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Synthesis and Investigation of Dithiocarbamate Derivatives as Polyfunctional Ingredients in Rubber Compounds

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ABSTRACT

The synthesis of dithiocarbamate derivatives and their potential application as accelerators and anti-degradants in rubber compounds have been investigated. The physico-mechanical properties of vulcanizates based on IR SKI-3 and their resistance to thermo-oxidative aging have been determined. The influence of the obtained compounds on the dynamic properties of the composition has been established. Partial replacement of captax with synthesized 2-fluorophenyl dithiocarbamate triethylamine allows maintaining the strength at the level of the control sample. At the same time, the rubbers exhibit increased resistance to dynamic loads and comparable values of the tangent of mechanical loss angle at high deformation levels compared to vulcanizates containing only captax. This effect is achieved by increasing the polarity of the radical and improving the mobility of the chains of rubber macromolecules, which is confirmed by the calculation of the time spectrum of relaxation for mechanical vibrations under shear deformations. Also, the synthesized product has a positive effect on the resistance of rubber to thermal-oxidative aging.

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1. INTRODUCTION

During processing, storage, and use, polymers are subjected to heat, light, oxygen, mechanical stress, and other influences. As a result, the properties of polymers change: mechanical strength decreases, elasticity diminishes, brittleness appears, color alters, smooth surfaces become rough, and so on. These property changes lead to a deterioration in quality and a reduction in the service life of polymer products [1].

Aging can be prevented by introducing small amounts of chemical substances—stabilizers—into the polymers. Their introduction enhances the polymer's resistance to external influences, expands the range of applications for polymer products, and increases their service life.

Some stages of the oxidation process can be suppressed with the help of vulcanization accelerators, and the addition of technical carbon binds radicals, significantly reducing the polymer's rate of oxidation.

The more antioxidants present in the mixture, the more effective their action. However, it is not sensible to add substances indiscriminately: for many compounds, an optimal concentration has been developed, above which efficiency does not increase and may even begin to decline [2,3].

The choice of an antioxidant can be made based on its effectiveness in inhibiting processes that lead to rubber aging. The chemical structure primarily influences the effectiveness of antioxidants and stabilizers [4-8]. When comparing the structure and effectiveness of rubber antioxidants, attention is paid to the presence of mobile hydrogen atoms in the antioxidants, the energy required to detach which is lower than the energy needed to detach hydrogen atoms from a carbocyclic polymer molecule. In the case of amine-type antioxidants, increased effectiveness is noted with an increase in conjugation within their molecules [8].

The favorable effect is achieved by introducing polar substituents such as -OH, -OMe, etc. (especially in ortho- and para-positions). For single-atom phenols, an increase in effectiveness is observed with the introduction of alkyl groups into their core, with efficiency rising as the number of carbon atoms in the alkyl chains increases from C1 to C4. Introducing a single substituent group in the ortho-position is more effective than in the para-position. The most active compounds contain substituents simultaneously in the 2-, 4-, and 6-positions. In the case of multi-atom phenols, favorable results are obtained by replacing hydrogen in one of the hydroxyl groups with an alkyl radical [9-11].

Diphenylolmethane is a better antioxidant than single-atom phenols. Efficiency decreases when hydrogen atoms in the CH2 group of this compound are substituted [12]. The solubility of stabilizers holds significant practical value, characterized by the maximum amount of substance that can be introduced into rubber, creating an equilibrium system rather than an oversaturated solution. This parameter determines the compatibility of the stabilizer with the elastomeric matrix, necessary to ensure uniformity of properties throughout the rubber product mass and prevent the stabilizer from blooming on the surface. It depends on the structure of the stabilizer and rubber, the molecular weight of the rubber, the presence of impurities in the rubber, and the composition of the rubber compound.

It has been noted that due to poor compatibility of some ingredients with rubber, at lower temperatures, dissolved ingredients in the rubber compound crystallize out of it. Naturally, such crystallization is expected to deteriorate the homogeneity of the rubber structure.

The solubility of antioxidants in rubbers significantly increases as the melting temperature of the antioxidants decreases. This corresponds to the well-known solubility rule.

Additionally, low-molecular-weight ingredients, particularly antioxidants, exhibit mobility in the rubber matrix, which decreases with increasing molecular size [13-14].

To determine solubility using model systems, equations for the entropy of dissolution and dilution are proposed, requiring values for temperatures, heat, melting entropies of substances, as well as their molar volumes. Additionally, there exist experimental and computational methods for determining the diffusion of antioxidants soluble in rubber.

An effective method for extending the service life of a polymer is the introduction of a highly active stabilizer into the system, which interacts with oxygen or other initiating agents at a rate significantly exceeding their participation in other elementary reactions. Many technical challenges are addressed by skillfully selecting the composition of the polymer blend and adding various ingredients. Unfortunately, all these solutions are specific. For each new product, it is necessary to empirically select the optimal combination of components depending on their properties. It is currently not possible to assess the upper limits of potential protective effects or recommend a scientifically justified strategy for finding new anti-ozonants.

A modern trend in the field of formulating polymer compositions is the use of ingredients that exhibit multifunctional properties, such as vulcanization accelerators and antioxidants, dispersants, and anti-tack agents [15-17]. Dithiocarbamates act as active structuring agents for certain rubbers. Antioxidants (anti-aging agents) are introduced into rubbers and tires to protect them from aging and oxidation. Compounds with amine and hydroxyl groups containing a mobile hydrogen atom typically possess antioxidant properties. These substances can influence the vulcanization kinetics as well as the structure of the vulcanization network. For example, amine-type stabilizers often increase the vulcanization rate, especially in the initial period.

