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ELASTOMERIC COMPOSITIONS BASED ON BUTADIENE-NITRILE RUBBER CONTAINING POLYTETRAFLUORETHYLENE PYROLYSIS PRODUCTS

Key-words: rubber, polytetrafluorethylene pyrolysis product, processing behavior, technical characteristic.

The effect polytetrafluorethylene pyrolysis products "Forum" on the properties of the elastomer compositions based on butadiene-nitrile rubber are investigated. It is established that introduction of modifying agent promote viscosity reduction, process acceleration of vulcanization and improve the technical properties of vulcanizate.

Ключевые слова: каучук, продукты пиролиза политетрафторэтилена, переработка, технические характеристики.

Изучено влияние продуктов пиролиза политетрафторэтилена на свойства эластомерных композиций на основе бутадиен-нитрильного каучука. Показано, что введение модификатора промотирует снижение вязкости, ускорение процесса вулканизации и улучшение технических свойств вулканизатов.

Introduction

Elastomers are one of the most important structural materials in modern engineering and occupy a unique place among a variety of polymeric materials. They are the only material capable of large reversible deformation in a wide range of temperatures; they possess high durability, wearability and water-resistance as well as a number of other valuable qualities [1].

At the same time, the products of elastomeric materials are determinative for different kinds of process equipment, automobiles, special purpose equipment. Failure of such determinative product leads to a loss of functional characteristics of machinery, mechanisms due to wear or destruction [2].

Despite the high importance of creating new formulations of rubber, it is advisable to carry out the modification of commercially produced rubber compounds. This would greatly save financial resources. Analysis of the literature data shows that the most common method of polymeric material modifying including rubber is the introduction of the modifying additive compositions in powder form.

The aim was to determine the influence of powdered polytetrafluoroethylene pyrolysis product on plasto-elastic properties and vulcanization kinetics of rubber compounds as well as on the basic operational properties of vulcanizates based on them.

Main part. The objects of the research were filled elastomer compositions on basis of synthetic butadiene-nitrile rubber (NBR) with the dosage of bound acrylonitrile 17-23% intended for the production of compacting rubber products for different purposes. The modifying additive was added in dosage of from 0.1 to 0.5 parts per hundred of rubber (phr). The samples without the additive were used as objects of comparison.

Polytetrafluoroethylene pyrolysis product is produced by the Institute of Chemistry, Far East Branch of the Russian Academy of Science, under the trade name "Forum". It's produced by thermal effects on the base polymer. The destruction of macromolecules of polytetrafluoroethylene in the most stressed areas of the sample followed by sublimation fragments of different molecular shape and mass is the most probable mechanism of this process. Macromolecular particles are the main products of the synthesis; they are characterized as "spray", which is formed by the interaction of molecular radicals - pyrolysis products of polytetrafluoroethylene and monomer molecules [3].

For the most part pyrolysis product PTFE contains sphere-like particles with an average diameter of 0.6 microns, which can be assembled into larger, easily breakable airflow conglomerates up to 15 μm. Particles can also sphere-like with the same dimensions as the diameters of the individual particles [4].

In accordance with studies [5-8], the powder particles contain the low-and high-molecular fractions of polytetrafluoroethylene. The molecules of low molecular weight part contain fluoroolefin end-groups with double bonds ($–CF=CF_2$) and side threefluoromethyl groups-CF_3. The material in these end-groups depends on the process conditions of block polytetrafluoroethylene pyrolysis.

The electronic picture of surface of the product "Forum" is presented in Fig. 1

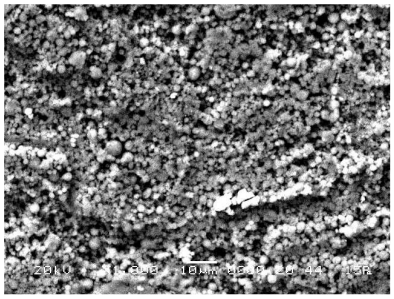

Fig. 1 – The electronic picture of surface of the product "Forum"

The Mooney viscosity test was carried out in viscometer MV2000 company «Alpha Technologies» according to ASTM D1646, and vulcanization kinetics parameters - on vibroreometre ODR2000 company «Alpha Technologies» by ASTM D2084. Physical and mechanical properties such as conditional tensile strength at break σ_p elongation at break ε_p were determined by tensiometer T2020DC company «Alpha Technologies» by ASTM D412. According to State Standard 9.024-74, State Standard 9.029-74 and State Standard 9.030-74 tests to determine resistance to heat ageing of rubbers in the unloaded and loaded conditions were carried out (the

accumulation level of relative compression set) and the action of liquid hydrocarbonaceous medium.

