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Application of carbon-mineral filler based on coal shale mining by-products in elastomeric compositions

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Abstract: The integration of biological and renewable resources as fillers or novel components in thermoplastics and rubbers has gained attention due to their potential to mitigate the environmental impact of petroleum- and natural gas-derived fillers. This study explored using a carbon-mineral filler, derived from coal shale processing by-products, as a partial or complete substitute for standard industrial fillers in rubber formulations for sealing materials. Six rubber compositions were produced, varying in the proportion of carbon-mineral filler replacing N550 semi-reinforcing carbon black, and were evaluated for viscoelastic, kinetic, physical-mechanical, structural, and operational properties. Fully substituting technical carbon with the carbon-mineral filler improved technological characteristics, reducing Mooney viscosity by 40.5% and increasing resistance to premature vulcanization by 53.6%. When up to 10 wt.% of N550 was replaced, the materials retained required strength and hardness. Moreover, the elasticity of rubbers increased by up to 1.5 times with higher filler content. Even at elevated substitution levels, sealing performance remained stable, while resistance to aggressive liquid media nearly doubled (up to 1.9 times). These findings suggest that the carbon-mineral filler can extend the service life of rubber sealing products while reducing reliance on conventional fillers.

Keywords: carbon-mineral filler, industrial elastomeric compositions, Mooney viscosity, relative compressive set

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1. Introduction

Technical carbon and white carbon black (hydrated silicon dioxide, $mSiO_2 \cdot nH_2O$) remain the most widely used reinforcing agents in elastomer composites based on both natural and synthetic rubbers. Their incorporation into rubber matrices substantially enhances mechanical performance, particularly strength and deformation characteristics. However, these improvements are now well-documented and understood, and further advancements using this conventional approach have reached a practical limit (Garishin et al., 2018; Basak et al., 2012). To achieve new breakthroughs, it is necessary to explore alternative, non-traditional fillers.

One promising strategy involves the use of finely dispersed clay minerals such as montmorillonite, halloysite, palygorskite, and shungite (Valera-Zaragoza et al., Shakun et al., 2014; Zoromba et al., 2015; Lua et al., 2016). These materials offer natural variability in particle morphology, which can be selected to suit specific application requirements. For instance, montmorillonite dispersion yields ultrathin plate-like structures (Xie et al., 2001; Garishin et al., 2009), palygorskite forms elongated needle-shaped particles (Tang et al., 2016), while shungite results in spherical globular particles (Ignatov et al., 2014). It is important to note that these mineral fillers are derived from soft, loose sedimentary rocks, which typically have a Mohs hardness between 1 and 4. Interestingly, after dispersion, the resulting filler particles exhibit significantly higher hardness and strength than the original mineral. Thus, low initial hardness of the raw mineral serves as an indicator of its favorable dispersibility and suitability for producing high-quality reinforcing fillers.

Incorporating dispersed clay particles into rubber enhances not only its physical and mechanical properties but also provides several valuable functional characteristics, such as improved thermal stability, flame resistance, reduced diffusion permeability, environmental safety, and lower overall production costs (Fengge, 2004). These composite materials represent structurally complex and heterogeneous systems, consisting of a soft, highly elastic, low-modulus rubber matrix reinforced with much harder and stronger dispersed filler particles. Such a structure leads to intricate mechanical behavior, including finite deformation, nonlinear elasticity, and viscoelastic responses, which arise from the coexistence of reversible and irreversible structural transformations during deformation. At present, elastomer composites containing mineral fillers are being actively investigated through both experimental studies and theoretical modeling (Rooj et al., 2012; Rooj et al., 2013; Zhang et al., 2012). From a practical standpoint, one of the most promising applications for these advanced materials is in the manufacturing of automotive tires and various technical rubber goods.

Elastomeric composites are considered highly promising structural materials, with their products widely utilized in industries such as automotive, aviation, aerospace, oil refining, and many others. In the development of these composites and the manufacturing of products from them, significant emphasis is placed on environmental sustainability, along with enhancing both economic and energy efficiency during production. Consequently, there is a growing need for the creation of new types of highly dispersed fillers, including those derived from natural sources. Such fillers should ensure an optimal balance of mechanical characteristics in polymer composites while offering clear advantages over conventional materials, making their development a critical and timely objective.

This study aims to explore the possibility of utilizing a by-product from oil shale extraction as a partial or complete substitute (10-90 wt%) for synthetic filler in specialized rubber compositions. The research focuses on assessing the rheological, kinetic, physical-mechanical, and performance properties of these modified formulations with the goal of lowering production costs and minimizing environmental pollution. For this purpose, an existing industrial rubber compound recipe designed for manufacturing sealing products was selected, where the conventional N550 technical carbon was replaced by the carbon-mineral filler derived from coal shale processing.

2. Materials and methods

2.1 Materials

The study utilized a carbon-mineral filler (CMF) derived from the by-products of coal shale mining at the Balausa deposit (Republic of Kazakhstan) through a preliminary flotation process. This filler has a chemical composition comparable to that of shungite rock (Table 1) but is distinguished by its higher carbon content and stable, uniform composition.

