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**Chemistry**

# FORMATION OF ELASTOMERIC COMPOSITION PROPERTIES IN THE PRESENCE OF BIOINGREDIENT

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**Abstract.** Peculiarities of formation of technological, vulcanization, dynamic, relaxation, and physicomechanical properties of elastomeric composition used for the tread production have been studied in the presence of bioingredient as a plasticizer-softener. Bioingredient is an organic component of sunflower oil winterization by-product (OSSO product). It was found that the OSSO product increases the cohesive strength of the rubber compound by 1.5 times in comparison with the industrial petrochemical lubricants. Under the same vulcanization conditions, the bioingredient provides 30–40 % higher resistance to reversion and relaxation processes at 373 K, lower dynamic losses, as well a high level of physical and mechanical characteristics.

**Keywords**: elastomeric composition, technologically active additive, bioingredient, sunflower oil winterization by-product, environmentally-friendly rubber.

## 1. Introduction

Almost all branches of industry consume products of rubber processing. Modern technology sets high standards for rubber products regarding their reliability, durability, and the range of operational parameters. So, the task of production technology of elastomeric materials (rubbers and products based on them) is to create optimal recipes and processing technologies, which not only meet technical requirements but which are safe and environmentally friendly.[1]

Among the components of elastomeric compositions, there are dangerous compounds, for example, vulcanization accelerators are capable of forming carcinogenic nitrosamines; high concentrations of vulcanization activator – zinc oxide – cause dysfunction of individual organs and systems of the human body; plasticizers based on petroleum raw materials contain carcinogenic polyaromatic hydrocarbons.[2] Particles formed during tires abrasion contain 61 wt % of rubber, 29 wt % of carbon black, 10 wt % of chemical additives; they are a significant source of carcinogens of various classes.[3,4] Today, the variety of rubbers, rubber compounds, and products based on them are strictly required by a number of environmental legislation. For example, European Directive 2005/69/EU limits the content of polyaromatic hydrocarbons in petrochemical lubricants-softeners and tires. Therefore, the increased requirements for environmental safety of rubber products in the processes of their manufacture and operation have contributed to the emergence of research on the use of raw materials of plant origin.

Thus, the scientists of the Ukrainian State University of Chemical Technology and the Institute of Chemistry of Macromolecular Compounds of the National Academy of Sciences of Ukraine synthesized organic compounds with a quaternized nitrogen atom (quaternary ammonium salts, QAS) using available plant raw materials such as furfural and castor oil and examined them as organic activators of sulfur vulcanization of elastomeric compositions based on carbon-chain diene rubbers of general purpose.[5-8] The influence of the QAS structure on the activity in the cross-linking process was determined. The directions of their effective application in the development of sulfur vulcanizing systems of elastomeric compositions of industrial type were proposed.

It is known[9] that the main properties of raw rubber, used in rubber products, are elasticity combined with low density and wear resistance. The latter is greatly increased by the introduction of active filler into raw rubber. Currently, the main highly active fillers are carbon black and silica acid filler (silica, white black). The application of silica has increased considerably over the past decades to compare with highly active grades of carbon black. The reason is that silica significantly reduces hysteresis losses and improves adhesion. Silica provides commercial products (including tires) with low rolling resistance and fuel consumption (respectively, exhaust emissions from the car are reduced), as well as good adhesion with wet or frozen road

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surfaces. In other words, it allows creating the so-called environmentally friendly, "green" rubber products.[10,11]

The ideology of creating "green" rubber products also involves changes in the structure of raw materials and their environmental friendliness by reducing the share of non-renewable raw materials, including ingredients of petroleum origin, *i.e.*, carcinogenic carbon black. To obtain amorphous silicic acid the multi-tonnage wastes of rice processing, such as rice husk (RH) with a high content of silicon(IV) oxide, can be used. The utilization of rice husk is an urgent problem, because it does not rot in the soil, and its combustion releases contaminants.[12,13] The mechanism of RH thermochemical conversion during heat treatment and development of production technology for the silicon(IV) oxide is described by many researchers.[14-17]

Over the last 15 years, an increase in the number of publications on the use of ingredients derived from rice husk for the production of tires and rubber products has been observed. These are short reports on the use of carbonized RH as a nanostructured filler,[18] products of heat-treated (873–1073 K) rice husk in elastomeric compositions based on butadiene-styrene rubber,[19] silica (as a product of rice husk combustion) for fuel-saving tires (Italian company Pirelli[20]). A series of publications devoted to the use of silicon-containing products of heat-treated RH in elastomeric compositions of model and industrial types is represented by authors from Ukraine.[21-25] In particular, Ovcharov and co-workers[25] determined the characteristics of heat-treated RH products, which are finely dispersed silicon, carbon-containing thermostable powders of amorphous-crystalline structure. A number of products was obtained from crushed rice husk under different heat treatment conditions and their efficiency as fillers for elastomeric compositions based on carbon-chain diene rubbers was evaluated. It was shown that the introduction of 20.0 wt % of carbonization products or silicon dioxide (obtained from RH), in contrast to the known semi-reinforcing fillers, has a positive effect on the plasticity and viscosity of mixtures based on butadiene-styrene rubber of SKS-30 ARK grade, the relative degree of crosslinking and kinetic parameters of sulfur vulcanization. It was established that RH products have a semi-reinforcing effect, providing vulcanizates with a high equilibrium shear modulus, high-temperature stability, and heat resistance in terms of elastic and strength properties. The temperature-time regime of products obtained from RH has a significant impact on the formation of elastomeric composition properties.

Rudnieva *et al.*[26] showed the possibility of using waxy substances obtained *via* extraction from sunflower husk as antiozonants in rubber for tires production.

To improve the quality of elastomeric compositions such additives (softeners, plasticizers) as mineral oils, paraffin (aliphatic), naphthenic (cycloaliphatic), and aromatic oils are traditionally used in rubber processing.[27,28] Aromatic extracts containing polycyclic aromatic hydrocarbons and, in particular, polyaromatic hydrocarbons, which are considered carcinogenic, are most often used in the production of tires. One possible solution is to replace aromatic extract with aromatic and paraffin oils with a reduced content of polycyclic compounds. Various ways of replacing mineral oils with oils of natural origin, in particular, vegetable oils, have been proposed. Bastioli *et al.*[29] patented an elastomeric composition, containing the following vegetable oil derivatives: a mixture of triglycerides, triglycerides of one or more long-chain carboxylic acids, esters of polyols.