Influence of modifying additive on the vulcanization grid parameters was assessed by concentration values of crosslinks by the Flory-Rener equation based on data on the equilibrium swelling in toluene at temperature (23 ± 2)°C [8]:

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

where M_c – average molecular weight of the chain segment enclosed between two crosslinks, kg/mol; V_r – volume fraction of rubber at swollen vulcanizate, м^3/mol; V_0 – molar volume of solvent, м^3/mol; χ – the Huggins constant which characterizes the interaction between the rubber and the solvent.

The viscosity of the material being processed 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 given speed for a particular stage of the process [9]. The results of identifying viscosity research of the elastomeric compositions are presented in Table 1.

Table 1 - Viscosity and kinetics of vulcanization of the elastomer compositions containing the product of PTFE pyrolysis

The modifying additive dosage, phr	The Mooney viscosity, conv.u.	Optimal time of vulcanization, min
0	85.1	15.5
0.1	84.5	15.3
0.2	83.3	15.1
0.3	82.8	14.9
0.4	83.1	14.4
0.5	83.5	14.5

The analysis of this data shows that the introduction of polytetrafluoroethylene pyrolysis product in the compositions leads to a decrease of viscosity. Thus, the minimum value of the elastomeric compositions viscosity based on NBR-18 is achieved at a dosage of 0.3 phr and is 82.8 conv. u Mooney, while the viscosity of the unmodified compositions is 84.1 conv. u Muni. Reducing the viscosity of the elastomer compositions is probably due to segments orientation facilitation of macromolecules in the direction of load application. The particles oligomeric fraction of modifying additive acting as a plasticizer contributes to this process.

Vulcanization is hemoreological process, as a result of chemical transformations the material passes from plastic and viscous-flow into highly elastic status. During vulcanization rubber macromolecules dimensional crosslinking occurs to form a vulcanization space grid. The main parameter characterizing vulcanization process is optimal time of vulcanization.

The obtained data (see Table 1) indicate that using the product "Forum" decreases optimal time of vulcanization. The minimum value of this ratio is achieved with a dosage of modifying additive of 0.4 phr. Perhaps the additive particles contribute to the segmental mobility facilitation of rubber macromolecules and to more uniform distribution of vulcanizing group components in a volume of elastomeric composition,which led to their more intensive interaction with rubber macromolecules at the double bonds and reduce the formation of vulcanization grid.

Since the compacting rubber products were exposed to elevated temperatures during operation, the thermal stability of elastomeric compositions was determined. Thermal ageing of the compositions in the unloaded state was performed in a heat chamber at 125 ° C for 72 hours, while in the loaded state (relative compression set) - for 24 hours. Change in elongation at break of $\delta_ε$ and the level of accumulation relative compression set are shown in Table 2.

It is seen that the imposition of polytetrafluoroethylene pyrolysis product promotes the thermal stability of the elastomeric compositions. Thus, the relative elongation of vulcanizates at break containing the product "Forum" is reduced by -13.6% at a dosage of 0.3 phr after thermal ageing, whereas the decrease of the indicator in the unmodified samples is 25%. PTFE pyrolysis product injection also reduces relative compression set savings at elevated temperatures. The minimum value of this ratio is achieved with a dosage of 0.2 phr, and it is 19.3%, while comparison sample - 24%.

Vulcanizates thermal stability increasing in unloaded condition is probably due to the fact that the application of modifying additive helps to reduce the rate of oxygen diffusion in the bulk of vulcanizate. This is probably achieved by the migration of low molecular weight fractions of "Forum" in the surface layers of the samples. This process helps to reduce the degree of exposure to elevated temperatures. Specific compression set reduction is probably determined by the acceleration of relaxation processes due to the increasing mobility of macromolecules segments.

