Elastomeric fire and heat-protective materials containing zirconium dioxide

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Abstract. Elastomeric fire-protective materials are widely used to protect special-propose structure in rocket, aviation and marine equipment. Important parameters of such materials are density and thermal conductivity. The reduction of these indicators while maintaining the rest of the set of materials properties is a complex and multifactorial task. A promising direction of its solution is the use of microspheres. The work shows that it is possible to increase the fire protection efficiency of elastomeric compositions, which contain transition metal oxides, with zirconium dioxide as an example. The effect of the introduction of zirconium dioxide in the form of a microdisperse powder, microspheres, and zirconium-aluminosilicate microfibers on the physical and mechanical, thermophysical, and fire protective properties of elastomeric compositions based on ethylene propylenediene rubber has also been considered.

1. Introduction

Products made of elastomeric compositions are used in rocket, aviation, and marine engineering, including for special purpose structures, which operate at extreme temperatures [1, 2]. Therefore, composite polymeric materials with heat resistance higher than 200 °C, whose products can be operated under extreme conditions for a long time, are of particular interest. The efficiency of elastomeric fire- and heatprotective materials (FHPM) is determined by a complex of endothermic physical and chemical transformations of their components and thermal degradation thereof, as well as by the processes of changing the chemical structure of the material: swelling, foaming, and coking. The combination of physical, chemical, and structural transformations in the material, as well as the introduction of ingredients with low heat and temperature conductivity into the composition of multicomponent FHPMs, ensures the effective performance of the heat protection function [3].

When an intense thermal effect occurs on a protective composite layer, processes of coke formation and structuring begin, which result in the formation of a protective layer with low thermal conductivity [3,4]. In most thermal barrier compositions, inorganic fillers have the function of the elements upon which primary carbon occurs and thereafter coke is precipitated, which is formed by the thermal decomposition of the materials.

However, when operated, a fire and heat protective material endures the exposure to not only elevated temperatures or pressures, but also to a high-speed heat flow, which results in the loss of the top layer of FHPM, thinning of the material itself and, as a result, a decrease in its efficiency.

To eliminate this negative effect, microfiber fillers are used that form a "grid", which increases the erosion resistance of the material. Such fillers include kaolin, basalt, carbon, and other fibers. The introduction thereof into polymers is accompanied with various interactions at the "polymer-filler"
interface, which affect the mechanical, physical, and chemical properties and the thermo-oxidative stability of a composite material [3, 4].

In particular, the use of fibrous materials in manufacturing high-temperature thermal equipment has resulted in energy savings of up to 40%. (in batch furnaces) and up to 25% (in continuous furnaces), a decrease in furnace dimensions due to the reduction of the masonry thickness and that of the furnace lining weight down to 10 times, a decrease in time of starting the operation down to 1.5-2 hours, an increase in the number of thermal cyclings up to 1000-2000, and a reduction of the labor intensity by several times when lining is assembled [8].

Some of the metals, which belong to d-elements, have properties that allow them to be used as protective and wear-resistant coatings, refractory materials for aircraft and rocket engines, components of multilayer coatings of laser mirrors and beam separators [9], for manufacturing refractories, and for increasing a campaign life (the number of meltings between two cold repairs of the lining) in glass and aluminium melting furnaces. Such refractory materials are used in the metallurgical industry for gutters, cups, when steels are continuously spilled, and crucibles for melting rare earth elements. They are also used in some ceramic metal coatings, which have high hardness and resistance to many chemical reagents and withstand short-term heating up to 2750°C [9-15].

As previously shown [16], the introduction of microdispersive zirconium dioxide contributes to an increase in the fire and heat protection efficiency of a material, however, some reduction in the strength of the material occurs. In order to overcome this disadvantage, it is possible to use more promising zirconium dioxide (ZSF) microspheres, which are stabilized with yttrium oxide and have a smaller particle size, and this increases the uniformity of the elastomeric composition and, simultaneously, reduces the density of a material due to the hollow structure of the microspheres. The diameter of the microspheres in the range of 20-100 μm is proportional to the wavelength of thermal infrared radiation and this provides the conditions of its maximum absorption by the microspheres. The wall thickness of the microspheres in the range of 1-10 μm assures the necessary strength of the material, which minimizes damage to the microspheres when a rubber mix is made and vulcanized.

The incorporation of microspheres into a polymer results in the formation of a porous structure. The thickness of the inter pore partition has a great influence on all properties of the material. It consists, essentially, of the wall thicknesses of two adjacent microspheres and a polymer interlayer there between. If the first factor is constant, reducing the thickness of the interlayer of a polymer matrix may reduce the average density of a material and decrease the pore size of the material as the number thereof increases. In addition, the effect of this variation in the structure on the material strength will be minimum, as the structure itself will approach the optimal one.

