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TECHNICAL PROPERTIES OF ELASTOMER COMPOSITIONS ON THE BASIS OF BUTADIEN-NITRIL OF RUBBER MODIFIED BY POLITETRAFTORETILEN

The effect of PTFE F4 and the product of thermal gas-dynamic synthesis "Forum" on the technical properties of the elastomer compositions based on butadiene-nitrile rubber NBR-18 are investigated. The addition of modifying agents improves following characteristics: the heat-ageing resistance of vulcanized rubber, swelling resistance in hydrocarbon liquids and abrasion resistance of elastomeric compositions.

Introduction. Elastomers are one of the major constructional materials in modern mechanical engineering. Its products are widely applied as sealing elements in various cars and mechanisms. Thus operability of the latters in many respects is defined by the quality of products and their efficiency resource [1].

Despite a high importance of new rubber compounding creation, it is reasonable to carry out batch-produced modification of rubber mixes. It allows making industrial rubber goods taking into account specific conditions of their operation. The analysis of reference data shows that the most widely used way of polymer material modifications including rubbers is structure introduction of composition components in the form of powders.

Main part. The aim of the work was a research of polytetrafluorethylene. (PTFE, fluoroplastic) the F4 brand, and also a product of thermodynamic (TGD) synthesis of polytetrafluorethylene (ultradisperse polytetrafluorethylene, UPTFE) the "Forum" brand affect technical properties of elastomer compositions. The research object was the filled elastomer composition on the basis of synthetic-butadiene-nitrile rubber with the associated acrylic acid nitrile content of 17–23%. The curing system consisted of N, N'-dithiodimorfoline (2.3 pbw), Thiuram D (1 pbw) and Sulfenamide C. (1.5 pbw). The filler was the combination of technical brands P-514 and P-803 carbon o in dosages of 40 and 90 pbw on 100 pbw rubber respectively. This elastomeric composition is intended for different function oil – gasoline-resistant industrial items production. Modifying agents were introduced in dosages from 0.1 to 0.5 pbw on 100 pbw rubber. Cured stocks without agents were an object of comparison.

The definition of physics and mechanical indicators of cured stocks before and after thermal aging were defined according to GOST 270-75 and GOST 9.024-74. Determination of rubbers resistance to wearing when sliding was carried out in accordance with GOST 426–77, and researches of

resistance to the hostile environment action – in accordance with GOST 4.030–74.

Cross linking density of modified cured stocks was determined by Florey Rener's equation on the data of equilibrium swelling in toluene at temperature (23±2)°C [2].

Polytetrafluorethylene represents friable, easy caked white powder of which particles have fibrous structure. It possesses a high corrosive and heat resistance, a low friction factor. PTFE – is a crystal polymer with melting temperature of the crystalline particles, equal 327°C, and amorphous segment vitrification temperature from – 100°C to – 120°C [3].

The "Forum" product is obtained by a thermal impact on the basic polymer. Thus the destruction of PTFE macromolecules proceeds in the most intensive sites with the subsequent fragment sublimation of a various form and masses. The obtained product precipitates on chamber walls in the form of an aerosol and represents a substance compounding sphere particles of 3–200 nanometers [4]. The researches having been carried out in works [4–7], show that particles of ultradispersed polytetrafluorethylene have the block structure consisting of polymeric and oligomeric fractions with various molecular weights and temperature of melting, possess an increased adhesion to metal surfaces and partial solubility of polymer (alcohol, acetone).

During the operation sealing industrial rubber products are treated to increased temperatures. Thus there are the irreversible changes of vulcanization structures connected with additional elastomer compositions structuring on the basis of butadiene-nitrile rubbers.

To define the influence of modifying agents on resistance to thermal aging physics and mechanical indicators of studied compositions before and after the increased temperature affect were determined. Investigated samples were subjected to thermal aging during 72 h at temperature 125°C. The results of researches are presented in Table 1.