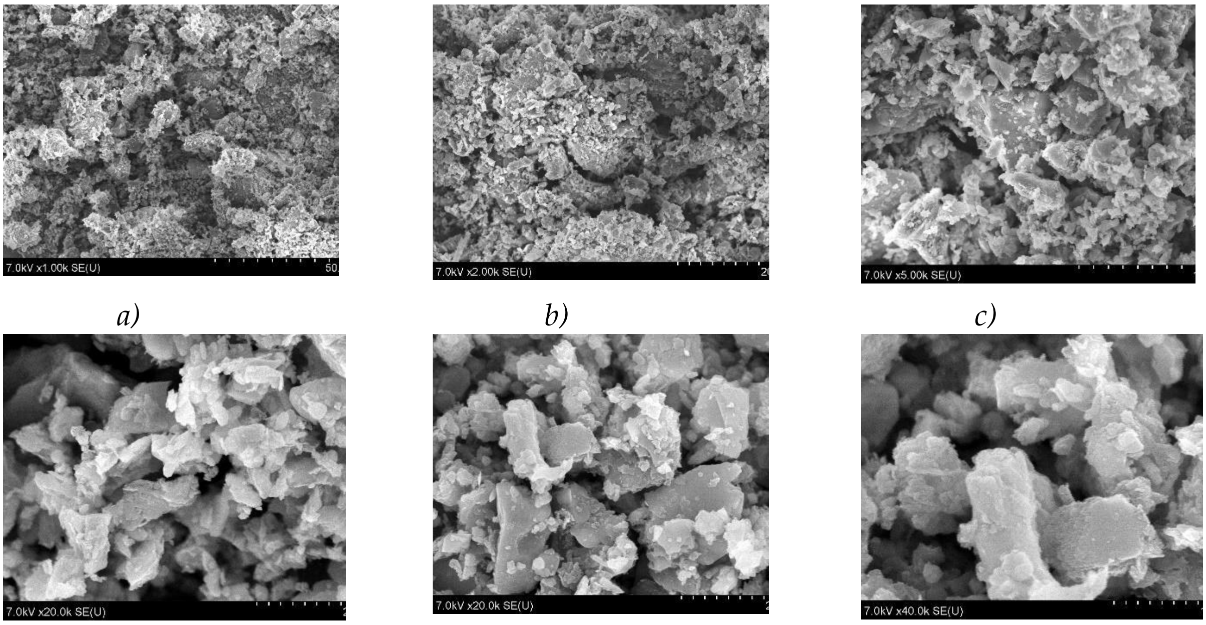
Table 1. Elemental composition of the surface of carbon-mineral filler

Elements	Content, %
C	38.34
O	35.85
Si	18.24

Al	1.20
S	1.41
Fe	1.82
K	0.79
Ba	2.23
Mg	0.05
P	0.04
Na	0.01
Ca	0.02

The CMF contains a relatively high level of metal impurities (≈6.16%) along with a measurable amount of sulfur (1.41%), both of which can significantly influence the kinetic behavior during the processing of rubber compounds.

The CMF is characterized by a structure composed of fragmented mineral aggregates interspersed with larger grains, which are surrounded by fragments of the rock matrix (Figure 1).



a) *b)* *c)*

d) *e)* *f)*

a) ×100, b) ×200, c) ×500, d) ×2000, e) ×2000, f) ×4000

Figure 1. SEM image of CMF at different magnifications

The physicochemical characteristics of the CMF are presented in Table 2.

Table 2. Physicochemical characteristics of CMF

Indicator name	Indicator value
Specific external surface area according to BET, m^2/g	21
Sorption volume, cm^3/g	0.02
Particle size, µm	5
Structure	crystalline

X-ray phase analysis conducted using a D8 Advance Bruker AXS diffractometer (Germany) revealed that the silicon in the CMF exists predominantly in a crystalline form (Figure 2).

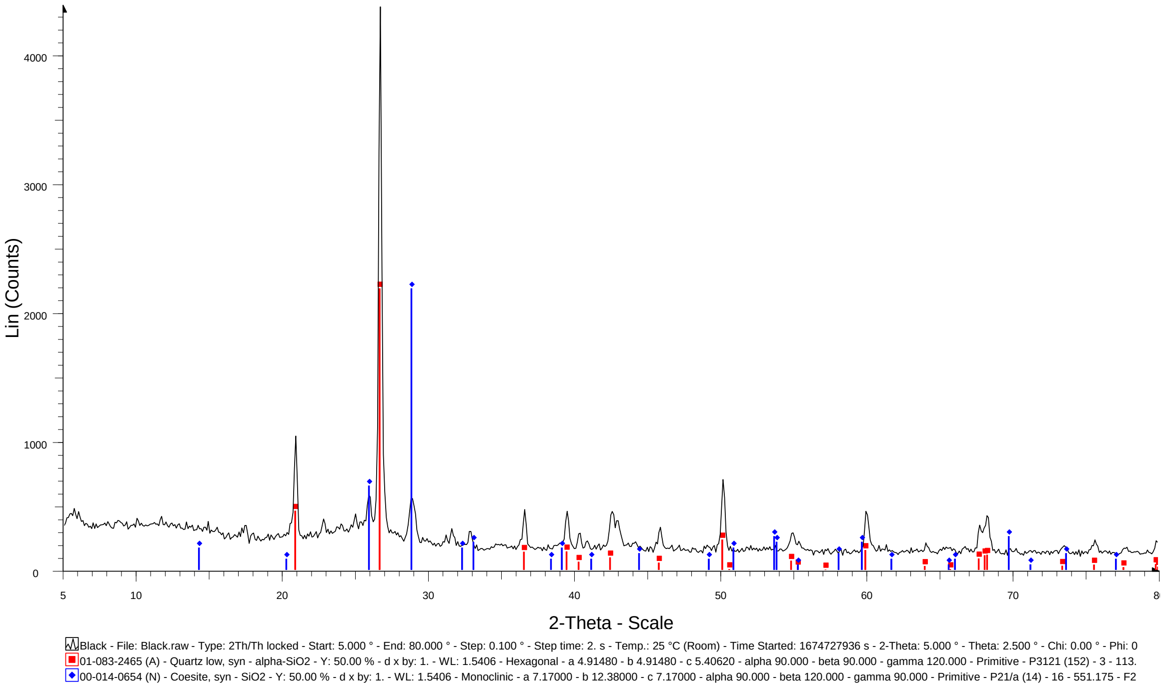


Figure 2. Diffractogram of the CMF sample

To evaluate the feasibility of incorporating CMF into production, studies were carried out using an existing industrial formulation of an elastomeric composition based on BNKS-18AMN synthetic butadiene-nitrile rubber (GOST R 54556-2011, 2013), specifically designed for manufacturing sealing products (Table 3). The formulation is presented solely for reference, as the exact industrial recipe cannot be disclosed by the authors.