2. Materials and Methods

The work studied the influence of zirconium microspheres (diameter 5-50 μm, content of ZrO₂ – 20.0-25. 0%) and zirconium-aluminosilicate microfiber (ZSM) (average diameter 3.25 μm, content of ZrO₂ – 14.0-18.0 %) on a complex of physical and mechanical, thermophysical and fire-protective properties of elastomeric fire and heat-protective materials (FHPMs) based on ethylene-propylenediene rubber, which contain 30 pts. wt. of a filler (BS-120) and a sulphuric accelerator-curative combination. The amount of the microspheres varied within 1-10 pts. wt., the microfiber content - 5-15 pts.wt. per 100 pts. wt. of the rubber.

We prepared the rubber compositions by mixing the ingredients in a two-roll open mill at ambient temperature. All of the ingredients were used as received. The ingredients were added step by step into the polymer matrix within 8 to 10 min. The vulcanization kinetics of compositions were followed with MDR 3000 Professional at 160°C. The MDR 3000 Professional was calibrated according to ASTM D2084 standard.

The compounds were compression-molded into square plates with a thickness of about 2.0 mm and vulcanized at 165 °C. Molding was performed at 165 °C under a pressure of 20 MPa. Specimens for tensile testing were dye-cut to dumbbell shapes with a length 20 mm from the rubber plates by a manual cutting press. The thickness of the specimens was measured by a manual gauge five times, and the minimum value was taken to estimate the stress. Tensile measurements were carried out on AG-Xplus (Shimadzu Europa GmbH) with a rate of grip separation of 500±50 mm/min at room temperature.
(23±2 °C). The results of the tensile measurements were averaged over 10–14 specimens dye-cut from two independently vulcanized rubber plates for each composition. The error bars provided are the standard errors.

3. Results and discussion
The influence of ZSM and the microfibers on the morphology of the elastomeric matrix was determined by means of Versa 3D electron scanning microscope. Zirconium-aluminosilicate microfibers were found to spread evenly over the volume of the elastomeric matrix without forming coarse agglomerates.

![Micrograph of material surface, which contains zirconium-aluminosilicate fibers.](image)

The study of the rheometric characteristics (MDR 3000 Professional, ASTM D2084-79) showed that the introduction of ZSF had little or no effect on the minimum and maximum torques compared to the control composition and considerably (by 53-55 %) increased the torque compared to a mix that contains microdisperse zirconium dioxide. At the same time, unlike compositions with aluminosilicate microspheres [17], the vulcanization curves of the compositions with ZSF have no additional peaks characteristic of the two-stage vulcanization.

It is also worth noting that when the content of microspheres increases in excess of 5 pts. wt., an increase in the Payne effect occurs, which appears to be due to a partial aggregation of the ZSF with white soot.

The introduction of microfibers has generally little effect on the vulcanization kinetics of a composition, however, when the fiber content increases above 10 pts. wt., an increase in the Payne effect is observed and this indicates an increase in the filler-filler interaction.

Zirconium microspheres have a smaller size than microdisperse zirconium dioxide, enabling their better distribution over the volume of a composition and, therefore, a greater homogeneity of the system and this affects the strength of the material: compositions, which contain ZSF, are 10-25% stronger than compositions with microdisperse zirconium dioxide and are not inferior to the control mix.

As shown by the data provided (table 1), introduction of the additives tested into rubber mixes makes it possible to maintain the stress-strain properties at the specified level. However, when the content increases more than 10 pts. wt., some reduction in physical and mechanical properties is observed, and this may be due to an increase in the interaction between the zirconium-containing components and the white soot.

| Process additives, parameter | Control | Z5  | Z10 | ZSF5 | ZSF10 | ZSM5 | ZSM10 |
|-----------------------------|---------|-----|-----|------|-------|------|-------|
| Microdisperse ZrO2         | -       | 5   | 10  | -    | -     | -    | -     |
| ZrO2 Microspheres          | -       | -   | -   | 5    | 10    | -    | -     |
| ZrO2 Microfiber            | -       | -   | -   | -    | -     | 5    | 10    |

Vulcanization characteristics of rubber mixes at 165 °C
### Vulcanizate properties (vulcanization 165 °C, 40 min.)

| Parameter | Value             |
|-----------|-------------------|
| $f_p$, MPa | 10.2              |
| $\varepsilon_{be}$, % | 643               |
| $\theta_{res}$, % | 20                |
| $\rho$, kg·m$^{-3}$ | 1060              |