It should be noted that the positive effect of classical technological additives on the properties of rubber compounds in some cases adversely affects the operational properties of tires. These disadvantages are eliminated by relatively new ingredients of rubber compound – technologically active additives (TAA), which allow regulating the technological properties of rubber compounds by influencing the intra- and intermolecular interactions in the rubber matrix. A keen interest in the application of TAA is caused by the multifunctionality of their action in rubber compounds.[30,31] Most TAA is produced on the basis of petrochemical raw materials but TAA based on materials of plant origin are receiving increased attention. The most available and renewable raw materials for the production of higher fatty acids and their salts are vegetable oils and by-products of their production.[31–35]

Taking into account that Ukraine is one of the world's leading producers of sunflower oil, tens of thousands of tons of oily spent adsorbent, which belongs to hazard class IV,[36] are obtained only at the purification stage. That is why the creation of technologies for processing and using by-products and wastes from the main stages of sunflower oil production is a topical issue. The lack of such technologies leads to the accumulation of mentioned products at working areas, then at landfills, and as a consequence, to the increase of environmental risks.

Analysis of scientific data on the chemical composition of by-products after the sunflower oil winterization[37] suggests that it can be an environmentally friendly raw material for obtaining ingredients of elastomeric compositions of non-petroleum origin. Previously,[38] we found that aluminosilicate adsorbent (obtained from a by-product of sunflower oil production) in the elastomeric composition based on butadiene-styrene rubber acts as a mineral filler of semi-reinforcing action, and improves operational properties of rubber compound. Thus, it was recommended to be used for manufacturing rubber products by the compression method. We also investigated the physico-chemical characteristics of the adsorbent of sunflower oil purification after its hydrophobization and subsequent heat treatment at 1073 K.[36] It was shown that the obtained experimental product is a porous fragment of solid foam of low density, annealing of which completely removes the organic component and thus increases the structure of the material. We examined the peculiarities of technological, vulcanization and physico-mechanical properties of elastomeric compositions based on cis-1,4-polyisoprene with experimental products ranging from 20.0 to 80.0 phr. The temperature stability and resistance to thermal aging were found to be increased. The adsorbent of sunflower oil purification can be also used in the elastomeric compositions based on a mixture of SKD and SKMS-30 ARKM-15 rubbers for the manufacture of the tread section of the tire.

After isolation of the hydrophobized aluminosilicate adsorbent from the by-product, almost 50 wt % of the organic component remains. It contains fats – glycerides of higher unsaturated and saturated aliphatic acids ($C_{18}$ to 95 %) and waxes – mixtures of high molecular mono- and diatomic alcohol ethers and saturated fatty acids from $C_{18}$ to $C_{32}$ (up to 28 wt %).[26,27] Based on the chemical composition and physical state (thick liquid), we assume that the organic component may be used as a non-petroleum technological additive of elastomeric compositions based on general-purpose rubbers. Therefore, the aim of this work was to study the effect of bioingredient (an organic component of the by-product after sunflower oil winterization – OSSO product) as a technological additive on the formation of technological, physico-mechanical, dynamic, and other properties of elastomeric compositions for tire production.

## 2. Experimental

### 2.1. Materials

The by-product after sunflower oil winterization was received from PJSC “Oleina” (Dnipro). The organic component of the by-product (OSSO product) was obtained according to the following method: a three-necked flask (volume 3500 $cm^3$), equipped with a thermometer and stirrer, was loaded with 300 g of oily spent adsorbent Randalite W24 and 2200 $cm^3$ of dichloroethane. The mixture was kept for 3 h under stirring at a temperature of 323–333 K, then cooled to room temperature and filtrated under vacuum. The residue on the filter was washed with 200 $cm^3$ of fresh dichloroethane and re-filtered. Dichloroethane was removed from the filtrate using a rotary evaporator, while 120–130 g of transparent, sticky to the touch, viscous mass of yellow-brown color remains in the cube.

The resulting product OSSO has the following characteristics: hardening temperature is below 318 K; drop point is 308 K; refractive index at 293 K is 1.475; average molecular weight (cryoscopic method) is 1325.68 amu. According to IR spectroscopy,[36] it was found that the OSSO product contains hydrocarbon radicals (stretching vibrations of CH-groups correspond to the absorption bands at 2965–2904 $cm^{-1}$ and 2872, 2849 $cm^{-1}$) and functional carboxyl-containing groups (stretching vibrations of C=O bond corresponding to absorption bands at 1734 $cm^{-1}$).

To evaluate the efficiency of the obtained bioingredient as a plasticizer-softener of the rubber compound, we studied an elastomeric composition used for the manufacture of tread section of tire. The OSSO product was compared with the Nytex 4700 commercial petrochemical plasticizer (Nynas company, Sweden) with a low level of polycyclic aromatic hydrocarbons. The amount of both samples was equal (11.0 phr per 100.0 parts of rubber base). It was also compared with the mixture consisting of 5.5 phr of OSSO + 5.5 phr of Nytex 4700. The study was conducted in a filled rubber compound based on a combination of synthetic diene rubbers of amorphous butadiene-α-methylstyrene rubber of SKMS-30 ARKM-15 brand and cis-butadiene rubber of SKD brand with the sulfuric vulcanizing system.

Masterbatch was obtained in a laboratory rubber mixer with a 2 $dm^3$ mixing chamber according to the traditional scheme. OSSO and Nytex 4700 were introduced using laboratory rollers. All rubbers and ingredients used in the work met the current standards.

### 2.2. Research Methods

Technological characteristics of rubber compounds and vulcanization rubbers were evaluated in accordance with current international standards and methods.[39-41] In particular, the rheological, vulcanization, dynamic, and relaxation properties of elastomeric compositions were determined according to the international standards DIN 53 529, ASTM D 6204, ASTM D 6601, ISO 13145. Non-rotor rheometer MDR 3000 (manufactured by German company Mon Tech) with Mon Control software was used. The MDR 3000 Professional rheometer is designed to determine the viscoelastic properties of elastomeric compositions before, during and after vulcanization. The device allows to study rubbers and ingredients, properties and characteristics of the products during processing and vulcanization of elastomeric compositions. The vulcanization rate, the conditional constant of the vulcanization rate, and the effective activation energy of the vulcanization process of elastomeric compositions according to rheometric data were calculated according to the methods described by several authors.[1,42] For example, the effective activation energy of the vulcanization process ($E$) of rubber compound is determined in regard to the conditional constants of the reaction rate at two temperatures according to formula (1):

$$E = \frac{4.576 \cdot T_1 \cdot T_2}{T_1 - T_2} \cdot \lg \frac{K_1}{k_2} \quad (1)$$

where $T_1$ and $T_2$ are absolute temperatures, K; $k_1$ and $k_2$ are conditional constants of vulcanization rate at temperatures $T_1$ and $T_2$.

