**Plastoelastic Properties of Elastomeric Compositions Containing Gas Pyrolysis Residue as a Plasticizer**

Murodjon Vapaev1, a), Elmira Teshabaeva2, b), Khushnudbek Samandarov2, c) and Jasurbek Sobirov2, d)

1*Tashkent Institute of Chemical Technology, 32 Navoi Street, Tashkent 100011, Uzbekistan*2*Tashkent State Transport University, 1 Temiryulchilar St., Tashkent 100167, Uzbekistan*

*a) Corresponding author: a)*[*murodjon.vapayev@mail.ru*](mailto:murodjon.vapayev@mail.ru) *b)* [*elmira-teshaboeva@mail.ru*](mailto:elmira-teshaboeva@mail.ru) *c)* [*xushnudbek6600@mail.ru*](mailto:xushnudbek6600@mail.ru) *d)* [*jasurbeksobirov19951908@gmail.com*](mailto:jasurbeksobirov19951908@gmail.com)

**Abstract.**  This study explores the performance of alternative plasticizers, including a by-product of gas pyrolysis, in comparison with the commonly used industrial plasticizer dibutyl phthalate (DBP), to determine their influence on the processing and technical characteristics of elastomeric composites. The findings suggest that the gas pyrolysis residue significantly contributes to the structural development of elastomeric materials through interactions involving donor-acceptor bonding, and concurrently helps suppress thermo-oxidative and photochemical degradation. Under thermal aging conditions, composites plasticized with the residue exhibited improved tensile strength over time relative to samples stabilized using the "Neozone-D" antioxidant. Meanwhile, elongation at break slightly decreased, and both the hardness and the –C–C– bond density within the vulcanization network increased. These results demonstrate that active compounds within the pyrolysis residue enhance structural reinforcement in elastomeric composites during prolonged exposure to heat.

**Keywords:** Composition, plasticity, kinetics, technology, viscosity, aging, plasticizer, elastomer, vulcanization, plasticization

**INTRODUCTION**

In transport engineering, aviation, metallurgy, the chemical and food industries, and agriculture, rubber products and tires based on elastomers are widely used. To improve their structure, ingredients derived from organic and inorganic substances are incorporated. It is important to develop ingredients that improve the technological properties of elastomer-based rubber products and tires, structurally adjust their physical-mechanical, dynamic, and special properties, taking into account specific requirements [1, 2].

Scientific research is focused on obtaining organic and inorganic ingredients from oil and gas refining products and recycled materials, developing methods for their modification, studying their physicochemical properties and structure, justifying their influence on the properties of compositions to tailor the structure of rubber products and tires based on elastomers to pre-determined requirements, and using them in the development of the composition and production technology of rubber products used in the transport, aviation, metallurgical, chemical, and food industries, as well as in agriculture [3, 4].

One method of elastomer modification is plasticization. Plasticization involves modifying the behavior of polymers through the addition of low-molecular-weight compounds known as plasticizers. These additives influence key characteristics such as system viscosity, molecular flexibility, and the dynamics of supramolecular arrangements. Their primary purpose is to enhance the processability and elasticity of polymer materials during manufacturing and application. [5, 6].

**OBJECTIVE AND METHODS**

This study was conducted to evaluate the potential of a tar-like by-product derived from gas pyrolysis resin-generated as waste during polymer manufacturing-as an effective plasticizing agent within elastomeric formulations.

**OBJECTS AND METHODS OF INVESTIGATION**

The materials utilized in this research included standard rubber formulations based on SKI-3, SKMS-30ARKM-15, and SKEPT elastomers, along with a secondary tar fraction derived from gas pyrolysis resin-a by-product originating from polymer manufacturing processes. The compounding of rubber mixtures was conducted using laboratory rolling mills and a Brabender Plastorder PIU-151 internal mixer equipped with a 75 cm³ chamber, operating at a rotor speed of 30 revolutions per minute and an initial temperature of 343 ± 3 K. The chamber was filled to 77% of its volume. The plasticizing agent was incorporated into the elastomeric matrix at varying concentrations of 2.5, 5.0, 7.5, and 10.0 parts by weight per 100 parts of rubber. A reference formulation lacking any plasticizer was employed as the control.