### Variation of vulcanizates properties after aging in air (125 °C, 72 h)

| Parameter | Value             |
|-----------|-------------------|
| $\Delta f_p$, % | -35.1             |
| $\Delta \varepsilon_{rel}$, % | -40.5            |

### Heat-protective and thermophysical properties of vulcanizates

| Parameter | Value             |
|-----------|-------------------|
| $\tau_{T, 100^\circ C}$, s | 200               |
| $CR$, % | 25.09             |
| $V_{lb}$, mm·min$^{-1}$ | 24.12             |

### Properties of vulcanizates for erosion waste

| Parameter | Value             |
|-----------|-------------------|
| $\sigma$, mPa | 37.3              |
| $\omega$, rps | 25                |
| $\Delta m$, % | 46.9              |
| $\tau_{ign}$, s | 20                |
| $\tau_{CS}$, s | 26                |

1. $M_{min}$ and $M_{max}$ – minimum and maximum torques; $\Delta M$ – difference between maximum and minimum torques; $\tau_S$ – induction period; $\tau_{ign}$ – optimal vulcanization time; $R_v$ – curing rate indicator; $\Delta G'$ – Payne effect; $f_p$ – nominal tensile strength; $\varepsilon_{be}$ – breaking elongation; $\theta_{res}$ – residual tension set; $\rho$ – density; $\Delta f_p$, $\Delta \varepsilon_{rel}$ – relative parameter variation after aging; $\tau_{T, 100^\circ C}$ – warmup time of unheated surface of sample to 100 °C; CR – coke residue after pyrolysis 600 °C, 30 min.; $V_{lb}$ – linear burning rate; $\sigma$ – tear strength of coked layer, $\omega$ – rotation speed, $\tau$ – heating time, $\tau_{ign}$, $\tau_{CS}$ – start time of ignition and coke peeling, respectively.

To evaluate the fire and heat resistance of the samples according to the technique developed, the following parameters were determined: the dependence of the temperature of the unheated surface of a sample on the time of exposure to the open flame of a plasmatron, the weight loss of a sample and the linear burning rate. When high temperature heating was applied, a temperature of about 2000 °C was created on a sample surface.

To assess the erosive resistance of the material under high temperature exposure conditions, a sample was placed on a rotating shaft and heated tangentially by a plasmatron. During the test, the start time of the sample ignition and the start time of the coke peeling were recorded. The diameter of a sample after the test was then determined. The burned layer was removed and the thickness of the unburned layer was determined.

The strength characteristics of coke are determined by taking into account the peeling forces, which are realized at the boundary between the coke layer and the undecomposed material at the moment of the coke layer breaking off under the action of the centrifugal forces, when a cylindrical sample rotates at a constant speed as it is heated at high temperature in the flame of the plasmatron. The peeling strength of the coked layer was determined by the formula (1):
where $\omega$ is the angular rate, rps; $R_0$ is the initial radius, mm; $R$ – radius before the boundary of the pyrolysis layer along which peeling occurs, mm; $\rho_c$ is the coke density, kg/m$^3$.

By adjusting the rotation speed of a sample, we can vary the mechanical impact on the sample within a wide range. The more the size of the coke residue is, when centrifugal ablation ($\Delta m$) takes place with the same rotation speed, the higher is the heat and fire-protective efficiency of a material.

The introduction of microspheres slows down the warmup rate of a sample when high temperature tests are carried out (figure 2). Due to additional structuring processes in the charring layer, samples, which contain microspheres, have a longer warmup time of the unheated surface of the sample to 100 °C (35-65 %) and their weight loss and linear burning rate are reduced.

![Figure 2. Dependence of warmup time of unheated surface of sample up to 100 °C on content of microspheres.](image)

As the morphological studies have shown, the resulting coke structure is more uniform and its pore diameter is smaller than that of the control sample, with the average pore diameter in the pre-pyrolysis zone decreasing from 350-420 mcm down to 110-120 mcm (figure 3 and 4).

![Figure 3. Structure of pre-pyrolysis layer of samples after test: a) control sample; b) containing 5 pts. wt. ZSF](image)
The heat-protective efficiency of the additives tested is confirmed by the methods of DTA and TG analyses (Q-1500D derivatograph, heating rate 5 °C/min): when ZSF is introduced, the start temperature of the weight loss increases slightly (figure 5), the coke number increases by 16% and the area of the endothermic peak, which characterizes the proportion of the incoming heat flow spent on the physical and chemical effects, which make it difficult to destroy the material, increases by 61.3%.