This study aimed to investigate the potential application of synthesized dithiocarbamate derivatives as vulcanization accelerators for rubber compounds and as antioxidants

2. METHODS

2.1. Raw Materials

All chemicals used in the synthesis of dithiocarbamate derivatives were purchased from OOO "RUTENIA", Russia.

The materials under investigation were rubbers based on synthetic isoprene rubber (SKI-3), manufactured by the Nizhnekamsk Synthetic Rubber Factory, Russia.

2.2. Synthesis of Dithiocarbamate Derivatives

The starting materials cyclohexylamine (99%, CAS 108-91-8), aniline (99%, CAS 62-53-3), 2-fluoroaniline (99%, CAS 348-54-9), triethylamine (99%, CAS 121-44-8), carbon disulfide (99%, CAS 75-15-0) and diethyl ether (99%, CAS 60-29-7) purchased from Sigma-Aldrich (Burlington, MA, USA) were used without further purification. Carbon disulfide and diethyl ether were purified using standard methods.

The target dithiocarbamate salts 1-3 were obtained by reacting the corresponding amines with excess carbon disulfide and an equivalent amount of triethylamine in diethyl ether under stirring at room temperature for 8 hours according to the following scheme (**Figure 1**).

The reaction involves several derivatives:

(i) Cyclohexyldithiocarbamate of triethylamine (**1**). To 80 mL of diethyl ether, 5 g (50.41 mmol) of cyclohexylamine, 5.75 g (75.62 mmol) of carbon disulfide, and 5.09 g (50.41 mmol) of triethylamine were added. The reaction mass was stirred at room temperature for 8 h. The resulting precipitate was filtered, washed with diethyl ether, and dried to acquire compound (**1**) as a pale-yellow solid. The yield of the target substance was 13.09 g (94%), Melting point = 94-95 °C.

(ii) Phenyldithiocarbamate of triethylamine (**2**). Obtained similarly to compound (**1**) from 5 g (53.69 mmol) of aniline, 6.12 g (80.53 mmol) of carbon disulfide, and 5.50 g (53.69 mmol) of triethylamine. Pale yellow solid. The yield of the target substance was 12.60 g (87%), Melting point = 92-93 °C.

(iii) 2-Fluorophenyldithiocarbamate of triethylamine (**3**). Obtained similar to compound (**1**) from 5 g (44.99 mmol) of 2-fluoroaniline, 5.13 g (67.50 mmol) of carbon disulfide, and 4.54 g (44.99 mmol) of triethylamine. Pale yellow solid. The yield of the target substance was 10.74 g (83%), Melting point = 91-92 °C.

The composition and structure of the obtained compounds were confirmed using chromatography-mass spectrometry. Mass spectra were recorded on an Agilent GC 5975/MSD 7820 chromatograph mass spectrometer. Elemental analysis was performed on a Perkin Elmer Series II 2400 instrument.

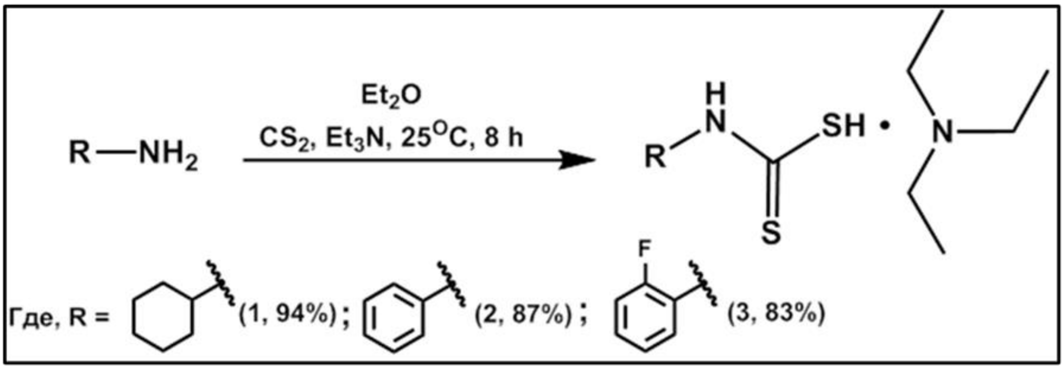

Figure 1. Reaction scheme for the preparation of dithiocarbamate derivatives (1-3).

2.3. Methods

The obtained compounds were tested as accelerators for vulcanization and anti-aging agents for elastomeric compositions based on IR SKI-3 (**Table 1**). SKI-3 rubber was chosen as one of the most widely used in the rubber industry. For comparison of the properties of the obtained vulcanizates, samples containing widely used vulcanization accelerator - captax (2-MBT) and antioxidant (IPPD) in the rubber industry were used.