To assess the plastoelastic behavior of the prepared compounds, measurements were carried out using the MV2000 shear disk viscometer in accordance with GOST 10722–76. Vulcanization kinetics were evaluated using the ODR2000 rheometer following GOST 12535–84. Hardness and elastic recovery were determined using Defo equipment under GOST 1020–95 standards. Additional mechanical and physical properties of the vulcanized samples were characterized in compliance with the applicable GOST protocols [7, 8, 9].

**MAIN BODY**

It is well-established that tar-like residues originating from gas pyrolysis resin are generated as by-products in the course of polymer production. Analytical observations indicate that the gas pyrolysis resin typically exists as a black, odorless solid (see table 1).

**TABLE 1.** Molecular Composition of By-Product from Gas Pyrolysis Resin

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Carbon Atom Count** | **Alkanes** | **Diene Fraction** | **Olefins Content** | **Cycloalkane Compounds** | **Arenes** | **Sum of Components** |
| 5 | 0,8 | 0,89 | 4,91 | 0,19 | 0 | 6,79 |
| 6 | 0,22 | 0,41 | 3,87 | 0,41 | 32,94 | 37,85 |
| 7 | 0,25 | 0,14 | 0,84 | 0,45 | 11,23 | 12,91 |
| 8 | 0,12 | 0,08 | 0,18 | 0,48 | 9,75 | 10,61 |
| 9 | 0,04 | 0,1 | 0,04 | 0,15 | 7,56 | 7,89 |
| 10 | 0,03 | 0,11 | 9,07 | 0,4 | 5,23 | 14,84 |
| 11 | 0,18 | 0,69 | 2,95 | 0 | 0,47 | 4,29 |
| 12 | 0 | 0,15 | 1,84 | 0 | 0 | 1,99 |
| Σ | 1,64 | 2,57 | 23,7 | 2,08 | 67,18 | 97,17 |

Here’s the English translation:

The gas pyrolysis resin is primarily composed of arenes and olefins, with hydrocarbon chains ranging from six to twelve carbon atoms. Quantitative analysis reveals that olefins constitute approximately 23.7%, while arenes account for about 67.18% of the total composition. Additionally, minor fractions of alkanes, dienes, and cycloalkanes are present in the resin. Both qualitative and quantitative spectral evaluations demonstrate a high degree of component compatibility, with spectral alignment in the range of 90–97%.

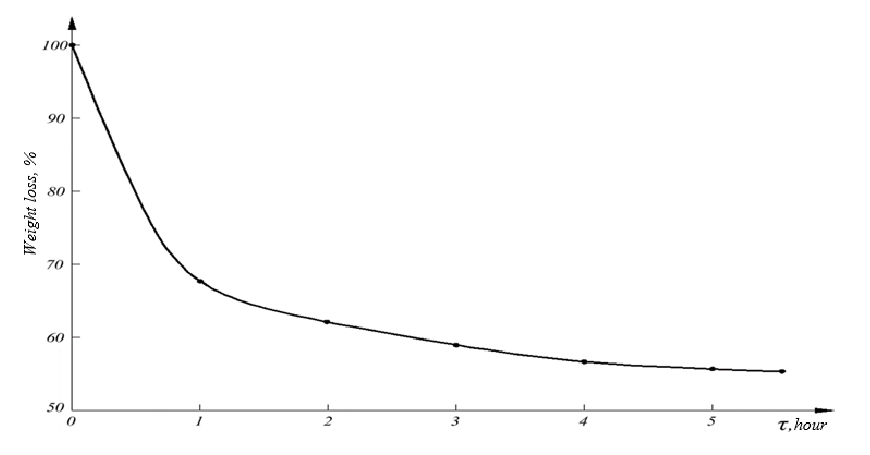
Gel permeation chromatography indicates that the resin possesses an average molecular weight of approximately 1000 g/mol. Infrared (IR) spectroscopy reveals distinct absorption bands corresponding to the vibrational modes of molecular groups: a peak at 3050 cm⁻¹, attributed to C–H stretching in aromatic rings, and additional bands at 2860, 2930, and 2975 cm⁻¹, associated with methylene and methyl C–H stretching [10, 11, 12].