Table 3. Recipe for industrial elastomeric compositions

Ingredient name	Ingredient content, wt. parts
BNKS-18 AMN	100.00
Sulfur	2.60
Vulcanization accelerators	2.45
Zinc white	5.0
Antioxidants	2.0
Filler: technical carbon grade N550	90
Plasticizer	35
Stearic acid	1
Total	238.05

The BNKS-18 AMN-based composition is utilized in the production of sealing rings that require high sealing performance. For this purpose, a semi-reinforcing grade of carbon black, N550, is used, featuring a specific external surface area of 41 m^2/g and an average aggregate size of 3 μm, as determined experimentally and in accordance with ASTM D1765-03. The structural characteristics of carbon black depend on its grade, which is defined by the size of primary particles and the morphology of aggregates. Based on these parameters, carbon black can exhibit either a highly aggregated or a less aggregated structure. Typically, aggregates are further combined into agglomerates held together by physical forces. Highly reinforcing grades of carbon black are distinguished by a greater proportion of branched aggregates, which create porous structures with a large surface area. This extensive surface promotes strong interactions with the rubber matrix, resulting in superior reinforcing effects (Balasooriya et al., 2019; Savetlana et al., 2017). Reinforcing fillers enhance the mechanical strength of rubbers and improve other key performance characteristics, such as tear resistance, wear resistance, and conditional stress at specific deformations. Conversely, when the structure of carbon black decreases, a higher proportion of spheroidal and ellipsoidal aggregates is observed (Jurkiewicz et al., 2018). Fillers with a low structure are less effective at reinforcement but are commonly used to reduce the production cost of rubber compounds. They also improve processing characteristics through hydrodynamic effects and can impart specific properties, such as improved heat and light resistance, to the final rubber product (Savetlana et al., 2017).

In the tested formulation, both partial replacement of N550 technical carbon with carbon-mineral filler in dosages ranging from 10 to 50 wt.% and its complete replacement in a dosage of 90 wt.% were carried out. With partial replacement, the total filler content in the elastomeric composition remained unchanged.

The concentrations of all other components in the formulation were kept constant, allowing for a clear assessment of the influence of the CMF on the technological and performance properties of the industrial elastomeric compositions.

2.2 Methods

The mixing of the components was carried out on RC-WW 330 150/150 laboratory roll mills (Rubicon, Germany) at a temperature of 45±5°C and a roll speed of 25 rpm. Following the mixing process, the rubber compound was used without any additional treatment. The introduction of the carbon-mineral filler was performed simultaneously with N550 carbon black in three successive stages.

In this study, the Mooney viscosity of the rubber compounds was measured using an MV 2000 shear disc viscometer (Alpha Technologies, USA) following the requirements of GOST R 54552-2011 (GOST R 54552-2011, 2013). The test involves immersing a metal rotor (disc) into a rubber compound sample placed inside a rigid cylindrical chamber, where specific pressure and temperature conditions are maintained. The rotor rotates slowly at a constant speed in one direction for a set period of time. The resistance of the rubber to this movement generates torque, which is recorded in conventional units and expressed as the Mooney viscosity of the sample.

The vulcanization and rheological characteristics of the rubber compounds were evaluated using kinetic vulcanization curves obtained with an ODR 2000 rheometer (Alpha Technologies, USA) in accordance with GOST 12535-84 (GOST 12535-84, 1985). This method involves measuring the torque generated during shear deformation of the sample, which is caused by the oscillations of a rotor equipped with a biconical disc operating at a specified frequency and amplitude under controlled temperature conditions. Test specimens weighing 10 g were prepared in any shape that allowed the chamber to be completely filled. The vulcanization of the BNKS-18 AMN-based elastomeric compositions was performed at 163°C for 30 minutes using a vulcanizing press, after which the samples were kept at room temperature for 24 hours prior to mechanical testing.

The evaluation of elasticity and strength properties of the elastomeric compositions was performed by determining the conditional tensile strength and elongation at break at a stretching speed of 500 mm/min using a T2020 DC10 SH tensometer (Alpha Technologies, USA). Testing was conducted on 15 standard specimens for each rubber formulation in compliance with GOST 270-75 (GOST 270-75, 1975). The method involves stretching the test samples at a constant rate until rupture, while measuring the force at specific elongation points, as well as recording both the force and elongation at the moment of sample failure.

The Shore A hardness of the elastomeric compositions was measured using a DIGI-TEST hardness tester (Bareiss, Germany) in accordance with GOST 263-75 (GOST 263-75, 1989). This method is based on determining the material's resistance to the penetration of an indenter into the rubber surface.

The relative residual compression deformation (RRCD) of the rubber samples was measured on nine specimens following the procedure outlined in GOST 9.029-74 (GOST 9.029-74, 1982). The RRCD value, expressed as a percentage and calculated with an accuracy of 0.01, was determined using Formula 1:

$$C=\frac{h_0-h}{h_0-h_s} \tag{1}$$

where h_0 – height of the sample before testing, mm;
h – height of the sample after «resting», mm;
h_S – height of the limiter, mm

The method involves subjecting the samples to static compression deformation, after which the RRCD value is used to assess the rubber's ability to maintain its elastic properties following aging under controlled conditions. The tests were performed at 25% compression and a temperature of 125±2°C. The final result was calculated as the arithmetic mean of the measurements obtained from all tested specimens, with a minimum of three samples required for accuracy.

