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PROPERTIES OF ELASTOMERIC COMPOSITIONS WITH FLUORINATED ADDITIVE

The effect of the product of pyrolytic synthesis "Forum" on the properties of the elastomer compositions based on EPDM rubber is investigated. It is established that introduction of modifying agent promotes viscosity reduction, cuts time attainment of optimum cure and improves the technical properties of vulcanizates.

Introduction. Among a variety of polymeric materials elastomers based on rubbers and their combinations, are in a unique position. They are the only materials capable of large reversible deformations in a wide range of temperatures; possess high strength, durability and water resistance, as well as a number of other valuable qualities [1]. However, to improve rubber products performance, improve the design and technology, it is of great importance to improve the quality of rubber, which can be achieved by the application of new types of elastomeric materials, and more rational way is to use traditional materials as modifiers. Modification of rubber allows purposefully regulating the technical properties of the elastomer compositions and vulcanizates based on them, depending on the operating conditions of finished products [1].

Main part. The aim is to study the influence of pyrolysis products of polytetrafluoroethylene (PTFE ultrafine, UPTFE) brand “Forum” on the properties of the elastomer compositions.

The object of the research was the filled elastomeric composition based on synthetic ethylene propylene rubber EPDM-50. As the vulcanizing system a combination of sulfur (1.75 parts per hundred rubber (phr)), thiuram D (1.75 phr), captax (0.75 phr), and zinc dimethyldithiocarbamate (1.75 phr).

The filler is a combination of carbon black grades P-514 and P-803, each dose is 66.15 phr. The modifying additive is added in dosages of from 0.1 to 0.5 phr. The object of comparison is an elastomeric composition containing no additive.

Determination of the viscosity of testing compositions was performed on Mooney viscometer MV2000 according to GOST 10722-76, and the kinetics parameters of vulcanization – on vibroreometre ODR2000 according to GOST 12535-84. Determination of resistance to thermal aging was determined by changes in physico-mechanical indicators according to GOST 270-75 and GOST 9.024-74.

According to GOST 426-77 the studies were conducted to determine the abrasion resistance when sliding on the abrasive cloth.

The impact of modifying additives on the vulcanized network parameters was evaluated by the concentration values of cross links and crosslink density, calculated by the Flory – Rener equation based on the data of equilibrium swelling in toluene at temperature 23(± 2) °C [2]:

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

where M_c – average molecular weight of the chain segment between two crosslinked chains, kg/mol; V_r – volume fraction of rubber in the swollen vulcanizate, m^3/mole; V_0 – molar volume of solvent, m^3/mole; χ – Huggins constant characterizing the interaction between rubber and solvent.

The “Forum” addition is a powder, its single particles tend to form agglomerates and larger associates, which are fragile structures, and can be destroyed by weak external influence. Fig. 1 shows an electronic snapshot of the surface additives.

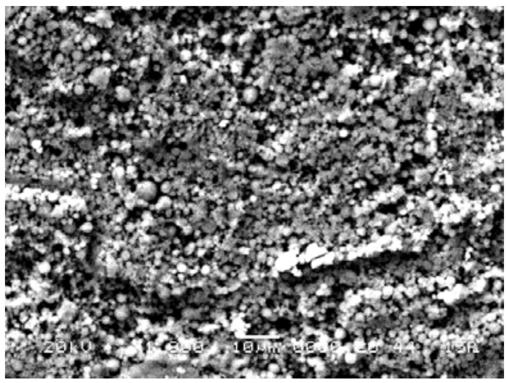

Fig. 1 Electronic picture of UPTFE surface

Studies have demonstrated [3-6] that the powder particles in the composition contain low and high fractions of polytetrafluoroethylene; wherein the molecules of a low molecular weight component comprise Fluoroolefin terminal double bond groups (-CF = CF_2), and side trifluoromethyl group -CF_3.

The material in these end-groups depends on the process conditions of the blocked polytetrafluoroethylene pyrolysis.

