N. R. Prokopchuk[1)], V. D. Polonik[1)]*, Zh. S. Shashok[1)]

Elastomeric compositions based on nitrile butadiene rubber containing polytetrafluorethylene pyrolysis products

The effect polytetrafluorethylene pyrolysis products „Forum" on the properties of the elastomer compositions based on nitrile-butadiene rubber were investigated. It was found that addition of the modifying agent in amount of 0.1 to 0.6 phr reduces viscosity, accelerates the vulcanization process and improves the technical properties of vulcanizates.

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

Mieszanki elastomerowe bazujące na kauczuku butadienowo-nitrylowym zawierające produkty pirolizy politetrafluoroetylenu

Badano wpływ produktów pirolizy politetrafluoroetylenu o nazwie „Forum" na właściwości mieszanek elastomerowych opartych na kauczuku butadienowo-nitrylowym. Stwierdzono, że dodatek środka modyfikującego w ilości od 0,1 do 0,6 phr powoduje redukcję lepkości, przyśpiesza proces wulkanizacji i poprawia właściwości techniczne wulkanizatów.

Słowa kluczowe: *mieszanka kauczukowa, produkt pirolizy politetraetylenu, właściwości przetwórcze, właściwości techniczne*

1. Introduction

Elastomers are one of the most important structural materials in modern engineering and occupy a unique place among a variety of polymeric materials. These are the only materials 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].

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 modification including rubber is the introduction of the modifying additive compositions in powder form.

The aim of this work was to determine the influence of powdered polytetrafluoroethylene pyrolysis product on plastoelastic properties and vulcanization kinetics of rubber compounds, as well as on the basic operational properties of vulcanizates based on them.

2. Experimental

The objects of the research were filled elastomer compositions on the basis of synthetic nitrile-butadiene

[1)] Belarusian State Technological University. Sverdlova Str.13[a], Minsk, Republic of Belarus, v.polonik@belstu.by

* The author for correspondence

Nikolai R. Prokopchuk (b. 02/07/1948, Mogilev), physical chemist. Corresponding Member of the National Academy of Sciences (2004), Doctor of Science (1989), Professor (1995), Head of Department (BSTU).

Graduated from the Belarusian Institute of Technology (1971). C 1971 at the Institute of Physical Organic Chemistry, Belorussian Academy of Sciences, since 1992 the Belarusian State Technological University, since 1996 head. Department of Technology of Petrochemical Synthesis and processing of polymeric materials of this university.

Research in chemistry, physics and technology of high-molecular compounds. Theoretically substantiated and experimentally confirmed the relationship between the activation energies of the degradation of polymers in the solid and liquid states; developed a method to estimate the total intermolecular interactions in the amorphous regions of polymeric materials. Created stabilized thermoplastic and elastomeric materials with enhanced photo and thermal stability, fatigue endurance, reduced toxicity. Developing environmental, resource and energy saving areas: recycling plastics; creating recipes modern paint materials.

Author of over 600 scientific papers and textbooks, including 2 monographs and 55 patents for inventions.

V. D. Polonik, junior scientific researcher

Zh. S. Shashok, Candidate of Technical Sciences, Assistant professor (BSTU)

rubber (NBR) with the content of bound acrylonitrile 17-23% intended for the production of rubber sealing products for different purposes. The modifying additive was introduced in rubber with the content from 0.1 to 0.5 parts per hundred rubber (phr). The samples without the additive were used as objects of comparison.

The polytetrafluoroethylene pyrolysis product is produced by the Institute of Chemistry, The Far East Branch of the Russian Academy of Science, under the „Forum" trade name. This product is not homogeneous. It's obtained by applying thermal effects on the base polymer. The most probable mechanism of this process is the destruction of polytetrafluoroethylene (PTFE) macromolecules in the most strained areas of the sample followed by the sublimation of fragments with different molecular shape and mass. The particles are the main product of the synthesis; they are characterized as a „spray", which is formed by the interaction of molecular radicals – pyrolysis products of polytetrafluoroethylene and monomer molecules [2].

For the most part the PTFE pyrolysis product contains sphere-like particles with an average diameter of 0.6 microns. These particles can be assembled into larger, easily breakable airflow conglomerates as large as up to 15 μm. The particles can also be petal-shaped with the same dimensions as the diameters of the individual particles [3].

The previous studies show [4-9] that, the powder particles contain both low and high molecular fractions of polytetrafluoroethylene. The molecules of low molecular weight part contain fluoroolefin end groups with both double bonds (–CF=CF_2) and side threefluoromethyl groups (-CF_3). The material in these end groups depends on the pyrolysis process conditions of polytetrafluoroethylene.