The preparation and vulcanization of rubber compounds were carried out following ISO 2393 ("Rubber test mixes (Preparation, mixing, and vulcanization) equipment and procedures"). Vulcanization of the rubber compound was conducted in a vulcanization press PHG-2 212/4 at a temperature of 155 °C for 20 minutes. The determination of vulcanization characteristics of rubber compounds was performed on an MDR 3000 Professional rheometer according to ASTM D 2084-79 ("Standard test method for rubber property-vulcanization using oscillating disk curemeter"). Dynamic characteristics of vulcanized rubbers were investigated following ASTM D 6601-02 ("Standard Test Method for Rubber Properties - Measurement of Cure and After-Cure Dynamic Properties Using a Rotorless Shear Rheometer") and ASTM D 5992-96 ("Dynamic Properties of Rubber Vibration Products"). Dynamic tests were conducted at a temperature of 100°C with a shear strain amplitude increasing from 1 to 100%. The frequency of mechanical vibrations was evaluated for each shear strain amplitude ranging from 1.67 to 30 Hz. The determination of elastic-strength properties of rubbers was carried out according to ISO 37-2020 ("Rubber, vulcanized or thermoplastic; Determination of tensile stress-strain properties") on a Shimadzu AG-X plus universal testing machine. Aging resistance tests of rubbers were performed according to ISO 188-2013 ("Rubber, vulcanized or thermoplastic; Accelerated aging and heat resistance tests"). To assess the effectiveness of the synthesized compounds as rubber anti-fatigue agents, a multiple elongation test was conducted according to ASTM D623-07 ("Standard Test Methods for Rubber Property; Heat Generation and Flexing Fatigue in Compression") under conditions of static deformation at 10% and dynamic deformation at 100%.

3. RESULTS AND DISCUSSION

The synthesized derivatives of dithiocarbamates, due to the presence of amino groups in their structure, may exhibit properties as chain-breaking antioxidant agents by scavenging peroxide radicals, as well as serve as highly active accelerators for vulcanization. The investigation of the synthesized compounds as multifunctional ingredients was conducted within a rubber compound based on IR SKI-3. To assess the impact of the synthesized compounds on the vulcanization rate, the vulcanization kinetics were studied (**Figure 2**).

As indicated by the presented data, cyclohexyl dithiocarbamate triethylamine shows minimal vulcanization activity, while phenyl dithiocarbamate triethylamine acts as a delayed-type accelerator compared to captax. In the rubber industry, where accelerators have poor solubility in rubber, synergistic combinations are widely used to more precisely regulate the vulcanization process, which is crucial for the production of rubber products as it helps reduce manufacturing costs. To enhance the activity of the synthesized phenyl dithiocarbamate triethylamine in the composition, diphenyl guanidine (DPG) was additionally introduced (3 parts by mass). DPG promotes better dispersion of fillers in the rubber mixture, which improves the homogeneity and quality of the material. DPG combines well with other additives, such as antiozonants and plasticizers, which allows the creation of rubber compositions with complex properties. However, even in this case, the obtained vulcanizates have low strength (less than 10 MPa) and high relative elongation (750-850%). Thus, the obtained samples are characterized by unsatisfactory physical and mechanical properties. Thus, further tests with them were not carried out.

It is known that electron-withdrawing substituents, by withdrawing electron density towards themselves, can increase the reactivity of multiple bonds. To enhance the vulcanization activity of the synthesized phenyl dithiocarbamate triethylamine, 2-fluorophenyl dithiocarbamate triethylamine (FFK) was synthesized. Complete substitution of captax (composition FFK-1) and IPPD (composition FFK-2) with FFK, as well as partial substitution of sulfur and captax (composition FFK-3), were conducted. The composition of the investigated compositions is provided in **Table 1**.

The synthesized 2-fluorophenyl dithiocarbamate triethylamine (FFK) not only affects the vulcanization kinetics but also the structure of the vulcanization network. Complete replacement of captax with 2-fluorophenyl dithiocarbamate triethylamine leads to a slowing down of the vulcanization process, a decrease in the density of spatial networks, and consequently, a deterioration in the elastic-strength characteristics of the sample (**Table 2**).

As a standalone vulcanization accelerator, 2-fluorophenyl dithiocarbamate triethylamine is not very effective; however, partial replacement of sulfur and captax with FFC (composition FFC-3) leads to a 52 % increase in vulcanization speed and a reduction in the average molecular weight of the chain segment between neighboring crosslinks from 29.4·105 to 24.1·105 mol/cm3 (an 18 % decrease).

The presence of an amine group in the FFC composition has a positive effect on the cohesive strength of rubber compounds, increasing it by 5-15 %.

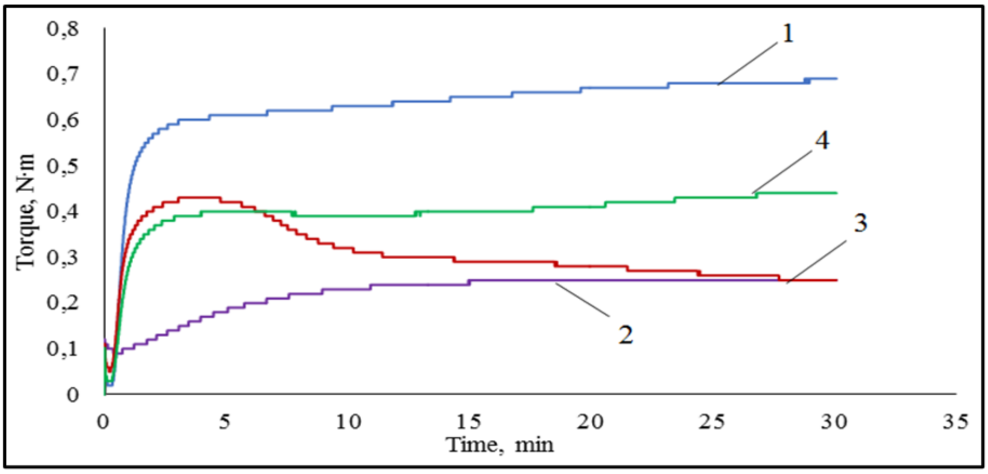

Figure 2. Rheometric curves of elastomeric compositions containing: 1 - 1.50 parts by mass of the industrial vulcanization accelerator captax; 2 - 1.50 parts by mass of the synthesized cyclohexyl dithiocarbamate triethylamine; 3 - 1.50 parts by mass of the synthesized phenyl dithiocarbamate triethylamine; 4 - 1.50 parts by mass of the synthesized phenyl dithiocarbamate triethylamine and 3.00 parts by mass of DPG.