**Chizmalar16_2**

**FIGURE 1.** IR spectrum of gas pyrolysis resin

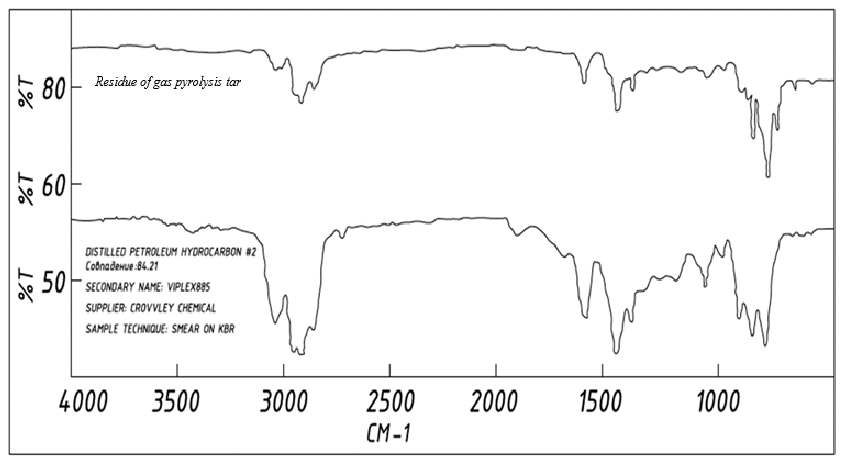
Characteristic absorption bands are also detected at 2860, 2930, and 2975 cm⁻¹, which correspond to the valence vibrations of C–H bonds in methylene and methyl groups. In addition, a strong absorption peak near 1710 cm⁻¹ indicates the presence of carbonyl (C=O) functional groups along the hydrocarbon chain. Asphaltic components exhibit a similar signal around 1730 cm⁻¹. Furthermore, the spectral region between 1500 and 1600 cm⁻¹ is associated with C=C stretching vibrations, characteristic of unsaturated structures such as aromatic or olefinic compounds. (Fig. 1).

Proton magnetic resonance (PMR) spectroscopy further confirms the presence of aromatic structures, as evidenced by proton signals at chemical shifts of δ = 6.10 ppm, 7.12 ppm, and 8.10 ppm. These signals are typical for aromatic rings and their substituted derivatives, indicating a significant aromatic content in the material. Studies have shown that its softening and melting point is about 120-140 °C. It is known that the boiling and flash points of organic substances used in the production of elastomeric compositions should not be lower than 180 °C [8, 9]. Therefore, we thermally treated the tar product of gas pyrolysis resin formed in the propylene production process at 240 °C (Fig. 2).

****

**FIGURE 2.** Influence of time on the thermal treatment process of the tar product of gas pyrolysis resin

As a result, a black liquid substance was formed with an approximate molecular weight of 900-1100. Its quantity decreased by 45%, and the composition was studied as a result of the study of the obtained substance in IR spectroscopy (Fig. 3).