Viscosity index of rubber compounds is one of the most important characteristics of their rheological properties, and also determines the dynamics of the recycling process. It is a measure of the force which must be applied to the material flow to implement it at a predetermined rate for a particular stage of the process [7]. Table 1 shows the results of the Mooney viscosity determination of the investigated elastomeric compositions.

Table 1

Viscosity study of elastomeric compositions

Dosage additives, phr	Mooney viscosity conv. u	Relaxation coefficient
0	49.8	0.62
0.1	47.4	0.64
0.2	45.9	0.64
0.3	46.4	0.64
0.4	45.8	0.64
0.5	45.6	0.65

As a result of studies, it was found out that the introduction of the fluorine-containing additive to elastomer compositions helps to reduce the viscosity. Thus, the minimum value of this indicator (45.6 conv. u., Mooney) is achieved at a dose 0.5 phr, whereas the viscosity of the composition under comparison is 49.8 conv. u.

This is accompanied by the acceleration of the relaxation processes of shear stresses. Thus, the relaxation coefficient of the composition containing 0.5 phr UPTFE is 0.65, whereas the non-modified sample – 0.62.

Reducing the viscosity of the elastomer compositions and acceleration of relaxation processes is probably due to the presence of low molecular weight fraction that facilitates the orientation of rubber macromolecules under applied load.

Vulcanization is a complex of physical-chemical processes occurring in the rubber compound, the basic processes are cross-linking of rubber macromolecules by chemical bonds of various energy and nature into a spatial vulcanized grid.

The properties of such grids are largely dependent on the distribution and concentration of chemical bonds, the average molecular weight and molecular weight distribution of rubber [8].

In the study of the kinetics of vulcanization of elastomer compositions (Table 2), it was showed that the introduction of ultrafine PTFE reduces the time required to reach the optimum vulcanization. Thus, the smallest value of the index equals to 30.2 minutes has a composition containing 0.3 phr of the studied additives, whereas the comparative sample - 31.9 min.

Swelling of rubbers is a diffusion process of a liquid absorption by a sample surface layer before the achievement of the maximum equilibrium swelling [8].

In Table 2 the results of determination of cross-links concentration, as well as of studied elastomer compositions swelling index are presented. Studies to determine the concentration of cross-linking (Fig. 2) showed that the use of ultrafine polytetrafluoroethylene in all dosages enhances the value of this indicator.

Table 2

Kinetics of vulcanization of elastomer compositions

Dosage additives, phr	Time to reach optimum vulcanization, min	Vulcanization rate, dNm/ min
0	31.9	2.3
0.1	31.0	2.1
0.2	30.6	2.3
0.3	30.2	2.3
0.4	30.4	2.2
0.5	30.7	2.3

The maximum concentration value of cross-linking equals to $7.22 \cdot 10^{-19}$ mol/cm^3 is achieved with a dosage 0.4 phr of the investigated additives, whereas the dosage in the comparison sample is $6.1 \cdot 10^{-19}$ mol/cm^3.

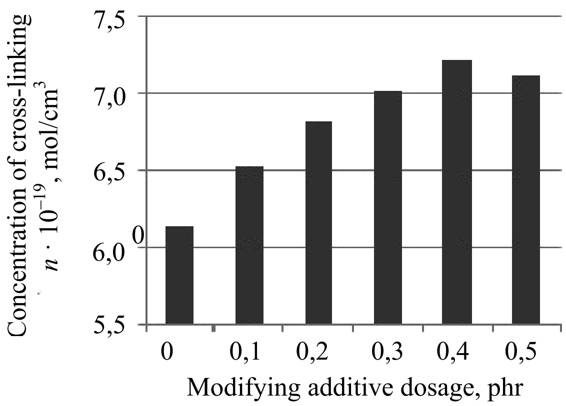

Fig. 2. The concentration of cross-linking testing compositions

Under the influence of elevated temperatures an irreversible change occurs in the structure of the vulcanizate which is associated with the oxidation of the matrix polymer chains and radicals formation.