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

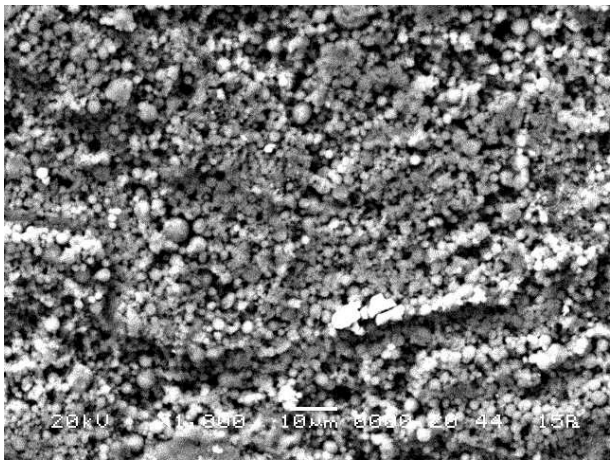

Fig. 1. *The electronic picture of surface of the „Forum" product*
Rys. 1. *Obraz elektroniczny powierzchni produktu „Forum"*

The Mooney viscosity test was carried out in the MV2000 viscometer according to ASTM D1646, and the vulcanization kinetics parameters were tested on ODR2000 vibroreometre according to ASTM D2084. The physical and mechanical properties such as conditional tensile strength at break σ_p elongation at break ε_p were determined by the T2020DC tensiometer according to ASTM D412. The viscometer, the vibroreometre and the tensiometer were produced by the «Alpha Technologies» company. According to the 9.024-74 State Standard, 9.029-74 State Standard and 9.030-74 State Standard tests to determine resistance to heat aging of rubbers in the unloaded and loaded conditions were carried out (the accumulation level of relative compression set) and to explore the action of liquid hydrocarbonaceous environments.

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

$$\frac{1}{M_c} = \frac{V_r + \chi \cdot V_r^2 + \ln(1 - V_r)}{\rho_k \cdot V_0 \cdot \left(V_r^{1/3} - 0.5 \cdot V_r\right)}$$

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, m^3/mol;

V_0 – molar volume of solvent, m^3/mol;

χ – the Huggins constant, which characterizes the interaction between the rubber and the solvent.

3. Results and discussion

The viscosity of the material 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 [8]. 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*
Tabela 1. *Lepkość i kinetyka wulkanizacji kompozycji elastomerowych zawierających produkt pirolizy PTFE*

The modifying additive content, phr	The Mooney viscosity, conv. u.	Time to reach vulcanization optimal degree, 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
0.6	83.7	14.7

The analysis of this data shows that the imposition of "Forum" product in the elastomeric compositions leads to a decrease of viscosity. Thus, the minimum value of the viscosity of elastomeric compositions based on NBR 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. Mooney. Reducing the viscosity of the elastomer compositions is probably due to segments orientation relief of macromolecules in the direction of load application. The particles oligomeric fraction of modifying additive acting as a plasticizer contributes to this process.

During vulcanization dimensional crosslinking of rubber macromolecules occurs to form a vulcanization space grid. The main parameter characterizing the vulcanization process is optimum vulcanization time.

The obtained data (see Table 1) indicate that the use of the „Forum" product decreases the time to reach an optimal degree of vulcanization. The minimum value of this ratio is achieved with a content of modifying additive of 0.4 phr. Perhaps the additive particles contribute to the segmental mobility relief of rubber macromolecules and to a more uniform distribution of vulcanizing group components in a volume of elastomeric composition. This leads to their more intensive interaction with rubber macromolecules at the double bonds and reduces the formation of vulcanization grid.

Since the sealing rubber products are exposed to elevated temperatures during operation, the thermal stability of elastomeric compositions was determined. Thermal aging 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 δ_ε and the level of accumulation of relative compression set are shown in Table 2.

Table 2. *Change in elongation at break of vulcanizates after thermal aging*
Tabela 2. *Zmiany wydłużenia przy zerwaniu wulkanizatów po starzeniu termicznym*

The modifying additive content, phr	δ_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
0.6	-16.4	21.9

It's 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 „Forum" product is reduced by -13.6% at a content of 0.3 phr after thermal aging, whereas the decrease of the indicator in the unmodified samples is 25%. The 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 parts by weight and is 19.3%, while comparison sample is 24%.

Vulcanizates thermal stability increase 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 amount of vulcanizate. This is probably achieved by the migration of low molecular weight fractions of „Forum" to the surface layers of the samples. This process helps to reduce the degree of exposure to elevated temperatures. The reduction of the specific compression set is probably the result of the acceleration of relaxation processes due to the increasing mobility of macromolecules segments.