****

**FIGURE 3.** Comparison of the IR spectrum of plasticizers and gas pyrolysis resin residue

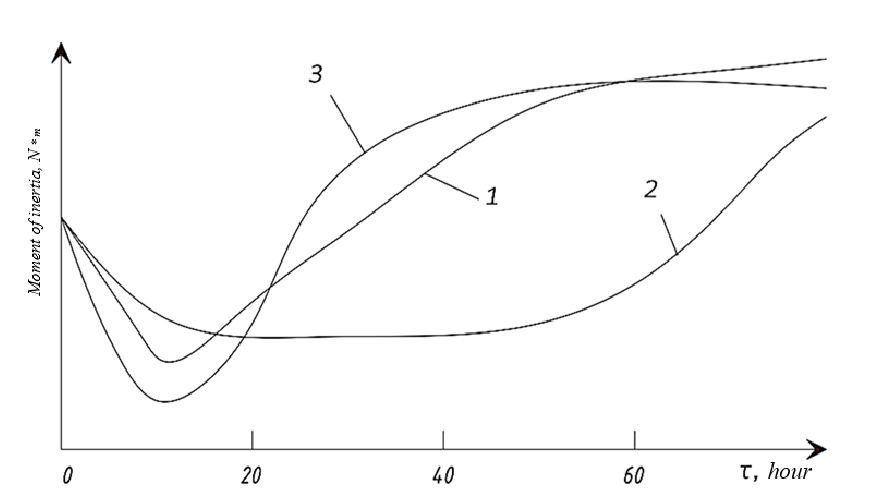
As illustrated in the figure, the molecular structure of the bottom residue from gas pyrolysis resin (BRGPR) exhibits similarities to that of the industrial plasticizer dibutyl phthalate (DBP), indicating its potential suitability for use as a plasticizing agent in elastomeric systems. One of the key rheological characteristics of rubber compounds is the Mooney viscosity index, which reflects the material's flow resistance under processing conditions. This parameter is crucial for understanding how the compound behaves during mixing and shaping, as it quantifies the mechanical energy required to induce flow at specific stages of manufacturing. Figure 4 presents the relationship between plasticizer dosage and Mooney viscosity in rubber formulations. Experimental evaluation of Mooney viscosity in compounds based on SKI-3 and SKEPT revealed that the incorporation of BRGPR significantly reduces viscosity in comparison with formulations lacking plasticizers. For instance, unmodified SKI-3 and SKEPT compounds exhibited Mooney viscosities of 15.7 and 75.0 arbitrary units, respectively. Upon the addition of 2.5 phr (parts per hundred rubber) of BRGPR, these values dropped to 7.6 and 61.1 units. Similarly, in formulations based on SKMS-30ARKM-15, the viscosity reduction observed with BRGPR was more substantial than that achieved using conventional DBP. The incorporation of plasticizers promotes more homogeneous distribution of ingredients within the rubber matrix. This also mitigates excessive heat buildup during mixing, which helps to prevent premature vulcanization and reduces the overall energy demand for processing. However, Mooney viscosity alone does not fully capture the complexities of elastomer processability. Therefore, additional parameters, such as stress relaxation behavior, are employed to characterize the viscoelastic response of rubber compounds. To assess these properties, stress relaxation measurements were performed using a viscometer that recorded the residual torque over time following the cessation of rotor motion. These data were used to calculate the relaxation coefficient (Kr), a critical metric in evaluating the ease of processing and structural relaxation behavior in elastomeric systems (table 2) [13, 14].