This process is characterized by the degree of changes in physical and mechanical properties (conditional strength at tensile δ_σ and relative elongation at break δ_ε) of elastomeric compositions. To determine the heat stability the investigated vulcanizates were subjected to thermal aging in an oven for 72 hours at a temperature 125°C. Results are presented in Table 3.

Table 3

Changes in the physical and mechanical properties of the elastomer compositions

Dosage additives, phr	δ_σ, %	δ_ε, %
0	17,09	–61,90
0,1	19,04	–57,14
0,2	18,73	–56,10
0,3	26,35	–55,81
0,4	21,23	–51,22
0,5	27,05	–53,33

The data presented in Table 3 show that the introduction of the product "Forum" in elastomer compositions based on EPDM increases the thermal stability of the vulcanizates.

It should be noted that the rate of elongation at break of the samples containing the modifying additive in the aging process is less reduced if it is compared with the unmodified samples.

Thus, the change in elongation at break of the vulcanizates containing 0.4 phr. UPTFE is -51.2%, whereas a decrease of this indicator in comparison samples is -61.9%. The observed increase in conventional tensile strength is due to the cross-linking process and recombination of macroradicals formed in the thermal aging process of the composition.

Increased thermal stability appamomu, due to the interaction of active end groups builder components elastomeric composition after result of which the by increasing the crosslink density is a decrease of the kinetic energy Macroradicals polymer matrix that prevents destructive processes and reduce the elasticity of the samples.

Wear of rubber due to friction on various surfaces is a major cause of failure of the rubber products. Thus, on the abrasive there are strips, coinciding with the direction of sliding. In this case, the wear is due to the fact that the counterface hard edges score (make microcuts) on the rubber surface layer [9]. Due to this fact, the basic method for reducing wear and improving performance of finished products is increasing resistance to abrasion by the use of anti-friction additives of different nature, including fluorine-containing ones.

Fig. 3 shows the results of abrasion resistance determination when sliding on the abrasion cloth.

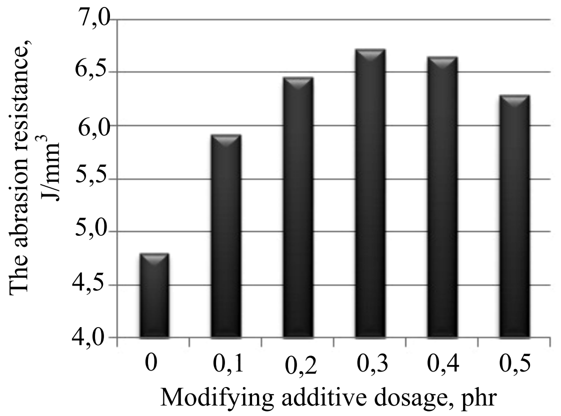

Fig. 3. Abrasion resistance of the testing compositions

Analysis of the data shows that the use of ultrafine polytetrafluoroethylene as a modifying additive can improve the abrasion resistance of the testing compositions.

In this case the maximum wear resistance will have the samples containing 0.3 phr. of the investigated additives. Thus, the abrasion resistance index value at the given dosage is 6.72 J/mm^3, whereas the comparative sample – 4.8 J/mm^3.

The increase of wear resistance of vulcanizates containing polytetrafluoroethylene pyrolysis product, is probably due to the collapse of the additive particles on nanofilms [10], which, filling microcracks on the sample surface, and aligning scuffs and roughness, and thereby, they help to reduce the penetration depth of the edges on the abrasive surface.

Conclusion. Thus, modification of elastomeric compositions by fluoride-containing compounds, including pyrolysis products of polytetrafluoroethylene, is an effective method for controlling the technological properties of mixtures and technical properties of the finished products. This improves properties such as thermal stability and wear resistance. The best complex of properties possesses the composition containing 0.4 phr of ultrafine polytetrafluoroethylene.

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