The vulcanization rate $V_c$ (taking into account the increase in the torsional moment $M_{tc(90)} - M_{ts}$) at the stage of vulcanization crosslinks formation was determined by the formula (2):[1]

$$V_c = \frac{M_{tc\,90} - M_{ts}}{t_{c\,90} - t_s} \quad (2)$$

where $M_{tc(90)}$ is the torsional moment on the vulcanization isotherm, which corresponds to the test time equal to the parameter $t_{c(90)}$, dN·m; $M_{ts}$ is the torsional moment on the vulcanization isotherm, which corresponds to the test time equal to the parameter $t_s$, dN·m; $t_s$ is the time of the vulcanization beginning, min; $t_{c(90)}$ is the optimal vulcanization time, min.

# 3. Results and Discussion

## 3.1. Technological Properties

In accordance with ASTM D 6204 standard the following characteristics were obtained using the MDR 3000 rheometer with shear deformation of 7 %, at the temperature of 373 K in the frequency range (Freg) of 0.1–20 Hz (Table 1): modulus of elasticity in shear (G'); shear loss modulus (G"); true dynamic viscosity (N'); apparent (conditional) dynamic viscosity (N"); complex dynamic viscosity (N*); the dynamic loss tangent (Tan. Delta) – the ratio of the loss modulus G" to the modulus of elasticity G'; an indicator that characterizes the shrinkage process of the rubber compound (Delta Tan. Delta).

**Table 1.** Technological characteristics of rubber compound of tread type according to rheometric data at 373 K in accordance with the ASTM D 6204 standard

| Additive and its amount (phr) | Index value | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Freq, Hz | G', kPa | G", kPa | N', Pa·s | N", Pa·s | N*, Pa·s | Tan. Delta | Delta Tan. Delta |
| Nytex 4700 (11.0) | 0.1 | 128.76 | 87.36 | 139 031 | 204 925 | 247 637 | 0.678 | |
| | 0.2 | 148.33 | 98.46 | 78 355 | 118 039 | 141 679 | 0.664 | |
| | 0.5 | 186.68 | 121.86 | 38 790 | 59 422 | 70 962 | 0.653 | |
| | 1 | 223.80 | 141.63 | 22 540 | 35 620 | 42 152 | 0.633 | |
| | 2 | 271.12 | 162.90 | 12 963 | 21575 | 25 170 | 0.601 | |
| | 5 | 338.70 | 193.56 | 6161 | 10 781 | 12 418 | 0.572 | |
| | 10 | 404.55 | 214.96 | 3 421 | 6 439 | 7 291 | 0.531 | |
| | 15 | 441.62 | 226.33 | 2 401 | 4 686 | 5 265 | 0.513 | |
| | 20 | 474.36 | 231.64 | 1843 | 3 775 | 4 201 | 0.488 | 0.190 |
| OSSO product (11.0) | 0.1 | 183.03 | 118.98 | 189 369 | 291 307 | 347 449 | 0.650 | |
| | 0.2 | 207.62 | 132.43 | 105 384 | 165 222 | 195 969 | 0.638 | |
| | 0.5 | 255.67 | 161.02 | 51255 | 81 383 | 96 178 | 0.630 | |
| | 1 | 301.77 | 185.48 | 29 520 | 48 029 | 56 375 | 0.615 | |
| | 2 | 360.27 | 211.25 | 16 811 | 28 669 | 33 234 | 0.586 | |
| | 5 | 443.00 | 250.29 | 7 967 | 14 101 | 16 196 | 0.565 | |
| | 10 | 523.88 | 278.10 | 4 426 | 8 338 | 9 440 | 0.531 | |
| | 15 | 568.60 | 293.35 | 3 113 | 6 033 | 6 789 | 0.516 | |
| | 20 | 609.60 | 301.78 | 2 402 | 4 851 | 5 413 | 0.495 | 0.155 |
| Nytex 4700 (5.5) + OCCO (5.5) | 0.1 | 141.22 | 94.60 | 150 558 | 224 765 | 270 531 | 0.670 | |
| | 0.2 | 163.19 | 107.55 | 85 586 | 129 864 | 155 530 | 0.659 | |
| | 0.5 | 204.75 | 133.02 | 42 343 | 65 172 | 77 720 | 0.650 | |
| | 1 | 245.54 | 154.74 | 24 627 | 39 079 | 46 192 | 0.630 | |
| | 2 | 296.65 | 177.81 | 14 150 | 23 607 | 27 523 | 0.599 | |
| | 5 | 369.76 | 212.78 | 6 773 | 11770 | 13 580 | 0.576 | |
| | 10 | 441.51 | 237.66 | 3 783 | 7 027 | 7 980 | 0.538 | |
| | 15 | 481.50 | 251.44 | 2 668 | 5 109 | 5 764 | 0.522 | |
| | 20 | 518.13 | 259.09 | 2 062 | 4 123 | 4 610 | 0.500 | 0.170 |

The effect of the studied factors on the technological properties of the elastomeric composition depending on the frequency of the rheometer test chamber oscillations was evaluated taking into account the oscillation frequency of production equipment of two technological stages:

I –preparation of rubber compound in a rubber mixer (oscillation frequency is 0.1–1.0 Hz);

II –processing (*e.g.*, injection molding) of rubber compound into semi-finished products (oscillation frequency is 2–20 Hz).According to the modulus of elasticity G' and the shear loss modulus G", the replacement of half of the Nytex 4700 softener for OSSO is accompanied by a 10 % increase in the mentioned values relative to the control sample (with 11.0 phr of Nytex 4700) at the preparation stage of rubber compound. A complete replacement of Nytex 4700 for OSSO product leads to an increase in the mentioned values by 30–40 % (Table 1). The compositions with the OSSO product had higher values of N', N" and N* relative to the control sample by 1.1, 1.3 and 1.4 times, respectively.

According to rheometric data obtained at the mixing stage at 373 K, the bioingredient OSSO in the amount of 11.0 phr and 5.5 phr is a worse softener of rubber compound based on the general-purpose raw rubbers in comparison with the commercial industrial softener Nytex 4700 of the same amount. The process of preparation (mixing) of the rubber compound in the presence of OSSO (compared to Nytex 4700) is accompanied by a slight decrease (by 4 %) in the value of Tan. Delta (Table 1), which is probably due to another hydrocarbon structure of the test product, its lower compatibility with the rubber matrix and other ingredients of the rubber compound.

