAS-4. It is the quaternary ammonium salt, which allows increasing the number of vulcanization bonds by more than 5 times compared to unmodified CRH and CRH modified with oxyethylated alcohol and ampholytic alkylphenol. Moreover, this effect exceeds the effect shown by BS-120. The higher the density of rubber crosslinking, the higher its resistance to deformation, which directly affects the conditional stress at 300% elongation (Fig. 9b) and other physical and mechanical properties of the elastomeric composition. The conditional stress at 300% elongation of rubbers containing 10.0 phr of CRH/QAS-4 is increased by 23%; the use of a similar dosage of other modified forms increases the elastic modulus of rubber by 11%.

The evaluation of the reinforcing effect of mineral additives in elastomeric compositions was carried out using a complex indicator – the reinforcement factor (I^3), taking into account the level of indicators of

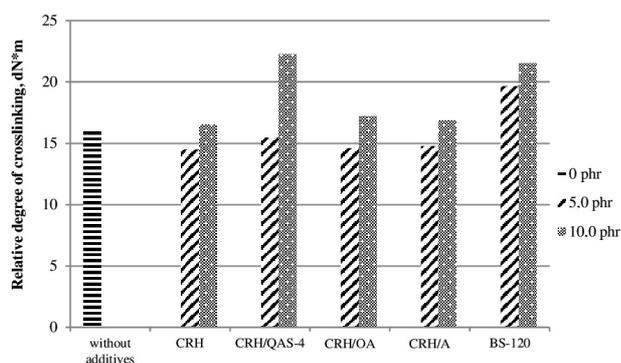


Fig. 7. The influence of the type and content of mineral additives on the relative degree of crosslinking of model elastomeric compositions

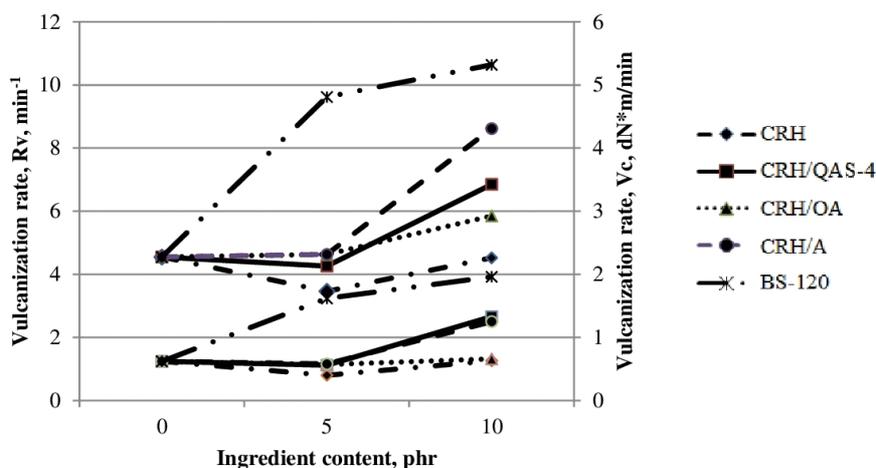


Fig. 8. The influence of the type and content of mineral additives on the vulcanization rate of model elastomeric compositions

conditional stress at 300 % elongation, conditional tensile strength, and tear resistance [15].

As can be seen from Fig. 10, an increase in the dosage of the mineral additive to 10.0 phr increases the rubber reinforcement factor. The modification of CRH with the studied surfactants allows increasing its reinforcing effect. For example, compared to rubber with 10.0 phr of unmodified CRH, rubber with CRH/QAS-4 has a reinforcement factor 2.6 times higher, rubber with CRH/OA – 1.9 times higher, and rubber with CRH/A – 1.6 times higher. The most effective was the modification of CRH with quaternary ammonium salt; the reinforcement factor of such rubber (10.0 phr) exceeds that of rubber with CRH/OA by 1.4 times, and the rubber with CRH/A by 1.7 times. The cationic nature of the quaternary ammonium salt in the CRH/QAS-4 composition probably reduces the agglomeration of particles of crushed rice husk in the elastomeric matrix, due to which the distribution of CRH improves and the efficiency of load redistribution in the elastomeric composition increases. The result is an increase in the conditional stress at 300% elongation, conditional tensile strength, and tear resistance of rubbers, and hence the formation of a reinforcing effect.