Table 1. Compositions of the investigated rubber compounds.

Ingredient Name	Composition, parts by mass per 100 parts by mass of rubber			
	Control sample	FFK -1	FFK-2	FFK-3
IR SKI-3	100	100	100	100
Zinc oxide activator	5	5	5	5
Stearic acid	1	1	1	1
Technical sulfur	1	1	1	0,5
Captax	1,5	–	1,5	0,5
IPPD	1	1	–	1
Synthesized compound	–	1,5	1	1

Table 2. Mechanical properties and thermal-oxidative aging resistance of the investigated compositions containing 2-fluorophenyl dithiocarbamate triethylamine.

Indicators	Control sample	FFK -1	FFK-2	FFK-3
Characteristics of rubber compounds				
Difference between maximum and minimum torque, N·m	0.67	0.16	0.54	0.75
Induction period, min	0.41	0.96	0.39	0.37
Optimal vulcanization time, min	9.34	16.2	10.29	8.13
Vulcanization rate index, min-1	0.94	0.72	0.91	1.42
The cohesive strength of the composition, kN/m	0.751	0.864	0.789	0.802
Properties of vulcanizates (vulcanization at 155°C, 20 min)				
Tensile strength, MPa	16.9	8.0	14.3	18.0
Relative elongation at break, %	550	610	600	620
Relative residual elongation after breakage, %	13	16	11	15
Fatigue endurance, thousand cycles	170	20	145	210
Rebound resilience, %	25	18	20	26
Shore A hardness, units	51	34	41	55
Changes in parameters after heat aging (100°C for 72 hours)				
Δfp, %	-24,8	–	-40,6	-10,8
Δε, %	-32,9	–	-24,6	-8,8

The synergistic effect of the combination of 2-fluorophenyl dithiocarbamate triethylamine and the industrial anti-ager IPPD is more notable: their joint introduction maintains the tensile strength at the level of the control sample while increasing the dynamic endurance of vulcanizates by 24%. The percentage of strength loss after thermal aging decreases from 24.8 to 10.8%.

Among the synthesized compounds, cyclohexyl dithiocarbamate triethylamine, phenyl dithiocarbamate triethylamine, and 2-fluorophenyl dithiocarbamate triethylamine replacing the cyclohexyl radical with a phenyl or fluorophenyl radical contributes to increasing the activity of these compounds as vulcanization accelerators and anti-agers. This increase can be explained by the enhanced polarity of the radical. The mechanism of inhibition of thermo-oxidative processes in polymers by the synthesized compounds can be viewed in terms of commonly accepted theoretical concepts of inhibited oxidation as a free-radical process [18]. Antioxidants play a role in converting active peroxide radicals of the oxidizing substrate into less active inhibitor radicals [19].

Presumably, the assumed mechanism of action of the investigated compounds in rubber thermo-oxidative aging processes involves the following radical reactions (using 2-fluorophenyl dithiocarbamate triethylamine as an example): hydrogen bonding occurs with free macro radicals R• formed during oxidation and polymer chain degradation, forming a less active N-centered radical (A) (**Figure 3**).

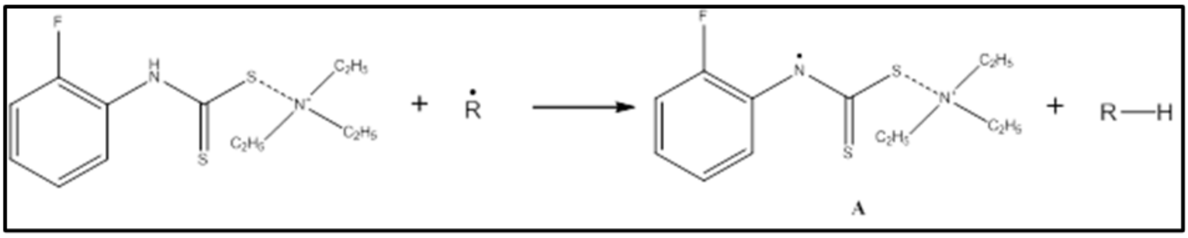

Figure 3. Hydrogen bonding occurs with free macro radicals R• formed during oxidation and polymer chain degradation, forming a less active N-centered radical (A).

A large amount of rubber works under conditions of cyclic loads (drive belts, conveyor belts, tires, shock absorbers). Thus, it is interesting to study the influence of 2-fluorophenyl dithiocarbamate triethylamine on the dynamic characteristics of samples. The tested rubbers do not contain active fillers; however, the apparent stiffness of the samples increases with the frequency of mechanical vibrations, albeit to a lesser extent. The rate of increase of this parameter is primarily determined by the shear strain angle. The intensity of the transition rate to a pseudo-glassy state begins to increase at 10% shear strain deformation (**Figure 4**).