Table 1

Physics and mechanical indicators of studied rubbers

| Dosage of an agent, pbw on 100 pbw rubber | The conditional durability at stretching, MPa | Relative lengthening at cutting, % | Factor of aging on conditional durability | Factor of aging on relative lengthening | Hardness according to Shor A, conventional unit. |
|---|---|------------------------------------|---|---|--|
| Without an agent | 10.7 | 200.0 | 1.00 | 0.75 | 77.4 |
| 0.1 PTFE | 11.3 | 210.0 | 0.99 | 0.81 | 75.9 |
| 0.2 PTFE | 10.1 | 180.0 | 1.12 | 0.80 | 74.5 |
| 0.3 PTFE | 12.3 | 210.0 | 1.15 | 0.81 | 73.4 |
| 0.4 PTFE | 12.0 | 200.0 | 1.18 | 0.82 | 72.5 |
| 0.5 PTFE | 12.0 | 210.0 | 1.15 | 0.81 | 72.0 |
| 0.1 UPTFE | 11.0 | 200.0 | 1.06 | 0.80 | 76.6 |
| 0.2 UPTFE | 11.3 | 220.0 | 1.01 | 0.82 | 75.4 |
| 0.3 UPTFE | 10.9 | 200.0 | 1.16 | 0.80 | 74.7 |
| 0.4 UPTFE | 10.5 | 180.0 | 1.27 | 0.89 | 73.4 |
| 0.5 UPTFE | 10.8 | 190.0 | 1.21 | 0.79 | 72.8 |

From the presented data we can see that with increase of fluoroplastic content in elastomer composition the conditional durability slightly increases at stretching. At fluoroplastic dosage from 0.3 to 0.5 pbw the increase of conditional durability is observed at stretching for 12% in comparison with the samples without agents.

In the course of researches the heat resistance increase of studied compositions was emerged: at polytetrafluorethylene dosage of 0.4 pbw the factor of aging increases in 1,1 times on relative lengthening at cutting.

The introduction of ultradispersed polytetrafluorethylene agent doesn't considerably impact the physics and mechanical indicators of studied elastomer compositions. At the same time their resistance to the high temperatures increases. So, at the dosage of 0.4 pbw UPTFE factors of aging on conditional durability at stretching and relative lengthening make 1.27 and 0.89, whereas in a model of comparison – 1.0 and 0.75 respectively.

The heat resistance of samples is probably connected with the interaction of modifying agent's particles with rubber macromolecules. Thus at the expense of additional coupling making the structure resisted to the increased temperatures [5] is formed.

The introduction of agents in all dosages results to the decrease in hardness of cured stocks. So, the minimum values of this indicator are observed at the samples containing 0.5 pbw of ultradispersed polytetrafluorethylene (72.8 conventional units, Shor A) and 0.5 pbw of polytetrafluorethylene (72 conventional units Shor A).

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.

From the presented data we can see that application of fluoroplastic in all dosages as a modifying additive agent decreases swelling extent of elastomer compositions in gasoline. So, the smallest indicator value is obtained at a dosage of 0.4 pbw and constitutes 18.9%, whereas at a compared sample – 21.8%. The maximum concentration of cross-links is thus observed ($8.46 \cdot 10^{-19}$ mol/cm³).

Table 2

Cross-linking degree of cured stocks

| Dosage of additive agents, pbw on 100 pbw rubber | Equilibrium degree of swelling <i>s</i> , % | Concentration of the cross-linkings of $n \cdot 10^{-19}$, mol/sm ⁻³ |
|--|---|--|
| Without an agent | 21,8 | 7,87 |
| 0.1 PTFE | 20.7 | 8.36 |
| 0.2 PTFE | 20.3 | 8.42 |
| 0.3 PTFE | 19.4 | 8.44 |
| 0.4 PTFE | 18.9 | 8.46 |
| 0.5 PTFE | 19.0 | 8.42 |
| 0.1 UPTFE | 19.6 | 8.71 |
| 0.2 UPTFE | 18.5 | 8.23 |
| 0.3 UPTFE | 18.3 | 8.31 |
| 0.4 UPTFE | 17.5 | 8.75 |
| 0.5 UPTFE | 16.7 | 9.97 |

The introduction of ultradispersed polytetrafluorethylene in the structure of elastomer compositions also reduces the swelling degree of cured stocks. Equilibrium degree of swelling at a dosage of 0.5 pbw decreases in 1.3 times, and the concentration of cross-links increases in 1.27 times in comparison with a sample not containing the modifying additive agent. Apparently it is connected with the formation of a denser coupling in the result of radical products of thermal fluoroplastic destruction and elastomer matrix macroradicals

interaction that leads to increase of hostile environment resistance.

Mixes on the basis of butadiene-nitrile rubbers are applied to manufacture industrial rubber products used in the conditions of wearing therefore wearing effect determination of fluorine-containing modifying agents of studied rubbers is of practical interest.

Abrasive wear is characterized by spur scratching of a used body's rough surface. The parallel strips coinciding with the direction of sliding are formed on an abrasive surface. The industrial rubber products used in a mode of friction should possess a high wear resistance. One of the ways of rubbers wear decreasing and increasing of their working capacity is rising of abrasion resistance and decreasing of the friction factor.