Elastomeric compositions of the industrial type

The study of CRH/QAS-4 was continued in the composition of industrial-type elastomeric compositions based on SKMS-30 ARKM-15 for the manufacture of molded rubber goods (ball mill seals). The rubber is filled with carbon black of N-550 grade (83.06 phr), chalk (68.05 phr), and kaolin (22.4 phr). We studied the compositions, in which kaolin was replaced with CRH/QAS-4 by half (11.2 phr) and completely (22.4 phr).

The study on the technological properties of rubber compounds showed that the complete replacement of kaolin with crushed rice husks modified with quaternary ammonium salt leads to a decrease in the viscosity of rubber compounds by 14% and an increase in thermoplasticity by 20% (Fig. 11).

The use of CRH/QAS-4 (22.4 phr) instead of kaolin leads to an acceleration of vulcanization by 13% and an increase in the degree of crosslinking by 21%. This effect is associated exclusively with the presence of QAS-4, since with the complete replacement of kaolin (20.0 phr) with unmodified CRH in the model elastomeric compositions based on SKMS-30 ARC, no significant difference in the effect on the sulfur vulcanization process was found (Table 3).

High values were demonstrated by rubbers with complete replacement of kaolin with CRH/QAS-4. In particular, these compositions have the maximum

values of relative elongation at break, rebound elasticity, tear resistance, and resistance to multiple deformations (Table 4), which is especially important for rubber molding rubber goods (ball mill seals).

For example, rubbers with 22.4 phr of CRH/QAS-4 are 25% higher than those with kaolin in terms of tear resistance and rebound elasticity. It should also be noted that the complete replacement of kaolin with CRH/QAS-4 allows, on average, reducing the loss of tensile strength of rubbers after heat aging by half (Fig. 12a) and reducing the loss of relative elongation at break by 1.5 times (Fig. 12b).

Studies have confirmed the effectiveness of crushed rice husk as a bio-ingredient for elastomeric compositions, which reduces dependence on traditional fillers and reduces the environmental burden. The modification of CRH with surfactants, especially the cationic quaternary ammonium salt QAS-4 (synthesized on the basis of furfural, which is obtained

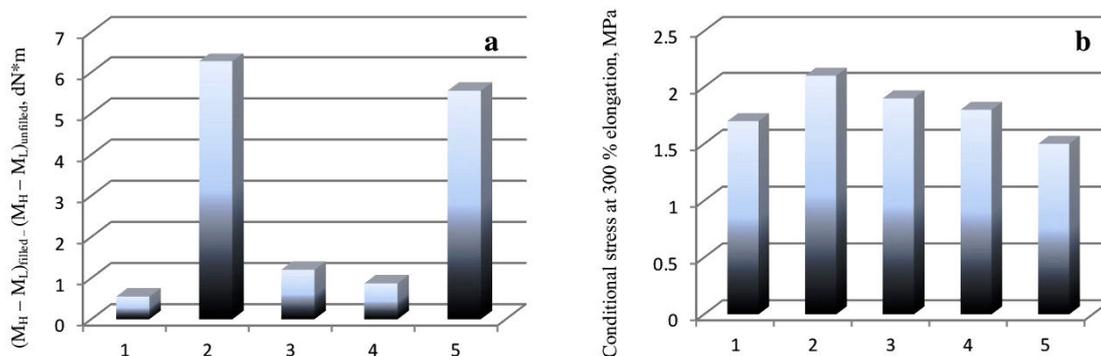


Fig. 9. The influence of the type of mineral additives (10.0 phr) on crosslinking effect (a) and conditional stress at 300% elongation (b) of model elastomeric compositions: 1 – CRH; 2 – CRH/QAS-4; 3 – CRH/OA; 4 – CRH/A; 5 – BS-120