At small shear strain angles from 1 to 3%, extremums are observed, which is associated with the heterogeneity of the structure of the formed vulcanizates and the formation of areas with different relaxation times. Higher levels of deformation lead to the material behaving essentially homogeneously and do not allow for an evaluation of the formed elastomer structure. For the base formulation (**Figure 4A**) containing a sulfur/captax ratio of 1/1.5 parts by mass and 1 part by mass IPPD, the obtained values of the accumulation modulus are 417 kPa and the overall crosslink density is $4.5 \cdot 10^{-4}$ mol/cm^3. Vulcanization in the absence of captax (**Figure 4B**) leads to a 27 % decrease in the accumulation modulus, with an overall crosslink density of $3.1 \cdot 10^{-4}$ mol/cm^3.

Replacing IPPD with 2-fluorophenyl dithiocarbamate triethylamine (**Figure 4B**) does not have a significant effect on the value of the accumulation modulus and overall crosslink density. Reducing the content of the vulcanizing group sulfur/captax to 0.5/0.5 parts by mass and introducing 1 part by mass of 2-fluorophenyl dithiocarbamate triethylamine into the base composition (**Figure 4D**) has the maximum effect on reducing the value of the accumulation modulus by 33% and reducing the overall crosslink density to 2.9·10^{-4} mol/cm^3.

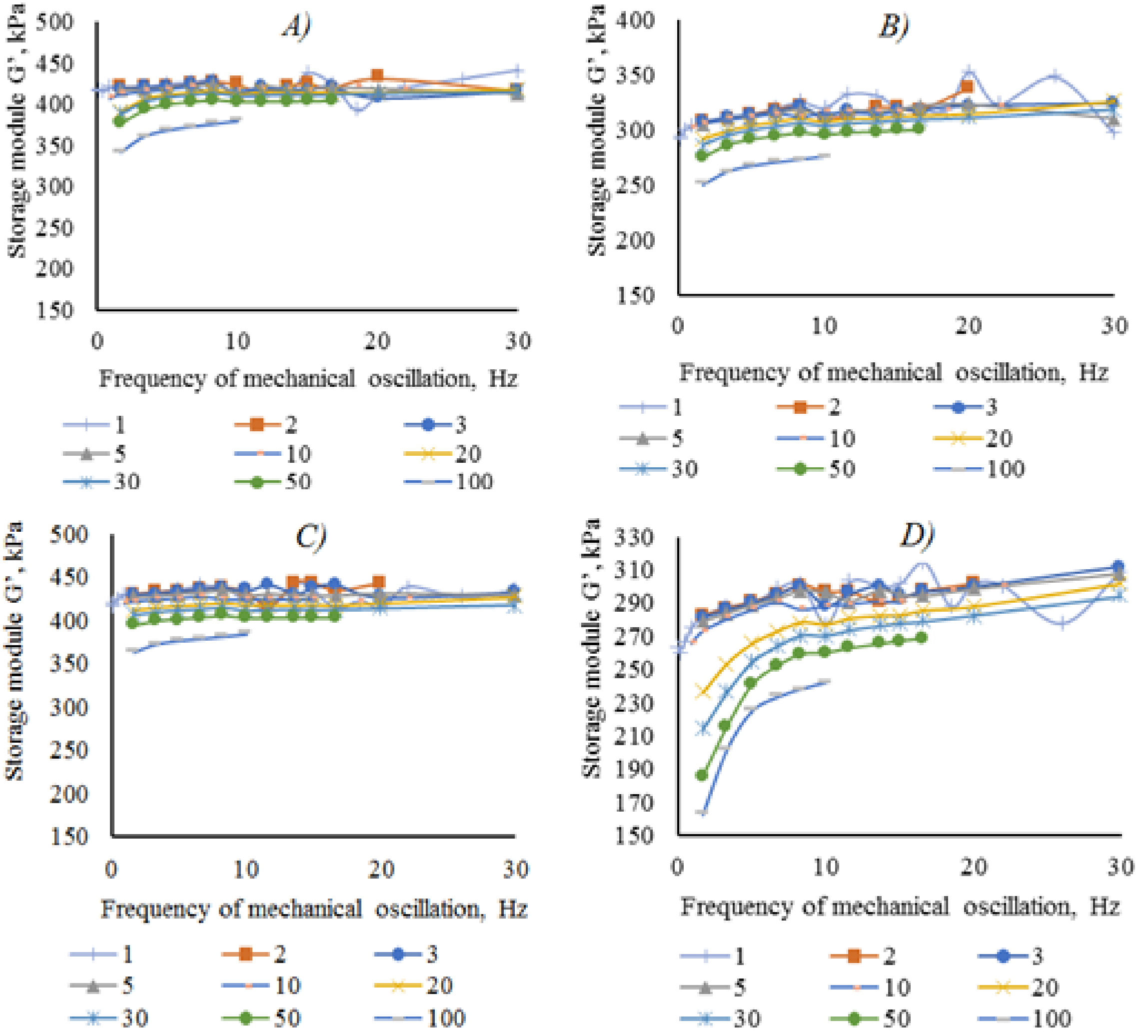

Figure 4. The influence of the frequency of mechanical vibrations on the storage modulus G' at different shear deformations: A - Control sample containing 1.50 wt. of captax; B - Sample containing 1.50 wt. 2-fluorophenyl dithiocarbamate triethylamine; C - Sample containing 1.50 wt. captax and 1.50 wt. 2-fluorophenyl dithiocarbamate triethylamine; D - Sample containing 1.00 wt. captax and 1.00 wt. 2-fluorophenyl dithiocarbamate triethylamine.