The resistance of the elastomeric compositions to aggressive liquid media was assessed by measuring the changes in mass and volume of the samples after exposure to a standard test liquid. To evaluate the chemical resistance of the rubbers, the samples were immersed in a 70:30 vol.% mixture of isooctane and toluene and kept at a temperature of 23±2°C for a period of 1 to 7 days, following the procedure specified in GOST 9.030-74 (method A) (GOST 9.030-74, 2006).

The equilibrium swelling method is one of the most commonly applied techniques for determining the cross-linking density of vulcanized rubber materials (Averko-Antonovich et al., 2002). For this study, five rubber samples were prepared, each measuring 200×10×2±0.2 mm. The samples were initially weighed using analytical balances and then immersed in toluene as the solvent. After reaching the equilibrium swelling state, the specimens were placed in an oven at 60±1°C for 24 hours to completely remove the absorbed solvent, followed by a final weighing to determine mass changes.

The volume fraction of rubber in the swollen unfilled vulcanizate V_r, m^3/mol, was calculated from the ratio:

$$V_r=\frac{P_{start}\cdot\frac{F}{\rho_r}}{P_{start}\cdot\frac{F}{\rho_r}+\frac{P_{swell}-P_{dry}}{\rho_s}} \tag{2}$$

where P_{start} – is the initial mass of the sample, kg;
F – mass fraction of rubber in the vulcanizate;
P_{swell} – mass of the swollen sample, kg;
P_{dry} – mass of the sample dried after swelling, kg;
ρ_r, ρ_s – densities of rubber and solvent (toluene), kg/m^3.

For filled rubbers, the value of V_r was converted to V_{r0} using the equation of Cannin and Russell (Ovcharov, 2001):

$$V_{r_0}=V_r\cdot(a\cdot e^{-s}+b) \tag{3}$$

where a and b are constants characterizing the system (for the rubbers under study, a = 0.56; b = 0.44);
z is the mass fraction of the filler in the vulcanizate.

The average molecular weight of the chain segment M_c enclosed between two crosslinks was determined using the Flory-Renner equation:

$$\frac{1}{M_c}=\frac{V_{r_0}+\chi\cdot V_{r_0}^2+ln(1-V_{r_0})}{\rho_\kappa\cdot V_0\cdot(V_{r_0}^{\frac{1}{3}}-0,5\cdot V_{r_0})} \tag{4}$$

where V_0 is the molar volume of the solvent, m^3/mol;

χ – Huggins constant, which characterizes the polymer-solvent interaction.

The value of χ for each sample was calculated according to Kraus, who assumed a linear relationship between χ and V_r:

$$\chi=0,37+0,52\cdot V_r \tag{5}$$

The number of cross-links n contained in 1 cm^3 of vulcanizate was calculated using the formula:

$$n=\frac{N_A\cdot\rho_\kappa}{M_c} \tag{6}$$

where N_A is Avogadro's number, $6.023\cdot10^{-23}$ mol^{-1}.

The cross-linking density ν, mol/m^3 was determined by the expression:

$$v=\frac{\rho_\kappa}{M_c} \tag{7}$$

where ρ is the density of the vulcanizate, kg/m^3.

Based on the study results, the obtained data were subjected to mathematical processing, which demonstrated that the relative measurement error at a confidence level of 0.95 did not exceed 5%. The analysis and processing of the experimental results were carried out in compliance with GOST 269-66 (GOST 269-66, 1993).

3. Results and discussion

3.1 Determination of viscosity according to Mooney

Figure 3 presents the results of measuring the Mooney viscosity (M_L) of rubber compounds formulated with different amounts of carbon-mineral filler based on BNKS-18 AMN.

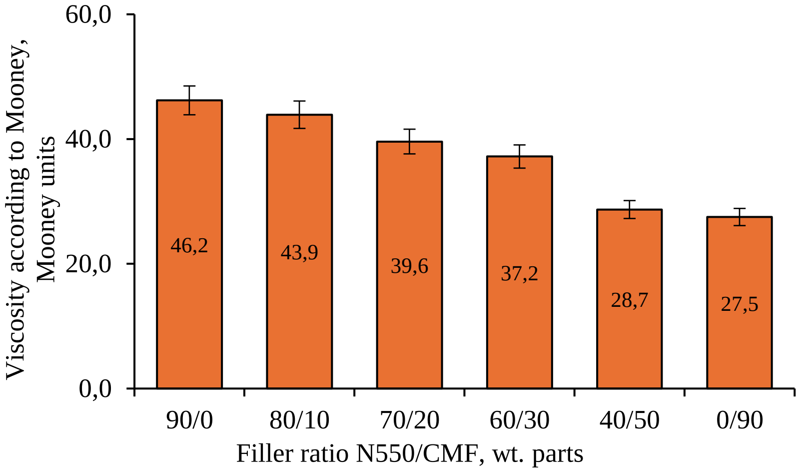


Figure 3. Dependence of the change in Mooney viscosity of rubber compounds on the dosage of CMF in elastomeric compositions based on BNKS-18 AMN

When N550 carbon black was replaced with CMF, the Mooney viscosity of the rubber compounds decreased by 5.0-40.5% as the CMF content increased. This reduction is attributed to the differences in the physicochemical surface properties of the fillers, particularly their specific external surface area. CMF has a surface area of 21 m^2/g, whereas N550 carbon black has a higher value of

41 m^2/g. Due to this difference, the ability of the combined filler system to form chain-like structures is significantly diminished, which weakens the physical interactions between the filler and the rubber matrix. As a result, the mobility of elastomer macromolecular segments increases, facilitating greater shear deformation and easier movement of macromolecules relative to one another, ultimately leading to lower viscosity (Fernandes et al., 2017). This decrease in viscosity is advantageous for processing, as it reduces the energy consumption required during the manufacturing of rubber compounds (Beknazarov et al.).