Rheometric tests of rubber compound under oscillation conditions of the rheometer chamber half-shape in the range of 2–20 Hz also show a lower softening effect of the OSSO product compared to Nytex 4700 (Table 1). The value of Delta Tan. Delta points to the advantage of Nytex 4700 industrial softener regarding the shrinkage of rubber compounds when processed into semi-finished products.

Taking into account that the minimum torsional moment (S'$_{min}$) at vulcanization temperatures correlates with the manufacturability of rubber compound at the temperatures of its preparation and processing, it should be noted a less positive effect of the experimental bio-ingredient on tread rubber compound at 428 and 438 K (Fig. 1), as compared with commercial Nytex 4700. In particular, the replacement of Nytex 4700 for the equal amount of the OSSO product increases the S'$_{min}$ by one-third.

The mix of the OSSO product and Nytex 4700 is intermediate in the effect between the individual test ingredients, indicating their additive effect on this process parameter.

Similarly, the replacement of Nytex 4700 for the OSSO product of the same amount affects the ductility of the rubber compound at 343 K (VC ISO 7323), reducing this value by 18 % and increasing the value of elastic renewal by 10 %. But the OSSO product shows a positive effect regarding the increase in cohesive strength of the rubber compound by 1.5 times compared to Nytex 4700 (Fig. 2).

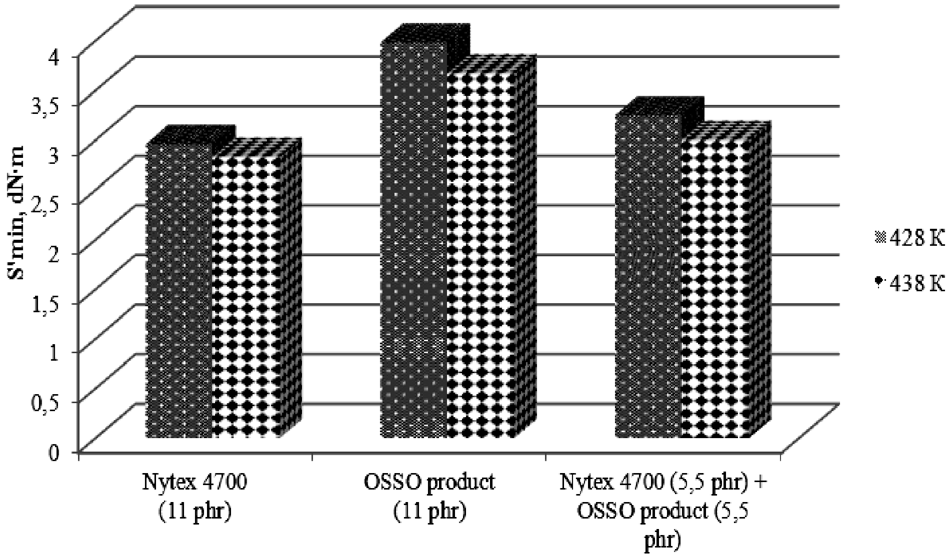

**Fig. 1.** Effect of the type and amount of test compounds on the minimum torsional moment (S'$_{min}$) of the rubber compound at different temperatures

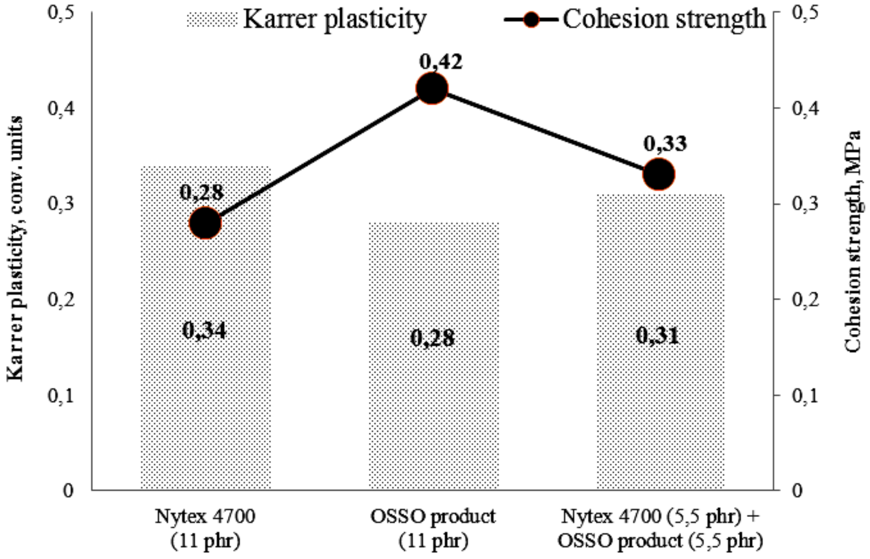

**Fig. 2.** Effect of type and amount of test compounds on Karrer plasticity and cohesion strength of rubber compound

Therefore, the evaluation of the technological properties of the filled rubber compound based on general-purpose raw rubbers for the manufacture of tire tread in the presence of the OSSO product as a plasticizer-softener in the temperature range from 343 to 438 K showed that the experimental bioingredient in the amount of 11.0 phr per 100.0 phr of rubber base has a less positive effect on the technological characteristics of the rubber than petrochemical lubricant Nytex 4700 of the same amount. However, the increase in cohesive strength of the rubber compound by 1.5 times (compared to industrial lubricants) is a positive effect of the test product. The joint use of the studied ingredients in a ratio of 1:1 is characterized by an additive effect on the formation of technological properties of the rubber compound.

## 3.2. Vulcanization Properties

The sulfur vulcanization process of tread type rubber compounds with the studied hydrocarbon compounds was evaluated according to the ASTM DIN 53529 standard using the MDR 3000 rheometer under the following conditions: T = 428 K; $\tau = 60$ min; H = 1.67 Hz; $\gamma = 1°$.

Analysis of the kinetic curves of rubber compound vulcanization, for example, at 438 K (Fig. 3), shows that the OSSO product, compared with commercial softener Nytex 4700, has another impact on the formation of elastomeric compositions properties at different stages of vulcanization: induction period, the formation of vulcanization network and the formation of vulcanization plateau.

The characteristics of the isotherms of rubber compound vulcanization at 428 and 438 K in the presence of the OSSO product and commercial Nytex 4700 are shown in Table 2.