The peaks observed in the loss modulus graphs are associated with stress relaxation in the material. At low frequencies of applied mechanical shear, stress is freely distributed within the macromolecules until a certain frequency is reached, where an extremum is observed. Further increasing the frequency leads to the formation of localized stresses with a random distribution (stress percolation), which is caused by the delayed relaxation of stress in polymer chains compared to the rapidly changing stimulus. Larger molecular weight fragments transition to a "pseudo-glassy" state first, followed by segments with smaller molecular weight, until the polymer is completely "frozen".

The quantitative relationship is represented by the dependence of the tangent of the mechanical loss angle on frequency.

The use of the mechanical loss coefficient tanδ is possible for describing changes in polymer structure. Typically, the maximum of this parameter is associated with the appearance of mobility in individual segments and the presence of a mobile phase with increasing temperature, like for example for studying the stereoisomeric composition and crystalline structure of polypropylene. For vulcanizates containing vulcanization accelerators, such transitions are observed from 3 to 2 at frequencies of 10 and 16.7 Hz at small shear deformations. In the absence of a vulcanization accelerator, the transitions occur from 4 to 3. In addition to the mentioned transitions, an extremum is formed around 13.7 Hz, indicating the presence of an additional region (phase) with a different relaxation time. Vulcanizates without captax and weakly crosslinked vulcanizates exhibit the highest level of loss modulus at small shear deformations (up to 5%), which may be attributed to the high mobility of their macromolecule fragments. For samples 2 and 3, at high shear deformations (100%), the loss modulus remains at the level of the control sample, while for weakly crosslinked samples, it increases by more than twice.

There are three fundamental relaxation processes - α, β, and λ - corresponding to three subsystems and three forms of molecular mobility. Low-frequency λ-processes represent slow physical relaxation processes associated with the mobility of domains - ordered microregions. Due to the presence of different ordered microregions with varying relaxation times depending on deformation levels, several λ-relaxation processes are distinguished (**Figure 5**). The activation energy of these processes changes little with temperature and is minimal among the three processes. For the shortest-lived λ1-process, τ1 = 0.1 s, and the long-lived λ3-process (determining viscous shear flow), τ3 = 10 s. In our case, the response time ranges from 0.033 to 0.59 s.

Changing the vulcanizing group leads to changes in the mobility of rubber macromolecule chains. This is also confirmed by calculating the relaxation time spectrum for these mechanical vibration frequencies under shear deformations (**Figure 5**), similar to the literature. The range of logarithm of frequency from 0 to 1.5 Hz corresponds to α- to λ-processes, as mentioned before. The absence of captax in the formulation or a general decrease in the content of vulcanizing groups leads to a reduction in the number of microvolumes with a high concentration of crosslinks in the disordered part of the elastomer.

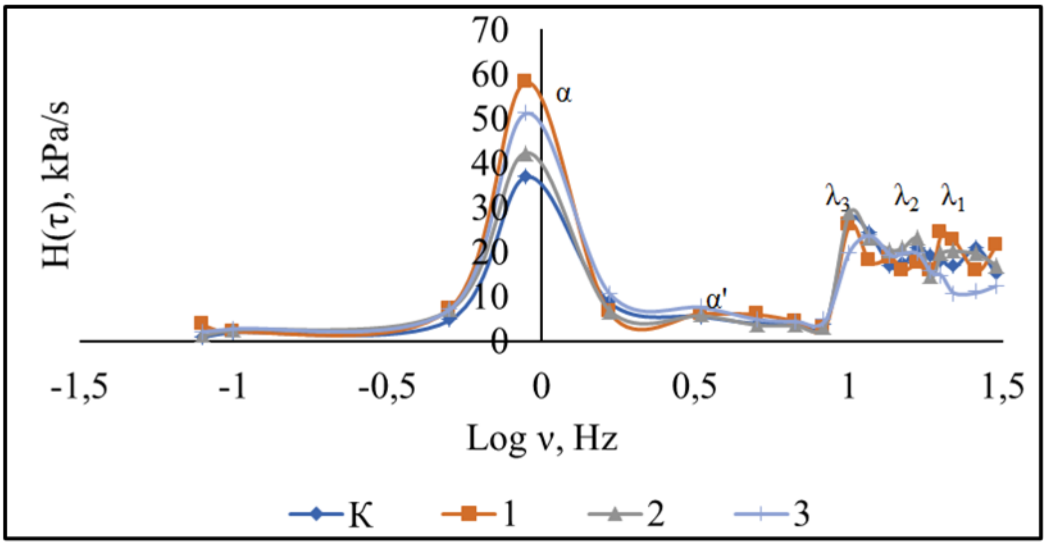

Figure 5. Continuous relaxation spectrum of the resulting rubbers: K - Control sample containing 1.50 wt. of captax; 1 - Sample containing 1.50 wt. 2-fluorophenyl dithiocarbamate triethylamine; 2 - Sample containing 1.50 wt. captax and 1.50 wt. 2-fluorophenyl dithiocarbamate triethylamine; 3 - Sample containing 1.00 wt. captax and 1.00 wt. 2-fluorophenyl dithiocarbamate triethylamine.