3.2 Determination of the kinetic parameters of the vulcanization process

Vulcanization of elastomeric compositions is the process in which rubber reacts with a vulcanizing agent, leading to the formation of a three-dimensional cross-linked network. During this process, the plasticity of the rubber decreases, while its elasticity and strength increase. At the initial stage, the rubber compound gradually loses its fluidity (sub-vulcanization). This is followed by the main stage, characterized by a sharp increase in strength as cross-linking intensifies. When the optimal vulcanization point is reached, the rubber achieves a balanced combination of physical and mechanical properties. After reaching this optimum, the material maintains its properties for a certain period, known as the vulcanization plateau. However, with prolonged vulcanization, reversion (over-vulcanization) occurs, leading to the breakdown of cross-links and a deterioration of rubber properties. By analyzing the kinetic parameters of the vulcanization process using rheometers, it is possible to track and evaluate all major stages of network formation and structural changes during vulcanization (Shutilin, 2003).

Table 4 shows the kinetic parameters of the vulcanization process of industrial rubber compounds based on BNKS-18 AMN with carbon-mineral filler.

Table 4. Kinetics of vulcanization of rubber compounds based on BNKS-18 AMN

Filler ratio N550 / CMF, wt. parts	M_L, dH·m	t_{s2}, min	ts(90), min	ΔM, dN·m
90 / 0 (industrial)	6.62	1.66	4.33	26.87
80 / 10	3.87	1.92	4.23	25.58
70 / 20	3.30	1.91	4.07	24.99
60 / 30	2.80	2.06	4.69	23.15
40 / 50	2.55	2.24	4.59	21.41
0 / 90	2.10	2.55	5.11	16.34

Notes:
1. M_L – minimum torque, dN·m;
2. t_{s2} – vulcanization start time, determined by an increase in minimum torque by 2 Nm, min;
3. $t_{c(90)}$ – optimal vulcanization time, min;
4. ΔM – difference between maximum and minimum torque, dN·m.

The analysis of the vulcanization kinetics revealed that partial substitution of N550 carbon black with CMF results in a 41.5-68.3% decrease in M_L compared to the control composition containing only carbon black. This reduction reflects the enhanced fluidity of the modified rubber mixtures (Brum et al., 2019). These findings align with the observed trends in Mooney viscosity changes, confirming the consistency of the results. Furthermore, the pronounced decrease in this parameter highlights the significant role of metal impurities present in the CMF (Table 1), which strongly affect the vulcanization kinetics (Kabulov et al., 2022).

It was found that partial replacement of N550 carbon black with CMF leads to a notable increase (up to 53.6%) in the onset time of vulcanization (t_{s2}), indicating higher resistance to sub-vulcanization. As a result, the optimal vulcanization time also rises by up to 15.3%. However, these effects are observed only at higher CMF concentrations (30-90 wt%). This behavior is likely associated with the high porosity of the CMF surface, which enhances the adsorption of vulcanizing system components. Such adsorption reduces their availability in the rubber matrix, thereby slowing down the vulcanization reaction (Dominic et al., 2019).

The analysis of the difference between the maximum and minimum torques (ΔM), which serves as an indirect measure of polymer crosslinking density (Ovcharov, 2001), showed that incorporating CMF derived from coal shale by-products into elastomeric compositions causes a reduction of up to 39.2% in this parameter compared to the industrial control formulation. This decrease suggests weaker interactions within both the «rubber-filler» and «filler-filler» systems. Such a reduction in interfacial bonding is expected to have a significant impact on the elasticity and strength of the resulting rubber materials.

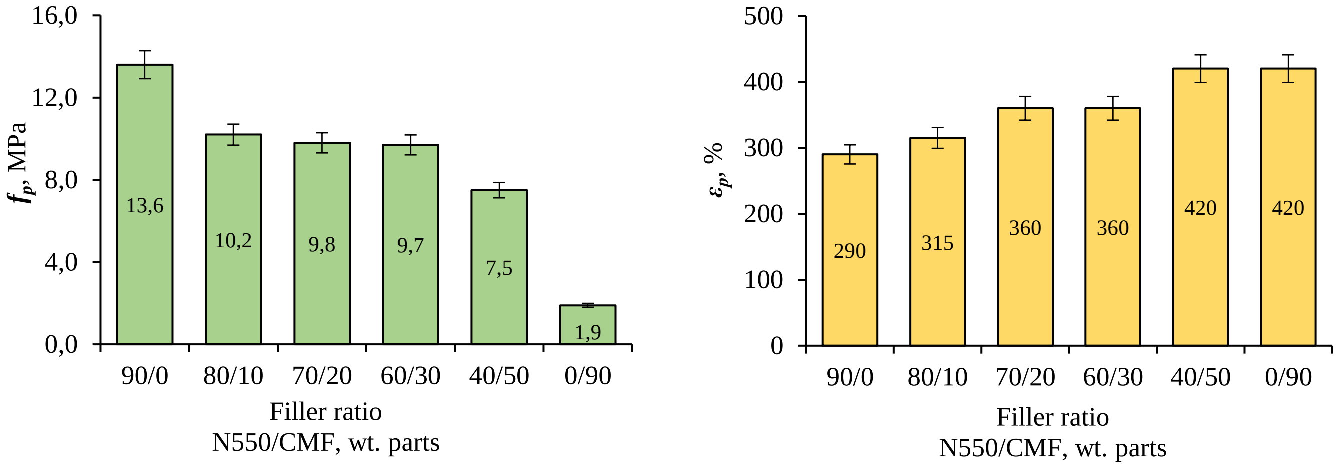
3.3 Study of the effect of CMF *on the physical and mechanical properties of elastomeric compositions*

To evaluate the impact of CMF on rubber performance, the physical and mechanical properties of the vulcanizates were examined. The analysis included measuring the conditional tensile strength (f_p), elongation at break (ε_p), and Shore A hardness.