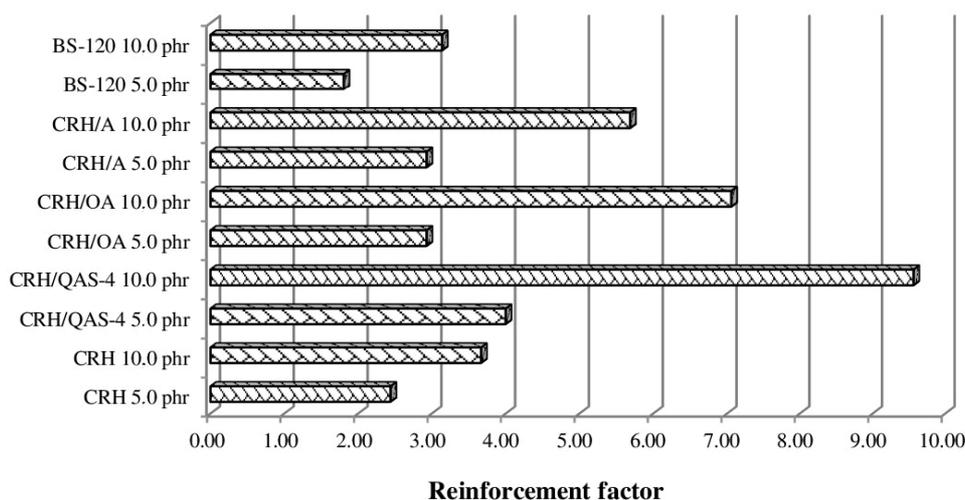


Fig. 10. The influence of the type and content of mineral additives on the reinforcement factor of model rubbers

from the sugar industry bio-waste), improves its adhesion to the rubber matrix, increases the degree of crosslinking, and improves the physical and mechanical properties of rubbers. Compositions with CRH demonstrate higher tear resistance and heat resistance compared to unfilled samples, although they are inferior in strength characteristics to rubbers with white soot because of the lower surface activity. Replacing kaolin with CRH/QAS-4 in elastomeric compositions for the manufacture of molded rubber goods preserves technological parameters and improves the performance of rubbers. Thus, the use of CRH, in particular in a modified form, is a promising direction for creating environmentally friendly and cost-effective elastomeric compositions.

REFERENCES

1. *A comparison of functional fillers – greenhouse gas emissions and air pollutants from lignin-based filler, carbon black and silica* / Meisel K., Rover L., Majer S., Herklotz B., Thran D. // *Sustainability*. – 2022. – Vol.14. – No. 9. – Art. No. 5393.
2. *Recent developments in synthesis, properties, applications and recycling of bio-based elastomers* / Burelo M., Martinez A., Hernandez-Varela J.D., Stringer T., Ramirez-Melgarejo M., Yau A.Y., Luna-Barcenas G.I., Trevino-Quintanilla C.D. // *Molecules*. – 2024. – Vol.29. – No. 2. – Art. No. 387.
3. *A review on mechanical improvements and environmental benefits of rice husk reinforced polymer composites* / Monga S., Kadian M., Nagoria S., Kumar S., Verma M. // *Curr. World Environ.* – 2024. – Vol.19. – No. 3. – P.1077-1100.