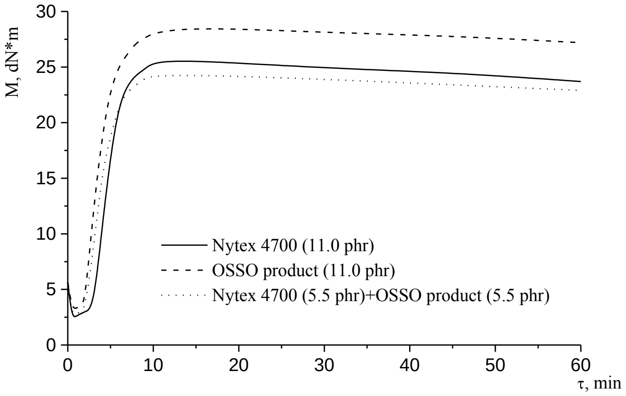

**Fig. 3.** Kinetic curves of sulfur vulcanization (T = 438 K) of elastomeric compositions based on a mix of butadiene and butadiene-α-methylstyrene raw rubbers in the presence of different types and amounts of test compounds

One can see that the OSSO product has a higher reactivity in the process of accelerated sulfur vulcanization of rubber compound compared with the commercial Nytex 4700. The most significant differences are observed for a maximum torsional moment and crosslinking degree on the vulcanization plateau (Fig. 3, Table 2). The joint use of the experimental product and Nytex 4700 leads to the antagonism effect regarding the values of $S'_{Max}$ and $S'_{Max} - S'_{Min}$.

Analysis of vulcanization isotherms of the rubber compound with OSSO (Fig. 3) shows that the formation of crosslinked structure has some differences from those of the rubbers with Nytex 4700 and with Nytex+OSSO. The time of induction period, the crosslinking rate in the main period and the width of the vulcanization plateau are observed to be different. For the rubber compound with OSSO the time of induction period (scorch time TS 1) is less by 20–30 % than that for rubber with Nytex 4700. However, vulcanization rates (including the increase in torsional moment $V_c$) and conditional constants $k_2$ at 428 and 438 K are inferior to those of the sample with Nytex 4700. For rubber with Nytex+OSSO the effective activation energy increases by 1.1 times (Table 2). The bioingredient under study provides the rubber compound with higher resistance to reversion by 10–30 % (T@Rev 98, Table 2).

**Table 2.** Vulcanization characteristics of elastomeric compositions in the presence of different types and amounts of test compounds at different temperatures (428 K – numerator, 438 K – denominator)

| Index | Type and amount of ingredient, phr | | |
|---|---|---|---|
| | Nytex 4700 (11.0) | OSSO (11.0) | Nytex 4700 (5.5) + OSSO product (5.5) |
| Relative degree of intercrosslinking ($S'_{Max} – S'_{Min}$), dN·m | $\frac{24.37}{23.35}$ | $\frac{24.90}{25.14}$ | $\frac{22.48}{21.65}$ |
| Scorching resistance (scorch time (TS 1)), min | $\frac{5.29}{3.34}$ | $\frac{4.12}{2.36}$ | $\frac{4.73}{2.53}$ |
| Time to reach 90 % vulcanization (TC 90), min | $\frac{13.45}{7.59}$ | $\frac{12.70}{6.87}$ | $\frac{13.69}{6.92}$ |
| Vulcanization rate ($V_c$), dN·m/min | $\frac{2.20}{4.05}$ | $\frac{2.03}{3.98}$ | $\frac{1.78}{3.53}$ |
| Conditional constant of vulcanization rate ($k_2$), $min^{-1}$ | $\frac{0.29}{0.54}$ | $\frac{0.27}{0.50}$ | $\frac{0.26}{0.52}$ |
| Effective activation energy of vulcanization (E), kJ/mol | 95.99 | 94.71 | 107.00 |
| Reversion time (T@Rev 98), min | $\frac{47.55}{24.41}$ | $\frac{52.70}{31.66}$ | $\frac{52.79}{26.20}$ |

The differences in the parameters of the vulcanization process proceeded in the presence of OSSO of different amounts and Nytex 4700 probably occur due to some change in the structure of vulcanization bonds and, accordingly, the properties of rubber. For example, for elastomeric composition with the OSSO product the values of Tan. delta@TC90 and Tan. delta@TC100 at the vulcanization optimum and on the vulcanization plateau of the product is 3–4 times higher than those for elastomeric composition with Nytex 4700. In particular, at 428 K the viscous deformation component of the elastomeric composition with bioingredient is 0.22 *vs.* 0.06 for elastomeric composition with Nytex 4700.

Thus, the comparison of the results obtained at 428 K and 438 K during the sulfur vulcanization process of tread-type elastomeric compositions with the bioingredient and commercial softener revealed differences in the processes parameters. These differences are associated with the initiation of vulcanization bonds at the beginning of sulfur vulcanization by the initial product, a higher by 10 % crosslinking degree, and the increase in the resistance to reversion by 1.1–1.3 times. It is shown that at the vulcanization optimum and on the vulcanization plateau the elastomeric composition with the OSSO product is characterized by 3–4 times higher value of "viscous deformation / elastic deformation" to compare with that of the composition with Nytex 4700 indicating a certain change in vulcanization bonds of rubber in the presence of a bioingredient. The joint use of the OSSO product and Nytex 4700 softener is accompanied by an antagonistic effect in a number of vulcanization parameters and is not effective.

## 3.3. Dynamic and Relaxation Properties

Dynamic and relaxation properties of tread-type elastomeric compositions were determined using MDR 3000 rheometer in accordance with the requirements of international standards ASTM D 6601 and ISO 13145.

Standard ASTM D 6601 involves the determination of the dynamic characteristics of elastomeric compositions after vulcanization at a certain temperature, which is lower than the vulcanization temperature, and allows to obtain the following characteristics: shear modulus (G'), kPa; shear loss modulus (G"), kPa; complex shear modulus (G*), kPa; loss factor Tan Delta (the dynamic losses tangent, as the ratio of the loss modulus to the modulus of elasticity: $\tan \delta = G''/G'$) (Table 3).

Tests of the samples (20 min, 433 K, 1.67 Hz, 7.0 % of deformation) were carried out on the vulcanization plateau to determine the above indices under deformation range of 1–100 % and the difference in modulus of elasticity at small (1.0 0 %) and large deformation amplitudes (100.0 %) – a complex dynamic modulus Delta

Strain, which quantitatively characterizes the Payne effect[43] (Table 3). The tests were performed for 3 and 5 min at a temperature of 873 K and a deformation frequency of 1 Hz.