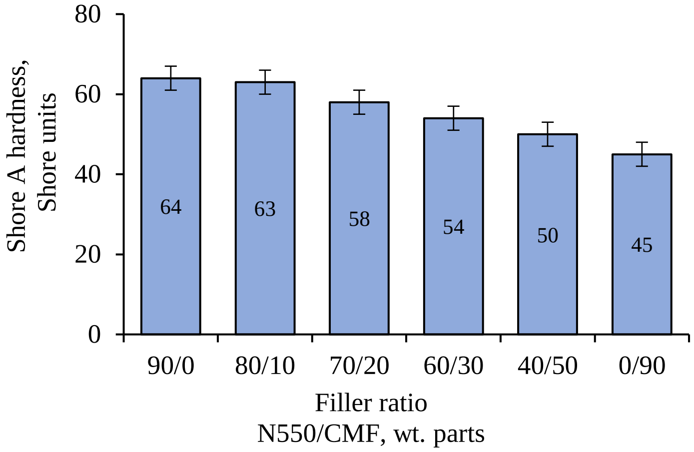
The industrial BNKS-18 AMN-based elastomeric composition is designed for the production of sealing products that must comply with the requirements of TU 2512-046-00152081-2003 (TU 2512-046-00152081-2003, 2003). According to this standard, the finished products should exhibit the following technical specifications:

- Conditional tensile strength (f_p): not less than 7.8 MPa;
- Elongation at break (ε_p): at least 150%;
- Shore A hardness: within the range of 60-85 units.

Figure 4 presents the results of testing the physical and mechanical properties of special-purpose rubber compounds in which CMF was used as a partial or complete replacement for N550 carbon black.



a) *b)*



c)

a) conditional tensile strength; b) relative elongation at break; c) Shore A hardness

Figure 4. Physical and mechanical characteristics of elastomeric compositions based on BNKS-18 AMN containing CMF in various dosages

It was found that partial substitution of N550 carbon black with CMF at dosages of up to 30 wt% results in a 28.7% reduction in conditional tensile strength (f_p). Despite this decrease, the strength values remain within the technical requirements for this type of rubber. However, when the CMF content exceeds 30 wt%, a sharp decline in tensile strength is observed (Figure 4*a*). The reduction in rubber strength in the presence of CMF can be attributed to its inert filler effect, which leads to non-uniform distribution of applied stress during tensile testing (Zhang et al., 2004; Şehriban et al., 2024). A similar trend was observed in the Shore A hardness values (Figure 4*c*). The hardness of the industrial composition was 64 Shore units, while formulations with CMF ranged from 63 to 45 Shore units, depending on the level of replacement. Conversely, relative elongation at break (ε_p) increased by up to 1.5 times with higher CMF dosages (Figure 4 *b*). This effect correlates with the observed changes in fp and is explained by a reduction in intermolecular forces between polymer chains, which enhances their mobility and flexibility (Karaagaç, 2014). The differences in strength characteristics of CMF-containing rubbers are most likely due to a lower crosslink density of the vulcanization network combined with a decrease in reinforcing filler content. At higher filler loadings, variations in particle structure and surface energy may cause filler agglomeration or dilution effects, which further reduce strength. This behavior suggests that CMF particles are less capable of bearing and distributing stress within the polymer matrix, leading to deterioration of the rubber's mechanical properties (Arayapranee et al., 2005).

3.4 Determination of the cross-linking density of rubbers

Rubber is produced through the vulcanization process, during which linear macromolecules of rubber are chemically cross-linked, forming a three-dimensional network structure. This transformation fundamentally alters the material’s properties, giving the final product its characteristic strength and elasticity. One of the key structural parameters of amorphous network polymers is the degree of cross-linking, which directly influences their performance. The physical and mechanical properties of vulcanized rubber are closely related to both the crosslink density and the overall architecture of the vulcanization network (Kimet et al., 2020).

To describe the spatial network structure of rubbers, key parameters are used, including the crosslink density (v) and the number of crosslinks per cubic centimeter of vulcanizate (n). These indicators provide essential information about the degree of network formation and are crucial for evaluating the performance characteristics of vulcanized rubber materials (Averko-Antonovich et al., 2002).

Table 5 presents the results of determining the spatial network indicators of the studied elastomeric compositions containing CMF in various ratios.

Table 5. Spatial network indicators of industrial rubbers

Filler ratio N550 / CMF, wt. parts	Name of indicators	
	$n \cdot 10^{-19}$, cm^{-3}	$\nu \cdot 10^{4}$, mol/cm^{3}
90 / 0 (industrial)	10.56±0.5	1.75±0.1
80 / 10	10.16±0.5	1.68±0.1
70 / 20	9.64±0.5	1.60±0.1
60 / 30	9.28±0.5	1.54±0.1
40 / 50	8.18±0.4	1.36±0.1
0 / 90	6.66±0.3	1.11±0.1

The analysis of the spatial network parameters of special-purpose rubber compounds in which CMF was used to replace the synthetic filler N550 demonstrated that the addition of CMF caused a reduction of up to 36.9% in the number of cross-links (*n*) compared to the formulation containing only carbon black. These findings are consistent with the results obtained from evaluating the vulcanization kinetics (Table 5). A less dense crosslinking network leads to increased elasticity of the vulcanizates, as it reduces the intermolecular interactions between macromolecular chain segments located between the network nodes (Zhovner et al., 2003). Moreover, due to their smaller particle size and larger specific surface area, carbon black particles facilitate a higher degree of crosslinking with the elastomer matrix compared to CMF (Savetlana et al., 2017).