Table 2 - Change in elongation at break of vulcanizates after thermal ageing

The modifying additive dosage, phr	$\delta_ε$, %	Accumulation level of relative compression set, %
0	-25,0	24,0
0.1	-15,0	19,8
0.2	-14,3	19,3
0.3	-13,6	19,6
0.4	-15,5	20,5
0.5	-16,2	21,1

Liquid hydrocarbon media in relation to rubbers are physically active media. It does not give rise to profound structural changes with the destruction of chemical bonds. When liquid hydrocarbons contact rubber products, a series of simultaneously proceeding processes such as sorption of medium by surface and volume of the rubber, medium diffusion through the rubber and extraction with soluble ingredients occur.

Resistance to liquid hydrocarbon media is an important indicator of operational reliability of rubber used for the production of compacting and cushioning rubber applied in sealing and gasketing products as swelling and erosion of ingredients occurring in contact with oils, greases and hydraulic fluids, reduces efficiency and durability of materials [10].

The data in Table. 3 show the results of determining the concentration of cross-linking as well as the degree of swelling and degree of erosion of the elastomeric compositions.

Presented numbers show that "Forum" using in the elastomeric compositions based on butadiene-nitrile rubber reduces diffusion of liquid medium deep into rubber products as well as reduces the bulk of extractable plasticizer.

Table 3 - The equilibrium degree of swelling of compositions under research containing product "Forum"

Modifying additive dosage, phr	Degree of swelling, %	Degree of erosion, %	Concentration of cross-linking $n \cdot 10^{-19}$, mol/cm^3
0	111,0	14,0	7,9
0,1	108,8	12,6	8,4
0,2	107,5	11,8	8,5
0,3	106,8	11,6	8,6
0,4	104,9	11,3	8,6
0,5	104,5	10,8	8,7

Thus, the degree of swelling of the composition based on NBR-18 in toluene is reduced by 7%, and the erosion - 30% as compared with the sample not containing the modifying additive. At the same time, increasing dosage of the modifying additive increases the concentration of vulcanizate crosslinking: $8{,}72 \cdot 10^{-19}$ mol/cm^3 in a sample containing 0.5 phr additives, whereas the comparison sample – $7{,}87 \cdot 10^{-19}$mol/cm^3.

The increased concentrations of crosslinking and, hence, the durability to the action of the liquid hydrocarbon medium, is apparently caused by the interaction of particles of the modifying additive with the components of vulcanizing systems. During vulcanization the formation of physical interaction additional linkages by the polar groups and the double bonds of rubber and additives active centres is possible.

Rubber compounds on the basis of NBR are used for the manufacture of rubber products operating under abrasion in harsh environments, so it seemed appropriate to determine the effect of modifying additives at the abrasion resistance of the studied elastomeric compositions.

Determination results of the abrasion resistance of the rubbers are shown in Fig. 2.

The presented data show that there is an increase in durability of the samples by using additives "Forum". Thus, the abrasion resistance index value for elastomer compositions on the basis of butadiene-nitrile rubber NBR-18 containing an additive in the maximum dosage is 14.2 J/mm^3, whereas the comparison sample - 8.4 J/mm^3.

The injection of the modifying additive into the elastomeric compositions helps to reduce the bulk of separated material during friction. This is probably due to the formation of zones of plastic deformation caused by the migration of low molecular weight fractions of the PTFE pyrolysis products in the surface layers of samples.

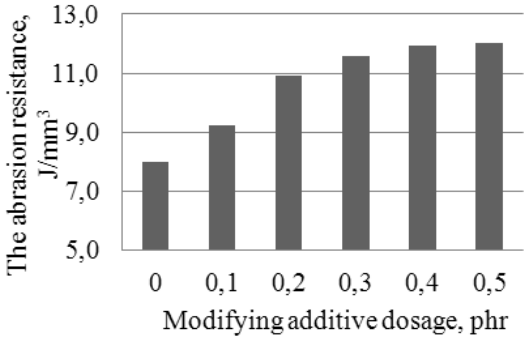

Fig. 2 – The abrasion resistance of the elastomeric compositions, containing PTFE pyrolysis product

Conclusion. The application of ultradisperse polytetrafluoroethylene as modifying additive to compositions on the basis of elastomeric butadiene-nitrile rubbers enables to reduce the viscosity of rubber compounds, to speed up the process of vulcanization grid formation, to improve the technical properties of the finished product such as heat resistance, resistance to attack by liquid hydrocarbon media, durability.

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