One can see that prescribed factors and test conditions (deformation level) significantly affect the dynamic properties of the elastomeric composition (Table 3). Rubber with 11.0 phr of bioingredient OSSO has a higher level of controlled dynamic parameters than similar rubber with Nytex 4700. The composition with OSSO+Nytex has the intermediate values of dynamic characteristics.

**Table 3.** Dynamic characteristics of the compositions using MDR 3000 rheometer (3 min – numerator, 5 min – denominator

| Additive and its amount (phr) | Index value | | | | |
|---|---|---|---|---|---|
| | Deformation, % | G', kPa | G", kPa | G*, kPa | Tan. Delta |
| Nytex 4700<br>(11.0) | 1 | $\frac{2933.81}{2040.49}$ | $\frac{459.63}{384.64}$ | $\frac{2969.60}{2076.46}$ | $\frac{0.157}{0.189}$ |
| | 2 | $\frac{2463.39}{1808.41}$ | $\frac{439.73}{378.19}$ | $\frac{2502.33}{1847.53}$ | $\frac{0.179}{0.209}$ |
| | 5 | $\frac{1874.83}{1462.46}$ | $\frac{359.26}{338.81}$ | $\frac{1908.94}{1501.20}$ | $\frac{0.192}{0.232}$ |
| | 10 | $\frac{1510.65}{1245.47}$ | $\frac{282.81}{287.97}$ | $\frac{1536.90}{1278.33}$ | $\frac{0.187}{0.231}$ |
| | 20 | $\frac{1215.21}{1050.52}$ | $\frac{223.37}{238.65}$ | $\frac{1235.57}{1077.28}$ | $\frac{0.184}{0.227}$ |
| | 50 | $\frac{874.50}{799.81}$ | $\frac{176.69}{186.57}$ | $\frac{892.17}{821.28}$ | $\frac{0.202}{0.233}$ |
| | 100 | $\frac{657.02}{646.85}$ | $\frac{155.34}{157.37}$ | $\frac{675.14}{665.72}$ | $\frac{0.236}{0.243}$ |
| OSSO product<br>(11.0) | 1 | $\frac{3924.27}{2638.43}$ | $\frac{751.76}{606.46}$ | $\frac{3995.63}{2707.28}$ | $\frac{0.192}{0.230}$ |
| | 2 | $\frac{3208.29}{2310.54}$ | $\frac{704.30}{574.62}$ | $\frac{3284.69}{2380.92}$ | $\frac{0.220}{0.249}$ |
| | 5 | $\frac{2359.00}{1845.75}$ | $\frac{566.52}{495.52}$ | $\frac{2426.07}{1911.11}$ | $\frac{0.240}{0.269}$ |
| | 10 | $\frac{1885.84}{1557.97}$ | $\frac{441.65}{419.81}$ | $\frac{1936.87}{1613.55}$ | $\frac{0.234}{0.270}$ |
| | 20 | $\frac{1499.98}{1299.77}$ | $\frac{346.26}{348.83}$ | $\frac{1539.43}{1345.77}$ | $\frac{0.231}{0.268}$ |
| | 50 | $\frac{1055.23}{970.92}$ | $\frac{266.46}{271.51}$ | $\frac{1088.36}{1008.17}$ | $\frac{0.253}{0.280}$ |
| | 100 | $\frac{778.77}{766.73}$ | $\frac{226.56}{229.80}$ | $\frac{811.06}{800.43}$ | $\frac{0.291}{0.300}$ |
| Nytex 4700 (5.5) +<br>OCCO (5.5) | 1 | $\frac{3158.57}{2166.39}$ | $\frac{567.76}{466.19}$ | $\frac{3209.19}{2216.02}$ | $\frac{0.180}{0.215}$ |
| | 2 | $\frac{2636.51}{1921.80}$ | $\frac{538.01}{449.37}$ | $\frac{2690.85}{1973.64}$ | $\frac{0.204}{0.234}$ |
| | 5 | $\frac{1984.45}{1558.23}$ | $\frac{442.18}{393.84}$ | $\frac{2033.12}{1607.24}$ | $\frac{0.223}{0.253}$ |
| | 10 | $\frac{1606.34}{1333.78}$ | $\frac{350.46}{333.15}$ | $\frac{1644.13}{1374.77}$ | $\frac{0.218}{0.250}$ |
| | 20 | $\frac{1293.84}{1131.14}$ | $\frac{277.33}{277.95}$ | $\frac{1323.23}{11.6479}$ | $\frac{0.214}{0.246}$ |
| | 50 | $\frac{930.40}{862.08}$ | $\frac{215.25}{219.60}$ | $\frac{954.97}{889.61}$ | $\frac{0.231}{0.255}$ |
| | 100 | $\frac{696.93}{685.15}$ | $\frac{186.66}{188.45}$ | $\frac{721.49}{710.60}$ | $\frac{0.268}{0.275}$ |

With increasing deformation intensity of vulcanizate samples from 1 to 100 % there is a decrease in the values of modulus of elasticity G', modulus of loss G" and complex shear modulus G*, which is the ratio of shear stress to shear strain at maximum amplitude; mathematically $G^* = (G'2 + + G"2)^{1/2}$. At the same time, the value Tan. Delta, which is the ratio of the modulus of loss to the modulus of elasticity $\tan \delta = G"/G'$, increases with increasing strain level of rubbers (Table 3). Since the value of $\tan \delta$ characterizes the share of energy dissipated by rubbers, the more this value, the more the sample is heated under sinusoidal oscillations. So, the obtained dependences of $\tan \delta$ level on the level of deformation of the rheometer half-form are quite logical. Also, the statement that, in regard to the dissipative energy loss, vulcanizates are arranged in a series according to the type and content of test compounds becomes objective. The series is as following: product OSSO (11.0 phr) > Nytex 4700 (5.5 phr) + OSSO (5.5 phr) > Nytex 4700 (11.0 phr). Hence, the compositions with the bioingredient OSSO as a softener are characterized by greater heat buildup during shear oscillations than those with the lubricant Nytex 4700.