3.5 Study of the effect of CMF on the relative residual compression deformation of rubbers

Modern technology heavily relies on rubber products, which are essential components in various machines and often directly influence their operational efficiency. When designing rubbers for such applications, it is crucial to consider both the operating conditions and the types of deformation the material will experience during service. Selecting the key performance indicators for rubber products is often the most challenging part of development. For non-stressed rubbers, these indicators typically include relative elongation, tensile strength, and elastic modulus. In contrast, for stressed rubbers, residual deformation becomes a critical parameter. Since the geometric dimensions of rubber products must remain nearly unchanged throughout their service life, the relative residual compression deformation (RRCD) is considered one of the most important indicators. It reflects the rubber's ability to maintain its elastic properties under continuous compression. A lower RRCD value indicates better performance and higher suitability of the rubber for long-term use (Ilyicheva et al., 2021).

Given that the BNKS-18 AMN-based compositions under study are designed for the production of sealing products, which are typically mounted in a fixed position and subjected to static compression deformation caused by the weight of the machinery and operational loads, tests were carried out to measure the RRCD of these materials (Figure 5).

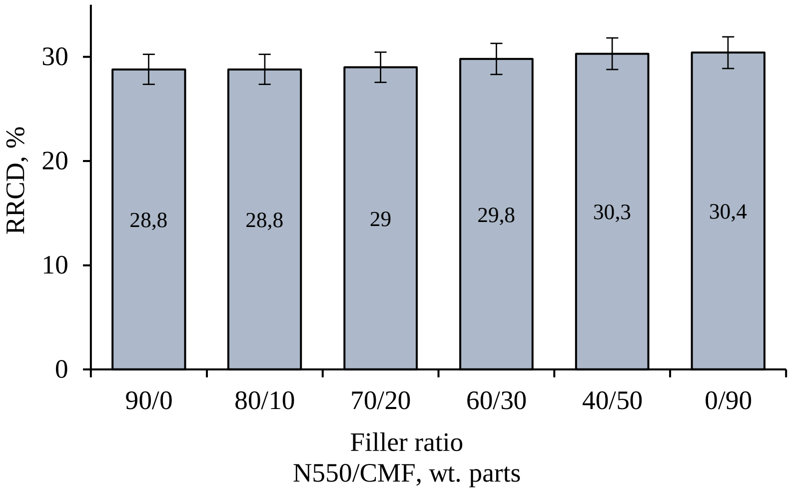


Figure 5. Dependence of the change in the relative residual compression deformation of elastomeric compositions on the filler ratio

Comparative analysis of the sealing performance of BNKS-18 AMN-based rubbers showed that replacing the semi-reinforcing N550 carbon black with CMF leads to a slight increase in RRCD values, by up to 5.5%, as the CMF content rises compared to the formulation with only industrial filler. This trend can be explained by the higher elasticity of the macromolecular chain segments between the network nodes in CMF-containing compositions. This enhanced flexibility facilitates the return of the polymer chains to their original conformation after compression, thereby maintaining the sealing properties of the material.

3.6 Study of the effect of CMF on the resistance of rubbers to aggressive environments

Rubbers are widely used for sealing devices because of their high elasticity, excellent shock-absorbing capacity, and other valuable performance characteristics. Typically, these seals operate in direct contact with hydrocarbon-based working media, which can significantly alter their composition and properties over time (Fedorova et al., 2022). Considering this, it was important to investigate how different dosages of CMF affect the resistance of BNKS-18 AMN-based rubbers to aggressive liquid environments. For this purpose, tests were conducted using a 70:30 mixture of isooctane and toluene as the standard medium (Figure 6).

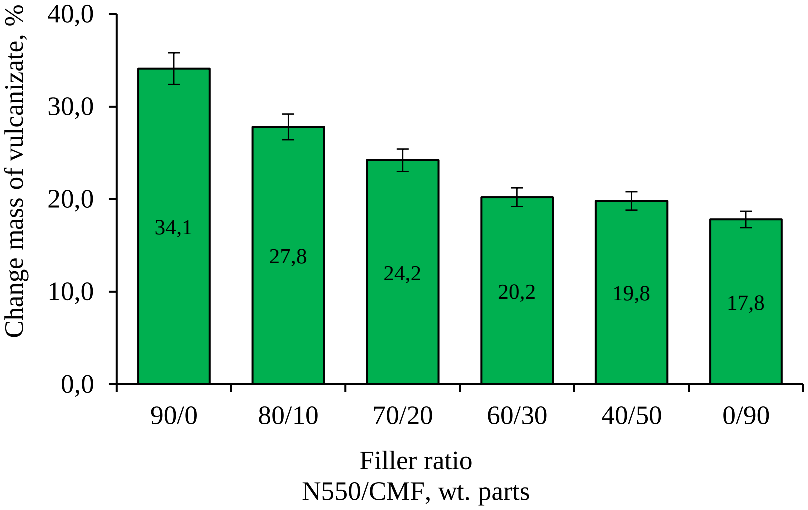


Figure 6. Dependence of the change in mass of rubbers on CMF after exposure to liquid aggressive media

The study of BNKS-18 AMN-based elastomeric compositions containing CMF demonstrated that increasing the CMF content enhances the resistance of vulcanizates to swelling in aggressive liquid media. Specifically, as the CMF dosage rises, the resistance improves by up to 1.9 times compared to the composition filled only with N550 carbon black. This behavior is likely linked to the physicochemical properties of the CMF surface. The interaction between aggressive liquids and filled rubbers largely depends on the wettability and activity of the filler, as well as the strength of the filler-rubber network it forms. Fillers are generally classified into active and inert types. Active fillers contribute to the higher strength and wear resistance of rubbers. Inert fillers, on the other hand, primarily impart special properties, such as heat resistance or enhanced chemical resistance (Vorobyova, 1981). Given these characteristics, the improved resistance of CMF-containing rubbers is most likely due to the inert nature of CMF, which limits the penetration of aggressive media into the rubber matrix.