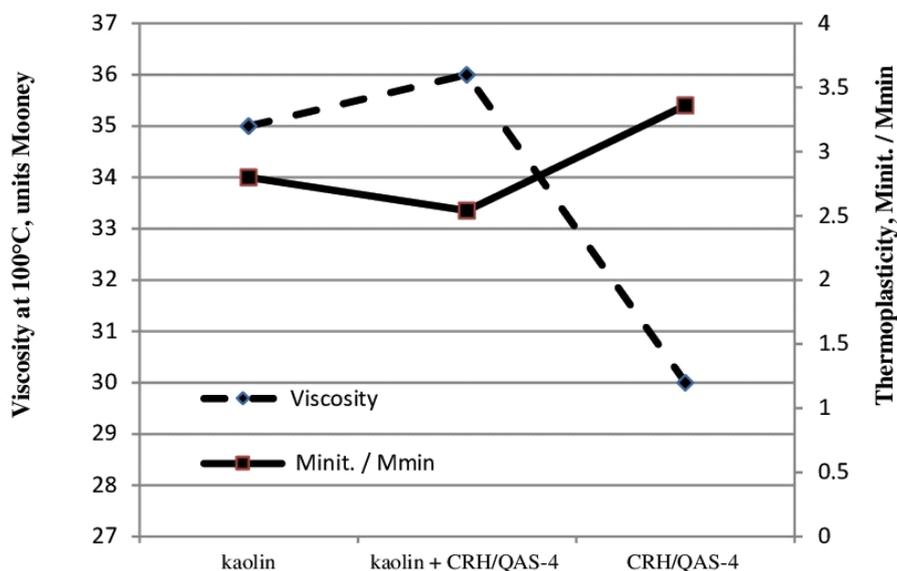


Fig. 11. Technological properties of industrial rubber compounds

Table 3

Parameters of sulfur vulcanization of industrial elastomeric compositions

Parameter	Value		
	kaolin 22.4 phr	kaolin 11.2 phr+CRH/QAS-4 11.2 phr	CRH/QAS-4 22.4 phr
Relative degree of crosslinking, ΔM , dN·m	37.02	34.98	44.83
Vulcanization start time, t_s , min	5.25	4.5	4.5
Time to reach optimum vulcanization, t_{c90} , min	13.75	15.5	13.25
Vulcanization rate calculated taking into account the increase in torque parameters, V_c , dN·m/min	4.21	3.14	4.74

4. *Composite elastomer materials based on new ingredients* / Ibadullaev A., Teshabaeva E., Vapaev M. // *Chem. Chem. Eng.* – 2021. – Vol.2. – No. 4. – P.32-44.

5. *Use of rice husk ash as filler in natural rubber vulcanizates: in comparison with other commercial fillers* / Sae-Oui P., Rakdee C., Thanmathorn P. // *J. Appl. Polym. Sci.* – 2002. – Vol.83. – No. 11. – P.2485-2493.

6. *Preparation of rice husk based carbon–silicon reinforcing agent and its enhancement capability for styrene butadiene rubber composites* / Zhang Y., Lin J., Zhang Q. // *Polym. Sci. Ser. A* – 2021. – Vol.63. – No. 3. – P.334-343.

7. *Soroka P.G., Oparin S.O. Vidtsentrovii mlin udarnoyi diyi.* – Patent UA 96082. MPK B02C 13/14. – No. a201006351, zayavl. 25.05.2010; opubl. 26.09.2011, byul. No. 18. – 12 p.

8. *Issledovanie vliyaniya sposobov podgotovki risovoi shelukhi na khimicheskii sostav syrevegogo materiala pri poluchenii SiO₂* / Gridneva T.V., Soroka P.I., Tertyishnyiy O.A., Ryabik P.V., Smirnova E.S. // *Voprosy Khimii i Khimicheskoi Tekhnologii.* – 2012. – No. 3. – P.50-53.

9. *Effect of calcination temperature and heating rate on the optical properties and reactivity of rice husk ash* / Chandrasekhar S., Pramada P. N., Majeed J. // *J. Mater. Sci.* – 2006. – Vol.41. – P.7926-7933.

10. *Cheremisinoff N.P., Cheremisinoff P.N. Elastomer technology handbook.* – London: CRC Press, 1993. – 1120 p.