**TABLE 2.** Stress relaxation indicators of the studied rubber compounds

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Ingredient Names | Amount of plasticizer added, parts by weight | Rubber compound based on / relaxation indicators of rubber compounds | | | | | |
| SKI-3 | | SKMS-30ARKM-15 | | SKEPT | |
| tgα´ | *K*р, % | tgα´ | *K*р, % | tgα´ | *K*р, % |
| Without additive | – | –1,581 | 48,41 | –0,52 | 52,07 | –0,640 | 48,00 |
| DBP | 2,5 | –0,428 | 81,54 | –0,60 | 53,18 | –0,618 | 53,18 |
| 5,0 | –0,480 | 82,76 | –0,59 | 53,48 | –0,646 | 53,44 |
| 7,5 | –0,769 | 83,75 | –0,57 | 54,27 | –0,645 | 55,27 |
| 10,0 | –0,863 | 85,30 | –0,56 | 60,22 | –0,638 | 55,33 |
| BRGPR | 2,5 | –0,987 | 77,63 | –0,57 | 56,13 | –0,645 | 53,90 |
| 5,0 | –0,987 | 79,85 | –0,55 | 56,50 | –0,635 | 57,20 |
| 7,5 | –0,835 | 81,93 | –0,48 | 60,89 | –0,628 | 57,32 |
| 10,0 | –0,850 | 83,60 | –0,48 | 64,14 | –0,623 | 58,80 |

The tangent of the angle of inclination of the tangent to the relaxation graph 1 second after the rotor stops (tgα´), or the slope of the relaxation curve in logarithmic coordinates (α), is a measure of the relaxation rate. The slope of the relaxation curve can be influenced by the polymerization process, molecular weight distribution, branching, average molecular weight, microstructure, filler content, their particle size, plasticizer content, additives, mixing method, etc. [15, 16]. The data clearly indicate that incorporating plasticizers into SKI-3-based elastomeric matrices significantly enhances stress relaxation behavior. Notably, when 2.5 parts by weight of plasticizer are added, the relaxation coefficient increases by approximately 51–69%. Among the tested plasticizers, dibutyl phthalate (DBP) and the gas pyrolysis resin bottom residue (BRGPR) had the most substantial effects. For rubber mixtures without any additives, the relaxation coefficient was 48.41%. This value rose to 81.54% and 77.63% following the addition of 2.5 phr of DBP and BRGPR, respectively. Furthermore, the inclusion of plasticizers not only promotes relaxation but also leads to a measurable reduction in the stress relaxation rate. Further experiments on rubber compounds based on SKMS-30ARKM-15 and SKEPT confirmed that BRGPR has a more pronounced impact on the relaxation coefficient than DBP. Specifically, in SKMS-30ARKM-15-based formulations, the addition of 2.5 phr of DBP resulted in a relaxation coefficient of 55.37%, whereas the same concentration of BRGPR increased it to 57.73%. The slope of the relaxation curve (tgα´) provides additional insight into this behavior. For example, in the SKEPT-based compound without additives, tgα´ was –0.640. With the addition of DBP and BRGPR at 2.5 phr, the values shifted to –0.645 and –0.660, respectively. These variations suggest that the observed changes are linked to the differing chemical structures and interaction mechanisms between the elastomer matrices and the plasticizers. The formation and characteristics of the vulcanization network are strongly influenced by the distribution and density of chemical cross-links, along with the average molecular weight and its distribution. In elastomeric systems modified with BRGPR, which serve as organomineral compositions, the vulcanization process demonstrates enhanced sulfur bonding kinetics.

The sulfur cross-linking with macromolecular chains, as illustrated in Figure 4, indicates that the development of the vulcanization network proceeds at a relatively high rate.

****.

**FIGURE 4.** Standard recipe - 1, 5 parts by weight - 2 and 10 parts by weight of gas pyrolysis resin bottom residue - 3

Experimental findings indicate that the bottom residue of gas pyrolysis resin enhances the adsorption of sulfur atoms onto the surface of filler particles, which in turn promotes the development of a more robust vulcanization network. This behavior suggests that the residue not only acts as a vulcanization activator but also accelerates the formation of cross-linked structures within the elastomer matrix. Compared to the conventional plasticizer dibutyl phthalate, the pyrolysis resin residue demonstrates superior influence on vulcanization kinetics, particularly under elevated temperature conditions, as illustrated in Table 3.