Figure 6 demonstrates test samples after testing to determine the erosion resistance under high-speed heat flow conditions. The control sample (figure 6a) is characterized with a large weight loss and a short start time of ignition. The presence of ZrO$_2$ intensifies the processes of coke formation, and the microfiber contributes to the creation of strong coke with low thermal conductivity (figure 6e).
The physical and chemical effects that occur as the high temperature heat flow passes through the cross section of the fire and heat protective material can be illustrated by the outline (figure 7), which was developed under the leadership of Prof. Kablov [18].

The processes, which occur in the coke and mineralized layers are important for the formation of the fire and heat-protective properties. It is these layers, which endure the main high-temperature impact.

Porous carbon-mineral coke, which consists of carbon, silicon oxide, and zinc oxide, is formed in the coke layer by pyrolysis of rubber and other organic components. It should be noted that coke structure is also significantly dependent on the introduction of microspheres: the ZSF enables the formation of microporous coke with less thermal conductivity at high temperatures. This is due to a decrease in radiative heat transfer in the small pores. The addition of microfiber components affects, to a greater extent, the strength of the resulting carbon-mineral coke structure by providing a micro-reinforcement effect.

4. Conclusions

Thus, the studies have shown that the introduction of zirconium dioxide enables an increase in the coke residue by 4-30 % and the heating time of the unheated sample surface up to 100 °C by 5-16 %, and reduces the linear burning rate by 10-40 %. The coke structure, which is thereby formed, is more regular and it has a smaller pore diameter than that of the control sample. However, due to the increase in the heterogeneity of the composition, some decrease in the physical and mechanical properties is
observed (10-30 %), which does not prevent their use. The introduction of microspheres enables the formation of a more regular dense fine-porous coke structure when high-temperature exposure is applied, and this, in turn, contributes to the increased warmup time of the unheated sample surface up to 100 °C and a reduced weight loss and linear burning rate. The presence of microfibers contributes to the creation of a "reinforcing grid," and this, in turn, results in an increased coke number and warmup time of the unheated sample surface up to 100 °C by 6 and 11 %, respectively.

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References
[1] Zaikov G, Kalugina E 2004 Book Heterochain Thermoresistant Polymers (Boston: Utrecht)
[2] Bleuel E, Boehme P 2002 Book of Abstracts, Proceeding of Polyurethanes Expo 2002 (Washington: American Plastics Council) p 234
[3] Mikhailin Yu 2008 Special Polymeric Composite Materials (St. Petersburg: Nauch. Osnovy Tekhnologii)
[4] Lomakin S, Zaikov G 2012 Bull. Kazan Technolog. University 7(15) 71
[5] Bartholmai M, Schartel B 2004 Polym. Adv. Technol. 15(7) 355 DOI: 10.1002/pat.483
[6] Kablov V, Novopol’tseva O 2017 Russ. J. Appl. Chem. 5(90) 797 DOI: 10.1134/S1070427217050214
[7] Kablov V, Novopol’tseva O 2018 Russ. J. Appl. Chem. 7(91) 1160 DOI: 10.1134/S1070427218070145
[8] Tarasov V 2013 Bulletin of MSTU. N.E. Bauman. Ser. "Engineering" 3 120
[9] Monte S 2012 Rubber World 40
[10] Rao T, Hussain I, Lee J, Kumar A, Koo B 2019 Appl. Sci. 9 3464 https://doi.org/10.3390/app9173464
[11] Chaudhary B, Panwar V, Roy T 2019 Bull. 76 511 https://doi.org/10.1007/s00289-018-2381-3
[12] 2015 Journal of Alloys and Compounds 643 S150
[13] Wongmaneerung R 2019 Key Engineering Materials 798 298
https://doi.org/10.4028/www.scientific.net/kem.798.298
[14] Kozulin A, Skripnyak E 2012 Izv. Vyssh. Uchebn. Zaved, Fiz. 7/2(55) 82
[15] Lin Vahabi Q, Vagner C, Cochez M, Ferriol M, Laheurte P 2016 Polymer Degradation and Stability 124 60 https://doi.org/10.1016/j.polymdegradstab.2015.12.004
[16] Kablov V, Novopol’tseva O 2017 Russ. J. Appl. Chem. 3(90) 401-405 DOI: 10.1134/S1070427217030120
[17] Kablov V, Novopol’tseva, O 2017 Russ. J. Appl. Chem. 2(90) 257 DOI: 10.1134/S107042721702015X
[18] Kablov V, Novopol’tseva O 2016 News of Volgograd State Technical University 4(183) 46