4. Conclusion

This study examined the effect of a natural carbon-mineral filler (CMF), derived as a by-product of coal shale mining at the Balausa deposit (Republic of Kazakhstan), on the properties of BNKS-18 AMN-based elastomeric compositions designed for the production of sealing products. The findings showed that complete replacement of N550 carbon black with CMF led to a decrease in Mooney viscosity of the rubber compounds by up to 40.5%, indicating improved processability compared to the industrial reference composition. Rheometric analysis revealed that increasing the proportion of CMF enhanced the resistance to premature sub-vulcanization, with a rise of up to 53.6%. In terms of mechanical properties, full substitution of N550 with CMF caused a reduction in conditional tensile strength by up to 86.0%, while the relative elongation at break increased by up to 1.5 times. Notably, replacing up to 10 wt% of carbon black with CMF allowed for the production of rubbers that met the required technical specifications for sealing applications. Furthermore, higher CMF loadings preserved the sealing performance (variation within 5.5%) and significantly improved the resistance to aggressive liquid media, with an increase of up to 1.9 times. Overall, these results demonstrate that carbon-mineral filler can serve as a sustainable and cost-effective alternative to conventional fillers in the rubber industry, offering environmental benefits while maintaining satisfactory performance in sealing products.

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6. Author Contributions

Conceptualization - V.B., A.K.; methodology - S.N., A.K.; software - V.B.; validation - A.K., V.B., S.N., A.K.; formal analysis - A.K., S.N.; investigation - V.B., S.N., A.K.; resources - A.K.; data curation - A.K., S.N.; writing-original draft preparation - A.K., V.B., S.N., A.K.; writing-review and editing - A.K., S.N.; visualization - V.B.; supervision - A.K.; project administration - S.N.; funding acquisition - S.N. All authors have read and agreed to the published version of the manuscript.

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Эластомерлік композицияларда көміртекті тақтатас өндірудің жанама өнімдеріне негізделген көміртекті минералды толтырғышты қолдану

Валерия Боброва, Сергей Нечипуренко, Андрей Касперович, Айгерим Кайайдарова

Аңдатпа. Биологиялық және жаңартылатын ресурстарды термопластар мен резеңкеде толтырғыш немесе жаңа компоненттер ретінде пайдалану олардың мұнай мен табиғи газдан алынған толтырғыштардың қоршаған ортаға әсерін азайту қабілетінің арқасында назар аудартады. Бұл зерттеу көміртекті тақтатастарды қайта өңдеудің жанама өнімдерінен алынған көміртекті минералды толтырғышты тығыздағыш материалдарға арналған резеңке композициялардағы стандартты өнеркәсіптік толтырғыштарды ішінара немесе толық ауыстыру ретінде пайдалануды қарастырады. N550 жартылай армирленген күйені алмастыратын көміртек-минералды толтырғыштың арақатынасымен ерекшеленетін және тұтқыр серпімді, кинетикалық, физикалық-механикалық, құрылымдық және пайдалану қасиеттеріне бағаланған алты резеңке композиция жасалды. Көміртекті көміртекті-минералды толтырғышпен толық ауыстыру технологиялық өнімділікті жақсартты, Муни тұтқырлығын 40,5%-ға төмендетті және мерзімінен бұрын вулканизацияға төзімділікті 53,6%-ға арттырды. 10 мас.% дейін ауыстырған кезде N550 материалдар қажетті беріктік пен қаттылықты сақтады. Сонымен қатар, каучуктердің иілгіштігі толтырғыштың мөлшері жоғары болған кезде шамамен 1,5 есе өсті. Толтырғыштың мөлшері артқан кезде де тығыздау тұрақты болып қалды, ал қатты сұйық ортаға төзімділік екі есеге жуық өсті (1,9 есеге дейін). Бұл нәтижелер көміртекті-минералды толтырғыш кәдімгі толтырғыштарға тәуелділікті азайта отырып, резеңке тығыздағыштардың қызмет ету мерзімін ұзарта алатынын көрсетеді.

Түйін сөздер: көміртек-минералды толтырғыш, өнеркәсіптік эластомерлік композициялар, Муни бойынша тұтқырлық, салыстырмалы қалдық қысу деформациясы

Применение углерод-минерального наполнителя на основе побочных продуктов добычи углистых сланцев в эластомерных композициях

Валерия Боброва, Сергей Нечипуренко, Андрей Касперович, Айгерим Кайайдарова

Аннотация: Использование биологических и возобновляемых ресурсов в качестве наполнителей или новых компонентов в термопластах и каучуках привлекло к себе внимание благодаря их потенциальной способности снижать воздействие на окружающую среду наполнителей, получаемых из нефти и природного газа. В этом исследовании изучалось использование углерод-минерального наполнителя, получаемого из побочных продуктов переработки каменноугольных сланцев, в качестве частичной или полной замены стандартных промышленных наполнителей в резиновых композициях для уплотнительных материалов. Было изготовлено шесть резиновых композиций, отличающихся соотношением углерод-минерального наполнителя, заменяющего полуармирующую сажу N550, и которые были оценены на вязкоупругие, кинетические, физико-механические, структурные и эксплуатационные свойства. Полная замена технического углерода углеродно-минеральным наполнителем улучшила технологические характеристики, снизив вязкость по Муни на 40,5%

и повысив устойчивость к преждевременной вулканизации на 53,6%. При замене до 10 мас.% N550 материалы сохраняли требуемую прочность и твердость. Кроме того, эластичность каучуков увеличилась почти в 1,5 раза при более высоком содержании наполнителя. Даже при повышенном количестве наполнителя герметичность оставалась стабильной, а стойкость к агрессивным жидким средам почти удвоилась (до 1,9 раза). Эти результаты свидетельствуют о том, что углеродно-минеральный наполнитель может продлить срок службы резиновых уплотнительных изделий, снижая при этом зависимость от обычных наполнителей.

Ключевые слова: углерод-минеральный наполнитель, промышленные эластомерные композиции, вязкость по Муни, относительная остаточная деформация сжатия