Next, we will answer for the allegedly obtained contradiction between G', G", G* and shear deformation values (Table 3): why with increasing the value of shear strain of rubber filled with carbon black, the values of dynamic parameters decrease? It is obvious that the introduction of a rigid filler in the elastic rubber increases the modulus of elasticity of elastomeric compositions (vulcanizates). However, the fact that the modulus G decreases significantly with increasing amplitude of shear deformation, – Payne effect (Fletcher-Gent effect), is much less obvious. The effect was studied in the 50-60 s of last century.[43] It is observed under cyclic loading conditions and small voltage amplitudes. The Payne effect depends on the filler content and disappears in unfilled elastomers. It is caused by the changes in the microstructure of rubber – damage and renewal of physical bonds that connect the groups of filler "filler-filler" and the spatial network formed from filler particles. The higher the degree of filling of the elastomeric composition and the more active the filler, the greater the Payne effect. The lower the value of the complex dynamic module Delta Strain ($G'_1$-$G'_{100}$), the more efficiently the filler is distributed in the volume of the elastomeric matrix.[43]

Given the fact that all rubbers contain equal amounts of carbon black as a filler and the studied organic substances as technological additives, we obtain the following sequence of their activities with a positive effect on the distribution of filler: Nytex 4700 > Nytex 4700 + OSSO product > the OSSO product). Thus, for the elastomeric composition with softener Nytex 4700 after 5 min of testing, the parameter Delta Strain, as a quantitative indicator of the Payne effect, was 1393.64 kPa, and for the elastomeric composition with the experimental product OSSO this value is equal to 1871.69 kPa. The established fact may be the result of a positive modifying effect of the product under study (in particular, its effect on the filler activity) or a negative effect – the deterioration of carbon black dispersion and an increase in the crosslinking degree of the filler.

This, obviously, explains the above-established fact of a higher value Tan. Delta (Table 3) for rubber with OSSO product compared to rubber containing Nytex 4700 softener.

According to the ISO 13145 standard, the tests for determining the dynamic and relaxation properties of rubbers were performed in 3 steps using the rheometer (after vulcanization of elastomeric compositions):

– the first step was realized under the following conditions: time 1 min, temperature 373 K;

– the second step was realized under the following conditions: deformation of 150 % with the definition of the following parameters:

shear modulus G', kPa;
shear loss modulus G", kPa;
mechanical losses tangent G"/G', Tan Delta;

– the third step was to determine the relaxation characteristics of the experimental samples:

maximum torsional moment, dN·m;
a torsional moment after 1 s of the test, dN·m;
a torsional moment after 20 s of the test dN·m.

Indices G', G" and $\tan \delta$ (Tan. Delta) were determined after rubbers vulcanization using a rheometer chamber for 20 min at a temperature of 433 K, deformation of 7 % and frequency of 1.67 Hz. Then the rubber sample, remaining in the molds, was cooled to 373 K. After holding at 373 K for 1 min with deformation of 150 % and frequency of 1.67 Hz the mechanical loss tangent Tan. Delta, as well as its components G' and G" were determined.

Data represented in Fig. 4 show that the complete replacement of Nytex 4700 lubricant for the OSSO product is accompanied by a simultaneous increase by one-third of the modulus of elasticity G' and the modulus of shear losses G". Since the value of Tan. Delta characterizes the share of energy dissipated by the sample, then the greater its value, the more the rubber is heated under dynamic loading (sinusoidal oscillations). So, the value of Tan. Delta (Fig. 4) indicates a certain reduction in heat buildup when the OSSO product is used. This may be due to changes in the concentration and nature of vulcanization crosslinks in vulcanizates in the presence of the OSSO product. The results of relaxation tests – both after 1 s and after 20 s – confirm this fact. For the compositions with the studied bioingredient OSSO the absolute values of torsional moment and the degree of their preservation are higher by 30–40 % in comparison with rubber containing only Nytex 4700 (Table 4).

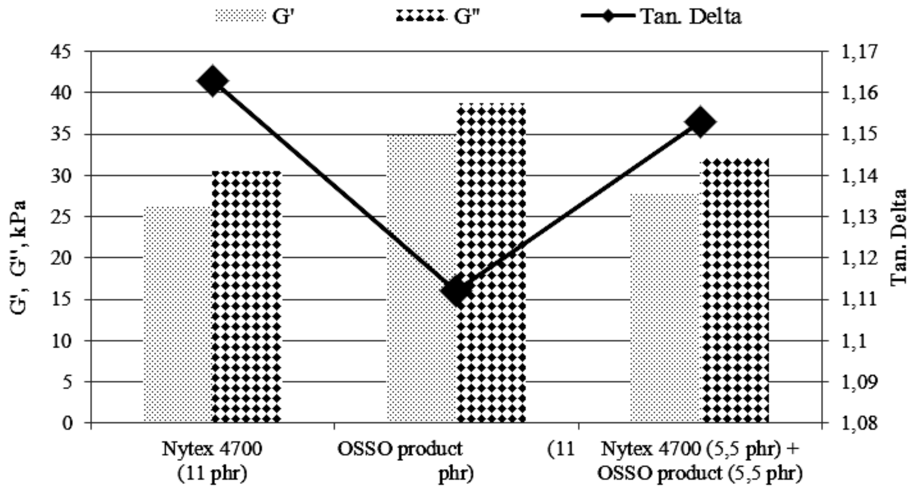

**Fig. 4.** Dynamic and hysteresis characteristics of tread-type vulcanizates in the presence of different types and amounts of test compounds

**Table 4.** Dynamic and relaxation characteristics of tread-type rubbers with different types and amounts of test compounds

| Index | Type and amount of ingredient | | |
|---|---|---|---|
| | Nytex 4700 (11.0) | OSSO product (11.0) | Nytex 4700 (5.5) + OSSO product (5.5) |
| Maximum torsional moment, dN·m | 9.22 | 11.66 | 9.85 |
| Torsional moment after 1 s of test, dN·m | 2.92 | 3.87 | 3.16 |
| Change in the torsional moment after 1 s of test, % | 68.37 | 66.79 | 67.89 |
| Torsional moment after 20 s of test, dN·m | 0.91 | 1.29 | 1.02 |
| Change in torsional moment after 20 s of test, % | 90.17 | 88.91 | 89.61 |

Thus, the comparison of the results on determination of the dynamic and relaxation properties of elastomeric compositions on the vulcanization plateau shows the following: thread-type rubbers with 11.0 phr of the OSSO product are characterized by the higher (up to 30 %) values of shear modulus, loss modulus, dynamic and mechanical losses tangent; the Payne effect is higher by one-third, the resistance to relaxation processes is higher by 40 % as compared to rubbers with Nytex 4700 commercial product.