**TABLE 3.** Influence of plasticizers on the structure of the vulcanization network and properties of vulcanizates of organomineral composition based on SKMS-30ARKM-15 (content 10 parts by weight per 100 parts by weight of rubber)

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Name of Plasticizers | Formed bonds, % | | | | Fp, MPa | KT, 373K, 72 hours |
| -C-Sx-C- | -C-S-S-C- | -C-S-C- | -C-C- |
| Vulcanization temperature of the composition based on SKMS-30ARKM-15 is 433K, time is 40 minutes. | | | | | | |
| Dibutyl phthalate | 33 | 32 | 22 | 13 | 10,6 | 0,75 |
| Gas pyrolysis resin bottom residue | 20 | 26 | 22 | 32 | 14,8 | 0,94 |

As a result, it was found that elastomeric compositions plasticized with cubic residue of gas pyrolysis resin have a great influence on the type, character, and number of cross-links formed during vulcanization, and vulcanizates with higher strength and coefficient of thermal wear were obtained compared to the composition plasticized with dibutyl phthalate plasticizer.

The findings suggest that the bottom residue of gas pyrolysis resin plays a critical role in shaping the structural and performance characteristics of elastomeric composite materials. This effect is likely due to donor–acceptor interactions that occur during the suppression of thermo-oxidative and photochemical degradation processes. When assessing the thermal aging behavior of composites plasticized with this residue, a time-dependent enhancement in tensile strength was observed—surpassing that of samples stabilized with Neozone-D. Concurrently, a slight decline in elongation at break and an increase in both hardness and –C–C– bond content within the vulcanization network were recorded [17, 18]. These outcomes support the conclusion that the active compounds in the gas pyrolysis residue promote additional structural development in the composite under the influence of prolonged heat exposure.

In further evaluations, rubber mixtures formulated with SKI-3 and SKEPT showed a notable decrease in the time required to achieve optimal vulcanization when plasticized with either DBP or BRGPR, as compared to mixtures lacking any plasticizers. In contrast, SKMS-30ARKM-15-based formulations did not exhibit a significant change in vulcanization time relative to the control sample. Nonetheless, the incorporation of BRGPR did lead to a slight improvement in the vulcanization rate under those conditions.

**CONCLUSION**

In summary, the investigation of plasto-elastic behavior in unfilled elastomeric formulations based on SKMS-30ARKM-15, SKI-3, and SKEPT revealed that the incorporation of BRGPR results in Mooney viscosity trends comparable to those observed with conventional industrial plasticizers. Across all tested systems, the viscosity profile remained consistent in terms of reduction and processing dynamics.

Moreover, the use of BRGPR was shown to notably enhance stress relaxation within the elastomeric matrix, exceeding the effectiveness of traditional plasticizers. This improvement indicates a more favorable viscoelastic response under processing conditions. Additionally, the presence of BRGPR was associated with a modest decrease in the time required to achieve optimal vulcanization, further supporting its efficacy as a functional plasticizing additive in elastomer technology.