The determination results of studied rubbers abrasion resistance are given in Table 3.

Table 3
Results of determination of rubbers abrasion resistance

| Dosage of additive agents, pbw on 100 pbw rubber | Abrasion I , mm ³ /J | Abrasion resistance, J/mm ³ |
|--|-----------------------------------|--|
| Without an agent | 0.1190 | 8.40 |
| 0.1 PTFE | 0.0908 | 11.01 |
| 0.2 PTFE | 0.0857 | 11.67 |
| 0.3 PTFE | 0.0828 | 12.07 |
| 0.4 PTFE | 0.0742 | 13.47 |
| 0.5 PTFE | 0.0776 | 12.89 |
| 0.1 UPTFE | 0.0884 | 11.31 |
| 0.2 UPTFE | 0.0834 | 11.99 |
| 0.3 UPTFE | 0.0758 | 13.20 |
| 0.4 UPTFE | 0.0723 | 13.82 |
| 0.5 UPTFE | 0.0706 | 14.16 |

The analysis of the presented data shows that the application of fluoroplastic as a modifying additive agent enables to decrease cured stock abrasion that leads to increase of their wear resistance.

So, the maximum value of resistance to abrasion is obtained at a dosage of 0.4 pbw PTFE. Thus the abrasion decreases in 1.6 times in comparison with not modified samples. It is necessary to note that some increase of rubbers abrasion is observed at a dosage of 0.5 pbw.

The application of ultradispersed polytetrafluorethylene also allows cured stock abrasion decreasing. Thus with increase in a dosage of a modifying additive agent the increase of elastomer compositions abrasive resistance is observed. The greatest value of an abrasive resistance indicator (14.16 J/mm³) is obtained at a dosage of 0.5 pbw.

It seems to be connected with the interaction of a modifying agent's particle with the elastomer

composition components. The formation of the surface layer possessing an increased abrasive resistance [6, 9] is thus possible.

Conclusion. Thus, updating of elastomer compositions on the basis of butadiene-nitrile rubbers with effective cure system by fluorine-organic compounds is an efficient method of higher ready goods technical properties. The complex of characteristics especially important for industrial rubber products is thus improved: the resistance of rubbers to thermal aging and hostile environment, as well as abrasive resistance increases. The rubbers containing ultradispersed polytetrafluorethylene in a dosage of 0.5 pbw on 100 pbw of rubber possess the best complex of technological and technical properties.

References

- Трение и износ плазмохимически модифицированных эластомеров / Э. Ф. Абдрашитов [и др.] // Трение и износ. – 2001. – Т. 22, № 2. – С. 190–196.
- Аверко-Антонович, И. Ю. Методы исследования структуры и свойств полимеров / И. Ю. Аверко-Антонович, Р. Т. Бикмуллин. – Казань: КГТУ, 2002. – 604 с.
- Петрова, Н. Н. Резины на основе пропиленоксидного каучука и политетрафторэтилена / Н. Н. Петрова, В. В. Портнягина // Каучук и резина. – 2007. – № 4. – С. 8–10.
- Бузник В. М. Морфология и строение микронных и наноразмерных порошков политетрафторэтилена, полученных газофазным методом / В. М. Бузник, В. Г. Курявый // Российский химический журнал. – 2008. – Т. LII, № 3. – С. 131–139.
- Металлополимерные нанокompозиты (получение, свойства, применение) / В. М. Бузник [и др.]. – Новосибирск: Изд-во СО РАН, 2005. – 259 с.
- Структура и свойства фторсодержащих нанокompозитов на основе вулканизированных каучуков / А. В. Струк [и др.] // Вес. Нац. акад. навук Беларусі. Сер. фіз-тэх. навук. – 2011. – № 1. – С. 25–31.
- Введение в физику нанокompозиционных машиностроительных материалов: монография / С. В. Авдейчик [и др.]; под науч. ред. В. А. Лиопо, В. А. Струка. – Гродно: ГГАУ, 2009. – 439 с.
- Федюкин Д. Л. Технические и технологические свойства резин / Д. Л. Федюкин, Ф. А. Махлис. – М.: Химия, 1985. – 240 с.
- Фторированные резины с улучшенными триботехническими свойствами / В. Г. Назаров [и др.] // Рос. хим. журн. (Журн. хим. общества им. Менделеева). – 2008. – Т. LII, № 3. – С. 45–55.

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