11. *Silica fillers for elastomer reinforcement* / Kohls D.J., Schaefer D.W., Kosso R., Feinblum E. // *Current topics in elastomers research.* – 2008. – P.505-517.

Table 4

Physical-mechanical characteristics of industrial rubber

Parameter	Value		
	kaolin 22.4 phr	kaolin 11.2 phr + CRH/QAS-4 11.2 phr	CRH/QAS-4 22.4 phr
Conditional stress at 300% elongation, f_{300} , MPa	8.4	6.9	6.5
Conditional tensile strength, f_p , MPa n.c.	10.6	11.3	9.3
120 ⁰ C×12 h	9.2	9.6	8.7
120 ⁰ C×24 h	7.7	8.8	7.9
120 ⁰ C×72 h	6.15	6.89	7.35
Relative elongation at break, ϵ , % n.c.	270	265	280
120 ⁰ C×12 h	250	250	265
120 ⁰ C×24 h	225	240	250
120 ⁰ C×72 h	210	235	240
Tear resistance, B, kN·m	42	45	53
Shore hardness A, H, arbitrary units	71	75	73
Rebound elasticity, S, %	32	34	40
Resistance to multiple deformations at $\epsilon=200\%$, N, thousands of cycles	36.70	38.25	39.40

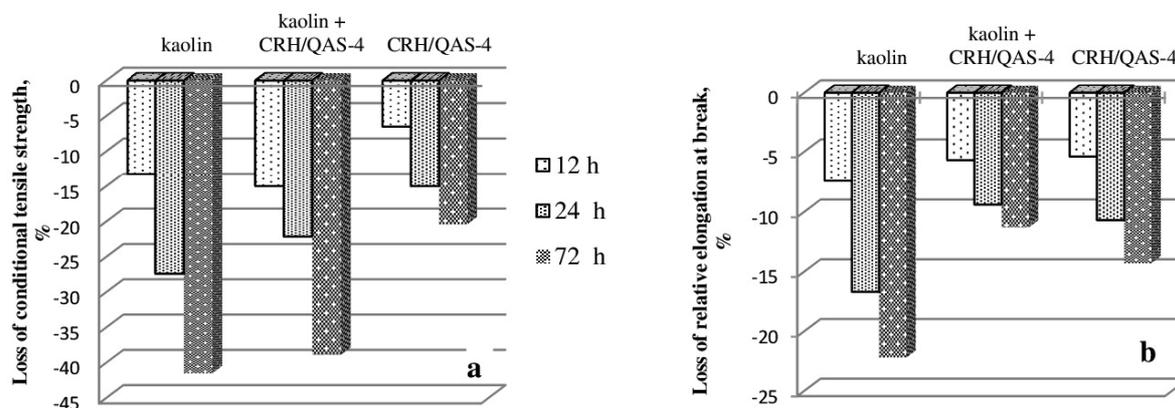


Fig. 12. Dynamics of loss of elastic-strength characteristics of rubber (conditional tensile strength (a) and relative elongation at break (b)) with partial and complete replacement of kaolin with CRH/QAS-4

12. Review: raw natural fiber-based polymer composites / Thakur V.K., Thakur M.K., Gupta R. // *Int. J. Polym. Anal. Charact.* – 2014. – Vol.19. – No. 3. – P.256-271.

13. Rice husk ash filled natural rubber compounds – the use of rheometric data to qualitatively estimate optimum filler loading / Costa H.M., Visconte L.L.Y., Nunes R.C.R., Furtado C.R.G. // *Int. J. Polym. Mater. Polym. Biomater.* – 2004. – Vol.53. – No. 6. – P.475-497.

14. The effect of filler–filler and filler–elastomer interaction on rubber reinforcement / Frohlich J., Niedermeier W., Luginsland H.-D. // *Compos. Part A: Appl. Sci. Manuf.* – 2005. – Vol.36. – No. 4. – P.449-460.