From **Figure 5**, a balance exists between the α, α'-processes, which are determined by the mobile weakly crosslinked phase of the vulcanizates, and the λ-processes, which determine the areas of increased crosslinking (domains) in rubbers. Weakly crosslinked vulcanizates exhibit the highest values of α and α'-processes. Additionally, a relatively high content of domains is noted in rubbers vulcanized without captax and with a content of 2-fluorophenyl dithiocarbamate triethylamine at 1.50 mass. Thermo-oxidative aging of the rubbers for 72 hours at a temperature of 125°C resulted in changes in their initial properties. The first notable change was observed in the storage modulus and overall crosslink density.

Rubbers containing captax exhibited increased values of the storage modulus, and consequently, the overall crosslink density was 7.6, 5.4, and $3.4 \cdot 10^{-4}$ mol/cm^3, respectively. For the rubber without captax, the magnitude of the loss modulus significantly decreased, leading to a decrease in overall crosslink density to $0.67 \cdot 10^{-4}$ mol/cm^3. The structural changes in the obtained rubbers are more clearly reflected in the continuous relaxation spectrum diagrams (**Figure 6**).

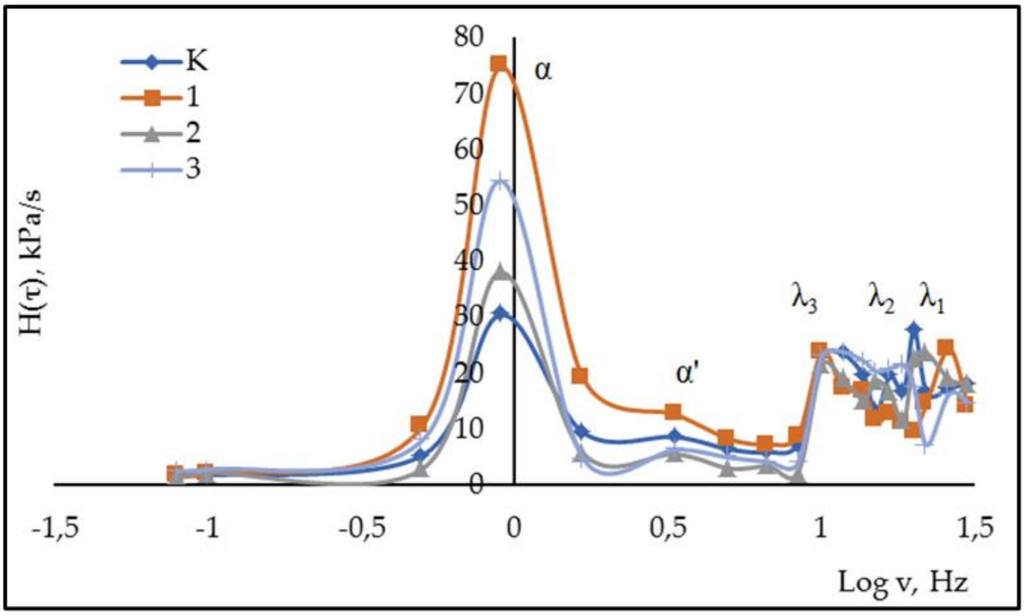

Figure 6. Continuous relaxation spectrum of the obtained rubbers after aging at 125°C for 72 hours: K - Control sample containing 1.50 wt. of captax; 1 - Sample containing 1.50 wt. 2-fluorophenyl dithiocarbamate triethylamine; 2 - Sample containing 1.50 wt. captax and 1.50 wt. 2-fluorophenyl dithiocarbamate triethylamine; 3 - Sample containing 1.00 wt. captax and 1.00 wt. 2-fluorophenyl dithiocarbamate triethylamine.

A significant increase in the intensity of α and α'-processes after aging rubbers without captax indicates the breakdown of formed crosslinks and an increase in the mobility of rubber macromolecules. A decrease in the intensity of the λ_3-process with a simultaneous increase in the λ_1-process indicates the breakdown of highly crosslinked domains into smaller sizes. For rubbers containing captax, as well as 2-fluorophenyl dithiocarbamate triethylamine or IPPD, α and α'-processes slightly decreased, but there was no change in the λ_3-process, indicating the preservation of the initial crosslinking. However, the intensity of the λ_2-process significantly increased, suggesting the formation of new structures during aging. Decreasing the vulcanizing group while introducing 2-fluorophenyl dithiocarbamate triethylamine or IPPD ensures better preservation of the initial structure, slightly increasing the λ_3-process and slightly decreasing α and α'-processes.

In other words, there is a balance in the combination of vulcanizing agents triethylamine fluorophenyl dithiocarbamate and captax in unfilled rubbers. The optimal ratio that allows for better preservation of the original properties of the rubbers after aging is a sample vulcanized with 1.50 mass parts of captax and 1.50 mass parts of 2-fluorophenyl dithiocarbamate triethylamine. The obtained relaxation spectra indicate that this sample practically does not alter the structure formed during vulcanization.

4. CONCLUSION

Therefore, partially replacing the industrial anti-aging agent IPPD and vulcanization accelerator 2-MBT with synthesized 2-fluorophenyl dithiocarbamate triethylamine allows for an increase in dynamic endurance of vulcanizates by 24 % while reducing the percentage of strength loss after heat aging from 24.8 % to 10.8 %. Decreasing the vulcanizing group leads to a reduction in the number of microvolumes with a high concentration of crosslinking chemical bonds in the disordered part of the elastomer, resulting in changes in the mobility of rubber macromolecule chains. This is also supported by calculating the relaxation time spectrum for mechanical oscillations at different frequencies during shear deformations. At high deformation values, the studied rubbers exhibit comparable values of mechanical loss tangent to vulcanizates containing captax.