## 3.4. Physical and Mechanical Properties

According to the current standards, the physical and mechanical properties of rubbers in the vulcanization optimum at 428 K were studied under different test conditions and different modes of deformation, both static and dynamic (Table 5).

Under normal test conditions, according to rheometric data, a positive correlation was found between the relative degree of crosslinking and the conditional stress of rubbers at 300 % elongation (Table 2, Table 5). It means that rubber with 11.0 phr OSSO was characterized by maximum conditional stress at 300 % elongation as compared to rubber with Nytex 4700 (11.7 MPa vs. 10.4 MPa). Rubber with Nytex 4700+OSSO product was characterized by minimum conditional stress at given elongation (Table 5). Composition with the studied bioingredient has a higher hardness, lower elasticity and tear resistance as compared to rubber with Nytex 4700. But generally, the values of physicomechanical characteristics of rubbers with the OSSO product, which were obtained under normal test conditions, meet the requirements of production control.

Vulcanizates with OSSO or with Nytex 4700 + OSSO have good indices of elastic strength and coefficients of temperature, heat resistance and ozone resistance (Table 5). The higher values of Goodrich heat buildup and Tan. Delta observed for the compositions with the studied bioingredient, are probably due to the differences in the crosslinking degree and the viscous deformation/elastic deformation ratio (Tables 1 and 2). Obviously, this is also the reason for less fatigue resistance of tread-type rubbers with the OSSO product (Table 5).

**Table 5.** Physical and mechanical properties of tread-type rubbers with different types and amounts of test compounds

| Index | Type and amount of ingredient | | |
|---|---|---|---|
| | Nytex 4700 (11.0) | OSSO product (11.0) | Nytex 4700 (5.5) + OSSO product (5.5) |
| Normal test conditions, 373 K | | | |
| Conditional stress at 300 % elongation, MPa | 10.4<br>– | 11.7<br>– | 9.9<br>– |
| Conditional tensile strength, MPa | 16.8<br>8.9 (0.53*) | 15.3<br>9.5 (0.62*) | 16.4<br>9.5 (0.58*) |
| Relative tensile elongation at break, % | 480<br>380 (0.79*) | 420<br>340 (0.81*) | 500<br>400 (0.80*) |
| Tear resistance, kN/m | 58<br>45 | 50<br>34 | 51<br>34 |
| Shore hardness, rel.units | 63<br>61 | 69<br>67 | 65<br>63 |
| Rebound elasticity, % | 26<br>32 | 22<br>28 | 24<br>30 |
| 373 K×12 h / 373 K×24 h | | | |
| Conditional tensile strength, MPa | 16.4 (0.98*)<br>15.0 (0.89*) | 15.2 (0.99*)<br>14.8 (0.97*) | 16.2 (0.99*)<br>15.7 (0.96*) |
| Relative tensile elongation at break, % | 360 (0.75*)<br>300 (0.63*) | 320 (0.76*)<br>290 (0.69*) | 390 (0.78*)<br>330 (0.66*) |
| Tear resistance, kN/m | 42<br>41 | 41<br>41 | 43<br>42 |
| Goodrich heat buildup, K | 307 | 314 | 309 |
| Multiple tensile fatigue at 100 % elongation, 250 cycles/min, cycles (normal conditions/393 K×12 h) | 497000<br>9000 | 485000<br>7708 | 645000<br>8833 |
| Multiple longitudinal bending fatigue, cycles | | | |
| – normal conditions visible | 105000 | 93000 | 88000 |
| till 12 mm | 236000 | 212000 | 189000 |
| – after aging visible | 83000 | 73000 | 68000 |
| till 12 mm | 152000 | 133000 | 121000 |
| Resistance of rubber to ozone aging in static conditions $(O_3)=(5\pm0.5)*10^{-5}$ vol. $\varepsilon_{stat.}$=10 %, 323 K, 24 h | | | |
| Conditional stress at 300 % elongation, MPa | 11.2 | 12.8 | 10.6 |
| Conditional tensile strength, MPa | 16.3<br>(0.97*) | 15.2<br>(0.99*) | 16.1<br>(0.98*) |
| Relative tensile elongation at break, % | 450<br>(0.94*) | 410<br>(0.98*) | 480<br>(0.96*) |

* Coefficient of temperature or heat resistance

Thus, the OSSO bioingredient (both alone and combined with Nytex 4700) as a softener for elastomeric compositions, which are used for manufacturing tire tread, provides good physical and mechanical properties of rubbers under different modes and test conditions. These properties are at the level of rubber with petrochemical lubricant Nytex 4700 and meet the requirements of regulatory and technical documentation.

## 4. Conclusions

Guided by global trends in resource-saving technologies for renewable plant raw materials, in particular, in the manufacture of environmentally friendly ingredients for the production of elastomer products based on secondary raw materials of oil and fat production, which is also relevant for Ukraine, we have studied the technological, vulcanization, dynamic, relaxation and physicomechanical properties of the elastomeric composition for the manufacture of tread section of tire in the presence of bioingredient – an organic component of the by-product after sunflower oil wintering (OSSO product) – which was used as a plasticizer-softener.

A systematic analysis of the effect of the studied OSSO on the complex properties of the elastomeric composition based on synthetic butadiene-α-methylstyrene and cis-butadiene rubbers in comparison with imported petrochemical lubricant Nytex 4700 in amounts of 11.0 phr and 5.5 phr shows the prospects of using bioingredient or its derivatives as technologically active additives based on domestic raw materials of plant origin.

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## ФОРМУВАННЯ ВЛАСТИВОСТЕЙ ЕЛАСТОМЕРНИХ КОМПОЗИЦІЙ ЗА НАЯВНОСТІ БІОІНГРЕДІЄНТА

***Анотація.*** *Досліджено особливості формування технологічних, вулканізаційних, динамічних, релаксаційних та фізико-механічних властивостей еластомерної композиції для виготовлення бігової частини протектора шин за наявності біоінгредієнта – органічного складника супутнього продукту після вінтеризації соняшникової Порівняно з промисловим нафтохімічним мастилом продукт ОССО в 1,5 разу підвищує когезійну міцність гумової суміші, зі збереженням параметрів вулканізації забезпечує на 30-40 % вищу стійкість до реверсії та релаксаційних процесів за 373 К, менший рівень динамічних втрат, високий рівень фізико-механічних характеристик.*

***Ключові слова:*** *еластомерна композиція, технологічно активна добавка, біоінгредієнт, супутній продукт після вінтеризації соняшникової олії, екологічно безпечна гума.*