**REFERENCES**

1. E. Kornev, Tekhnologiya elastomernykh materialov: uchebnik (ISTEK, Moskva, 2009), 502 p.
2. A. A. Dontsov, Protsessy strukturirovaniya elastomerov (Khimiya, Moskva, 1978), 287 p.
3. M. E. Solov’ev and N. D. Zakharov, Optimizatsiya fiziko-khimicheskikh eksperimentov modifitsirovannogo izmelchennogo vulkanizata, Kauchuk i rezina **8**, 9–10 (1984).
4. E. M. Ginting, N. Bukit, D. Gultom, E. Frida, and B. F. Bukit, Preparation and characterization of oil palm empty bunches powder as a filler of polypropylene-natural rubber, Int. J. Civ. Eng. Technol. **10**(6), 453–464 (2019).
5. V. A. Shershnev, Development of concepts regarding the role of activators in sulfur vulcanization of hydrocarbon elastomers, Kauchuk i Rezina **1**, 31–36 (2012).
6. G. Heideman, J. W. M. Noordermeer, R. N. Datta, and B. Van Baarle, Zinc-loaded clay as an activator in sulfur vulcanization: A new alternative to zinc oxide, Rubber Chem. Technol. **77**, 336–352 (2004).
7. O. V. Karmanova, L. V. Popova, and O. V. Poimenova, Development of activation systems for efficient vulcanization of elastomers, Vestn. VGTUIT **3**, 126–129 (2014).
8. T. V. Rogativa, V. F. Shumskii, V. S. Kutianina, and I. P. Getmanchuk, Effect of the technological additive Technol on the rheological properties of styrene-butadiene rubber, Kauchuk i Rezina **3**, 24–28 (2004).
9. H. Chen, C. Wang, C. Hu, J. Zhang, S. Gao, W. Lu, and L. Chen, Vulcanization accelerator-enabled sulfurized carbon materials for high capacity and high stability in lithium–sulfur batteries, J. Mater. Chem. A **3**, 1392–1395 (2015). doi:10.1039/C4TA05938G.
10. S. Liu, J. Yu, K. Bikane, T. Chen, C. Ma, B. Wang, and L. Sun, Rubber pyrolysis: Kinetic modeling and vulcanization effects, Energy **155**, 215–225 (2018). doi:10.1016/j.energy.2018.04.144.
11. M. Wang, J. Zhu, S. Zhang, G. You, and S. Wu, Factors influencing the vulcanization induction period of natural rubber composites: A combined molecular simulation and experimental study, Polym. Test. **80**, 106075 (2019). doi:10.1016/j.polymertesting.2019.106075.
12. E. Teshabayeva, S. Axmadjanov, S. Turobdjonov, and M. Tursunaliev, Properties of elastomer compositions filled with a multifunctional filler, AIP Conf. Proc. **3045**, 06007 (2024). doi:10.1063/5.0145712.
13. E. U. Teshabayeva, S. A. Axmadjanov, M. M. Tursunaliev, and Kh. T. Ergashova, Gas pyrolysis resin as a plasticizer for composite elastomer materials, E3S Web Conf. **383**, 04036 (2023). doi:10.1051/e3sconf/202338304036.
14. E. A. Maxsetbaev, S. M. Turobjonov, A. Ibadullaev, and E. U. Teshabayeva, Poluchenie, svoystva i primenenie kubovogo ostatka gazopiroliznoy smoly v proizvodstve i pererabotke elastomerov, Kompozitsionnye materialy **1**, 166–169 (2024).
15. A. Ibadullaev, E. Maxsetbaev, and A. Babaev, Properties of elastomer compositions with the application of gas pyrolysis resin residue as a plasticizer, AIP Conf. Proc. **3045**, 060005 (2024). doi:10.1063/5.0197534.
16. A. Ibadullaev, E. U. Teshabayeva, and Ya. O. Seidabdullaev, Kataliticheskaya aktivnost’ Mo(V), zakreplennogo na neorganicheskikh napolnitelyakh, v polimerizatsii pentozansoderzhashchikh monomerov, in Proc. Int. Conf. “Catalytic Processes of Oil Refining, Petrochemistry and Ecology” (2013), p. 161–163.
17. E. U. Teshabayeva, A. Ibadullaev, and V. N. Juraev, Sozdanie i primenenie ingredientov na osnove mestnykh syr’evykh resursov i otkhodov proizvodstv v elastomernykh kompozitsionnykh materialakh, Khim. Khim. Tekhnol., 66–71 (2016).
18. A. Kh. Yusupbekov, D. Ya. Yuldashev, and F. Z. Yusupbekova, Rol’ poverkhnostno-aktivnykh veshchestv pri sozdanii energosberegayushchey tekhnologii polucheniya kompozitsionnykh elastomernykh materialov, Kompozitsionnye materialy **4**, 14–18 (2001).