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

Resistance to liquid hydrocarbon medium is an important indicator of operational reliability of rubber used for the production of sealing and cushioning rubber applied in sealing and gasketing products because swelling and erosion of ingredients occurring in contact with oils, greases and hydraulic fluids reduce efficiency and durability of materials [9].

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

Table 3. *The equilibrium degree of swelling of compositions under research containing product „Forum"*
Tabela 3. *Stopień pęcznienia równowagowego na podstawie badań kompozycji zawierających produkt „Forum"*

The modifying additive content, 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
0.6	104.5	10.7	8.7

The numbers presented show that the of use „Forum" in the elastomeric compositions based on NBR can

decrease the diffusion of liquid medium deep into rubber products, as well as can reduce the amount of extractable plasticizer.

Thus, the degree of swelling of the NBR based composition in toluene is reduced by 7%, and the erosion by 30% as compared to the sample not containing the modifying additive. At the same time, the increased content of the modifying additive raises the concentration of vulcanizate crosslinking: $8{,}7 \cdot 10^{-19}$ mol/cm^3 in a sample containing 0.6 phr additives, whereas in the comparison sample – $7{,}8 \cdot 10^{-19}$ 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 studied elastomeric compositions.

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

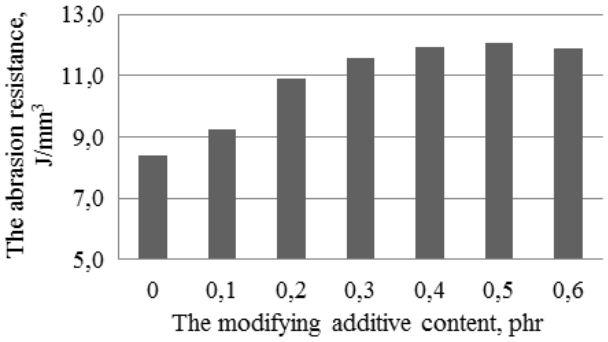

Fig. 2. *The abrasion resistance of the elastomeric compositions, containing PTFE pyrolysis product*
Rys. 2. *Odporność na ścieranie kompozycji elastomerowych zawierających produkt pirolizy PTFE*

The presented data show that there is an increase in durability of the samples after the „Forum" additives are used. Thus, the abrasion resistance index value for elastomer compositions on the basis of butadiene-nitrile rubber containing an additive in dosage of 0.5 phr is 14.2 J/mm^3, whereas in the comparison sample is 8.4 J/mm^3.

The injection of the modifying additive into the elastomeric compositions helps to reduce the amount 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 the samples.

3. Conclusion

The application of the polytetrafluoroethylene pyrolysis product as a modifying additive to compositions on the basis of elastomeric nitrile butadiene rubbers in amount of 0.1 to 0.6 phr contributes to reducing the viscosity of rubber compounds, to speeding up the process of vulcanization of rubber compounds, to improving the technical properties of the finished product such as heat resistance, durabilityand resistance to liquid hydrocarbon media. The optimal dosage of modyfying additives is 0.4 phr.

References

1. *Kercha Y.Y., et al., Structural and chemical modification of elastomers [in Russian], Navuk. Dumka, Kiev (1989).*
2. *Struck A.V., et al., Structure and properties of fluorine-containing nanocomposites based on vulcanized rubbers [in Russian], Weight. Nat. Acad. Navuka of Belarus, Ser. fiz-TECH. Navuka, No.1, 25-31 (2011).*
3. *Kuryavyi V.G., et al., The morphological structure of the PTFE ultradisperse pyrolysis products [in Russian], Advanced Materials, No.6, 71-73 (2002).*
4. *Vopilov Y.E., et al., Properties of ultradisperse PTFE fractions which are soluble in supercritical carbon dioxide [in Russian], High-molecular structures, T. 54, Series A, No 6, 842-850 (2012).*
5. *Bouznik V.M., et al., Particle size and shape of ultradisperse polytetrafluoroethylene obtained in thermal gas-dynamic method [in Russian], Advanced Materials, No 2, 69-72 (2002).*
6. *Avdeychik S.V., et al., Engineering fluorocomposites: structure, technology, applications: monograph [in Russian], Grodno State University, Grodno (2012).*
7. *Averko-Antonovich I.Y., Methods of research of structure and properties of polymers [in Russian], KSTU, Kazan (2002).*
8. *Shutilin Y.F., Handbook on properties and applications of elastomers: monograph [in Russian], Voronezh state tehnol. acad., Voronezh (2003).*
9. *Uralsky M.L., Control and regulation of technological properties of rubber compounds [in Russian], Khimiya, Moscow (1983).*

List of abbreviations:
Phr – parts per hundred rubber;
NBR – nitrile butadiene rubber;
PTFE – polytetrafluoroethylene
Conv. u. – conventional unit