15. Shvarts A.G., Knyazeva L.A. Vliyanie rezhima smesheniya na svoistva smesei, modifitsirovannykh N-nitrozodifenilaminom // *Kauchuk i rezina.* – 1982. – No. 6. – P.24-26.

Received 07.07.2025

Revised 24.08.2025

Accepted 30.12.2025

Published 25.02.2026

ЕЛАСТОМЕРНІ КОМПОЗИЦІЇ З БІОІНГРЕДІЄНТАМИ НА ОСНОВІ РИСОВОГО ЛУШПИННЯ

Л.О. Соколова, В.І. Овчаров, О.О. Тертишний, Т.В. Гриднєва, В.О. Тищенко

В умовах глобального зростання вимог зеленої хімії та циркулярної економіки використання подрібненого рисового лушпиння (ПРЛ) як біоінгредієнта еластомерних композицій пропонує екологічно стійку альтернативу. У даній роботі встановлено, що модифікація ПРЛ поверхнево-активними речовинами, зокрема катіоноактивною четвертинною амонієвою сіллю (ЧАС-4), синтезованою з біовідходів цукрової промисловості, значно покращує взаємодію лушпиння з каучуковою матрицею, підвищує ступінь зшивання та покращує фізико-механічні властивості гум, такі як опір роздиранню і теплостійкість. Експериментальні результати свідчать, що композиції з ПРЛ, модифікованим ЧАС-4, демонструють переваги у технологічності переробки, включаючи збереження пластичності гумових сумішей та прискорення сірчаної вулканізації, а також вдосконалення експлуатаційних характеристик промислових гум у порівнянні з традиційними наповнювачами. Використання ПРЛ, особливо у модифікованій формі, є перспективним напрямом для створення екологічно безпечних та економічно ефективних еластомерних композицій.

Ключові слова: еластомерна композиція; біоінгредієнт; рисове лушпиння; четвертинна амонієва сіль; властивості гумових сумішей та гум; поновлювана біосировина; екологічна безпека.

ELASTOMERIC COMPOSITIONS WITH RICE HUSK-BASED BIO-INGREDIENTS

L.O. Sokolova^{a,}, V.I. Ovcharov^a, T.V. Hridnieva^a, O.A. Tertishniy^b, V.O. Tyshchenko^c*

^a Ukrainian State University of Science and Technologies, Dnipro, Ukraine

^b Dnipro State Agrarian and Economic University, Dnipro, Ukraine

^c Zaporizhzhia National University, Zaporizhzhia, Ukraine

* e-mail: sokolovalina18@gmail.com

In the context of the global growth of green chemistry and the circular economy, the use of crushed rice husk (CRH) as a bio-ingredient in elastomeric compositions offers an environmentally sustainable alternative. It has been found that modification of the husk with surfactants, in particular the cationic quaternary ammonium salt (QAS-4) synthesized from sugar-industry biowaste, significantly improves the interaction between the husk and the rubber matrix, increases the degree of crosslinking, and enhances the physical and mechanical properties of the rubbers, such as tear and heat resistance. Experimental results showed that compositions with CRH modified with QAS-4 demonstrate advantages in processability, including preservation of the rubber compound's plasticity and acceleration of sulfur vulcanization, as well as improved performance characteristics of industrial rubbers compared with traditional fillers. The use of CRH, especially in a modified form, is a promising direction for creating environmentally friendly and cost-effective elastomeric compositions.

Keywords: elastomer composition; bio-ingredient; rice husk; quaternary ammonium salt; properties of rubber compounds and rubbers; renewable bioresource; environmental safety.