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6. AUTHORS' NOTE

The authors declare that there is no conflict of interest regarding the publication of this article. The authors confirmed that the paper was free of plagiarism.

7. REFERENCES

[1] Helberg, J., and Pratt, D. A. (2021). Autoxidation vs. antioxidants–the fight for forever. *Chemical Society Reviews*, *50*(13), 7343-7358.

[2] Abirov, R. Zh., Ivakhnenko, O. P., and Eremin, N. A. (2016). Polymer flooding technology investigation in reservoir conditions of the N-Field. *Herald of the Kazach-British Technical University*, 13(4(39)). 7-10.

[3] Deng, C., Huang, J., Qi, Y., Chen, D., and Huang, W. (2022). Distribution patterns of rubber tire-related chemicals with particle size in road and indoor parking lot dust. *Science of The Total Environment*, *844*, 157144.

[4] Shilov, I. B., Shirokova, E. S., and Voronchikhin, V. D. (2024). Reaction of o-phenylenediamine with epichlorohydrin and evaluation of the product as a rubber antiaging agent. *News of higher educational institutions. The Series "Chemistry and Chemical Technology"*, *67*(1), 97-103.

[5] Garaeva, G. R., Gladkikh, S. N., and Belinskii, M. A. (2017). One-package epoxy adhesive materials with high heat resistance. *Polymer Science, Series D*, *10*(1), 40-44.

[6] Sidorov, O. I., Pil'chenko, V. A., Sidorova, N. I., Bochkova, T. V., Elizarov, V. I., and Bodrikhin, E. V. (2021). Investigation of the Rheokinetics of Curing and Properties of an Epoxyurethane Thermal-Protective Coating. *Polymer Science, Series D*, *14*, 588-593.

[7] Liu, R., and Mabury, S. A. (2020). Synthetic phenolic antioxidants: A review of environmental occurrence, fate, human exposure, and toxicity. *Environmental science and technology*, *54*(19), 11706-11719.

[8] Cataldo, F., Faucette, B., Huang, S., and Ebenezer, W. (2015). On the early reaction stages of ozone with N, N′-substituted p-phenylenediamines (6PPD, 77PD) and N, N′, N ″-substituted-1, 3, 5-triazine "Durazone®": an electron spin resonance (ESR) and electronic absorption spectroscopy study. *Polymer Degradation and Stability*, *111*, 223-231.

[9] Azaizeh, H., Halahlih, F., Najami, N., Brunner, D., Faulstich, M., and Tafesh, A. (2012). Antioxidant activity of phenolic fractions in olive mill wastewater. *Food Chemistry*, *134*(4), 2226-2234.

[10] Morlière, P., Patterson, L. K., Santos, C. M., Silva, A. M., Mazière, J. C., Filipe, P., Gomes, A., Fernandes, E., Garcia, M. B. Q., and Santus, R. (2012). The dependence of α-tocopheroxyl radical reduction by hydroxy-2, 3-diarylxanthones on structure and micro-environment. *Organic and biomolecular chemistry*, *10*(10), 2068-2076.

[11] Cainelli, G., Angeloni, C., Cervellati, R., Galletti, P., Giacomini, D., Hrelia, S., and Sinisi, R. (2008). New Polyphenolic β-Lactams with Antioxidant Activity. *Chemistry and biodiversity*, *5*(5), 811-829.

[12] Kochergin, Yu. S., and Zolotareva, V.V. (2020). Regulation of properties of epoxy polymers based on diphenylolmethane using oligobutadiene rubber with terminal carboxyl groups. *Bulletin of BSTU named after V.G. Shukhov*, (6), 127-135.

[13] Kablov, V. F., Novopoltseva, O. M., Kryukova, D. A., Keibal, N. A., Burmistrov, V., and Kochetkov, V. G. (2023). Functionally active microheterogeneous systems for elastomer fire-and heat-protective materials. *Molecules*, *28*(13), 5267.

[14] Fedosov, S. V., and Bakanov, M. O. (2020). Application of «micro-processes» method for modeling heat conduction and diffusion processes in canonical bodies. News of Higher Educational Institutions. *The Series "Chemistry and Chemical Technology"*, *63*(10), 90-95.

[15] Kayushnikov, N., Prokopchuk, N.R., and Uss, E.P. (2017). Tire elastomer compositions with zinc-containing technological additives. *Proceedings of BSTU, 2*(199), 75-83.

[16] Novopoltseva, O.M., Kochetkov, V.G., Burmistrov, V.V., Butov, G.M., and Solopov, V.A. (2019). Research of adamantyl-containing compounds as ingredients of polyfunctional rubber compounds, *Izvestiya of the Volgograd State Technical University*, 5(228), 66-70.

[17] Sun, Y., He, J., Zhong, B., Zhu, L., and Liu, F. (2019). A synthesized multifunctional rubber additive and its improvements on the curing and antioxidative properties of styrene-butadiene rubber/silica composites. *Polymer Degradation and Stability*, *170*, 108999.

[18] Luo, K., You, G., Zhang, S., Zheng, W., and Wu, S. (2020). Antioxidation behavior of bonded primary-secondary antioxidant/styrene-butadiene rubber composite: Experimental and molecular simulation investigations. *Polymer*, *188*, 122143.

[19] Ismail, M. N., Yehia, A. A., and Korium, A. A. (2002). Preparation and evaluation of some novel organo-phosphorus compounds as antioxidants and antifatigue agents in rubber. *Journal of Applied Polymer Science*, *83*(14), 2984-2992.