REFERENCES

- Meisel K, Rover L, Majer S, Herklotz B, Thran D. A comparison of functional fillers – greenhouse gas emissions and air pollutants from lignin-based filler, carbon black and silica. *Sustainability*. 2022; 14: 5393. doi: 10.3390/su14095393.
- Burelo M, Martinez A, Hernandez-Varela JD, Stringer T, Ramirez-Melgarejo M, Yau AY, et al. Recent developments in synthesis, properties, applications and recycling of bio-based elastomers. *Molecules*. 2024; 29: 387. doi: 10.3390/molecules29020387.
- Monga S, Kadian M, Nagoria S, Kumar S, Verma M. A review on mechanical improvements and environmental benefits of rice husk reinforced polymer composites. *Curr World Environ*. 2024; 19(3): 1077-1100. doi: 10.12944/CWE.19.3.4.
- Ibadullaev A, Teshabaeva E, Vapaev M. Composite elastomer materials based on new ingredients. *Chem Chem Eng*. 2021; 2(4): 32-44. doi: 10.51348/ZNKZ7723.
- Sae-Oui P, Rakdee C, Thanmathorn P. Use of rice husk ash as filler in natural rubber vulcanizates: in comparison with other commercial fillers. *J Appl Polym Sci*. 2002; 83: 2485-2493. doi: 10.1002/app.10249.
- Zhang Y, Lin J, Zhang Q. Preparation of rice husk based carbon–silicon reinforcing agent and its enhancement capability for styrene butadiene rubber composites. *Polym Sci Ser A*. 2021; 63: 334-343. doi: 10.1134/S0965545X21030147.

7. Soroka PG, Oparin SO, inventors; Ukrainian State University of Chemical Technology, assignee. *Vidtsentrovnyi mlyn udarnoyi diyi* [Centrifugal impact mill]. Ukraine patent UA 96082. 2011 Sep 26. (in Ukrainian).

8. Gridneva TV, Soroka PI, Tertyishnyi OA, Ryabik PV, Smirnova ES. Issledovanie vliyaniya sposobov podgotovki risovoi shelukhi na khimicheskii sostav syrievogo materiala pri poluchenii SiO₂ [A study of the influence of rice husk preparation methods on the chemical composition of the raw material in the production of SiO₂]. *Voprosy Khimii i Khimicheskoi Tekhnologii*. 2012; (3): 50-53. (in Russian).

9. Chandrasekhar S, Pramada PN, Majeed J. Effect of calcination temperature and heating rate on the optical properties and reactivity of rice husk ash. *J Mater Sci*. 2006; 41: 7926-7933. doi: 10.1007/s10853-006-0859-0.

10. Cheremisinoff NP, Cheremisinoff PN. *Elastomer technology handbook*. 1st editon. London: CRC Press; 1993. 1120 p. doi: 10.1201/9780138758851.

11. Kohls DJ, Schaefer DW, Kosso R, Feinblum E. Silica fillers for elastomer reinforcement. In: *Current topics in elastomers research*. 1st edition. Bhowmick AK, editor. 2008. p. 505-517. doi: 10.1201/9781420007183.

12. Thakur VK, Thakur MK, Gupta RK. Review: raw natural fiber-based polymer composites. *Int J Polym Anal Charact*. 2014; 19(3): 256-271. doi: 10.1080/1023666X.2014.880016.

13. Costa HM, Visconte LLY, Nunes RCR, Furtado CRG. Rice husk ash filled natural rubber compounds – the use of rheometric data to qualitatively estimate optimum filler loading. *Int J Polym Mater Polym Biomater*. 2004; 53(6): 475-497. doi: 10.1080/00914030490450100.

14. Frohlich J, Niedermeier W, Luginsland HD. The effect of filler–filler and filler–elastomer interaction on rubber reinforcement. *Compos Part A Appl Sci Manuf*. 2005; 36: 449-460. doi: 10.1016/j.compositesa.2004.10.004.

15. Shvarts AG, Knyazeva LA. Vliyanie rezhima smesheniya na svoistva smesei, modifitsirovannykh N-nitrozodifenilaminom [The influence of the mixing mode on the properties of mixtures modified with N-nitrosodiphenylamine]. *Kauchuk i Rezina*. 1982; (6): 24-26. (in Russian).