Study of the Local and Imported Rubber Products Made from Fluoroelastomer

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Abstract. The paper provides the results of the studies of the domestic and imported fluoroelastomer O-rings for cylinders with antifreeze cooling. It revealed that the imported materials were more efficient as they featured better compressive strain properties since they provided the acceptable sealing ability when subjected to antifreezes at elevated temperatures, as compared to the domestic materials. The different properties are explained by significantly different filler components and fluoroelastomer chemistry. The comparative analysis showed that the domestic O-rings had a higher compression set both in the coolant medium and in air. The high compression set and subsequent loss of the sealing effect can be caused by low quality of the rubber and inadequate formulation of the rubber mixture.

1. Introduction

The development of the construction, automotive, aviation, aerospace, oil, chemical, cable industries and electronics is making new demands on materials: lower environmental pollution, lower cost, lower energy intensity, and higher reliability.

Fluoroelastomers have an excellent resistance to oils, fuels, lubricants, the majority of mineral acids, many alicyclic and aromatic hydrocarbons which act as solvents for other rubbers. They are inert to gasoline, petroleum, chlorinated solvents. As fluoroelastomers can dissolve in some ketones and esters they are used to manufacture sealants and adhesives. Fluoroelastomers are mainly used to manufacture products which should have a high heat resistance during operation and high resistance to aggressive media [1-7].

Today, a key challenge is to increase the resistance of rubbers to hot-air ageing and heat ageing. Fluoroelastomers have an extremely high heat-ageing resistance. Fluoroelastomers have a very high hot-air ageing resistance and can function at temperatures above 200 °C for a long time [8]. In addition to high heat resistance, fluoroelastomers are distinguished by their high weather and ozone resistance, superior chemical and biological inertness (as compared to all other rubbers), good wear and abrasion resistance, adequate dielectric properties, uninflammability, and heat ageing resistance [9].

Today, fluoroelastomers are used for shaft sealing, valve stem seals, seals in engine cylinder heads and filters, diaphragms, fuel pumps, O-rings (cylinders with antifreeze cooling), etc. [6, 10, 11]. An O-ring is a circular ring with a round cross-section. A ring packing prevents an unintended loss of fluid. A material of O-ring is selected according to the operating conditions. First of all, elastomer should be resistant to media within the warranty storage and operation period in the range of medium temperatures, pressures, and other factors that affect a sealing device [3]. In order to ensure leak-tightness of a sealing device, contact stresses should be generated at metal-elastomer interface. It is achieved by deformation
of a rubber O-ring within the specified limits [4]. Under current conditions of import substitution, the relevant objective is to conduct comparative studies of the domestic and imported fluoroelastomer O-rings for cylinders with antifreeze cooling.

2. Materials and methods
The samples of O-rings were studied:
   Sample 1: black, imported,
   Sample 2: beige, domestic.

   The thermal analysis was recorded using thermal gravimetric analysis TG 209 F1. For thermal decomposition, the samples were heated from 30 °C to 600 °C at a rate of 10 °C/min in argon atmosphere according to GOST 29127 [12].

   The resistance of O-rings to coolants was studied using Binder heating chamber at a temperature of 110±5 °C according to GOST 9.030 [13].

   The physical mechanical performance was determined using the LRX Plus material testing machine by Lloyd Instruments according to GOST 270 [14].

3. Results and discussion
Fluoroelastomers are fluorine-containing polymers with a saturated skeleton, which are made by polymerization of fluorinated monomers such as vinylidene fluoride, hexafluoropropylene, and tetrafluoroethylene. As a result, high quality rubber is formed, and it has an exceptional resistance to oils and chemicals at elevated temperatures. Today, this material is mainly used to manufacture O-rings for heavy-duty applications. Fluoroelastomers are mixed with various additives to improve the properties. Fluoroelastomers can recover quickly or have the elastic properties typical of true elastomers, and their mechanical properties are similar to those of general-purpose synthetic rubbers.

   Sealing ability can be influenced by various aspects of formulation, mixing, and curing. In view of this, the first stage involved the comparative studies of the sample compositions.

   There are many material analysis techniques, among them is thermogravimetric analysis. This technique is used to determine the composition [15-17].

   The analysis of Figure 1 and table 1 showed that the sample was made from high molecular weight block copolymer of vinylidene fluoride with hexafluoropropylene (FKM) and filled with carbon black (minimum 22 % wt.), and sample 2 was made from the copolymer of vinylidene fluoride with hexafluoropropylene (SKF-26 [9], domestic) and did not contain carbon black. It has been reported that [8] that the addition of special oxidized carbon black to the fluoroelastomer-based mixture can improve creep resistance.
Figure 1. TGA curves of sample 1 (TG-1, dTG-3), sample 2 (TG-2, dTG-4)

Table 1. TGA results of the samples

| Component name                          | Content (wt. %) | Sample 1 | Sample 2 |
|-----------------------------------------|----------------|----------|----------|
| Low-molecular-weight organic components (plasticizers, softening agents) |                | 1.5-2    | 1.5-2    |
| Vinylidene fluoride                     |                | 8        | 56       |
| Hexafluoropropylene                     |                | 52       |          |
| Carbon black                            |                | 22-25    | -        |
| Inorganic components                    |                | 11-12    | 41-43    |

Therefore, the samples of imported and domestic O-rings are made from high molecular weight block copolymer of vinylidene fluoride with hexafluoropropylene, the key difference of sample 1 of the imported O-ring is carbon black as a filler, which can have a significant influence on the properties of O-rings.

It is known [8, 18-20] that the repeated exposure of rubber products to oils and solvents during the operation can result in swelling and accelerate their ageing. The effect can depend heavily on the type of aggressive medium. In view of this, pH of antifreezes was studied. Fleet Charge and G-energy antifreezes differ in water content (45-50 % wt.), glycol content (42-50 % wt.), as well as in the type of additives, which can have a significant influence on the performance of O-rings.

A chemical damage of materials can result from reactions between rubbers and components of the environment or their absorption by a material. It leads to the swelling of rubber and decrease in its strength. Damage has a greater extent at higher temperature and concentration of corrosive agent. Rubbers absorb various substances to which they are exposed directly, most notably, organic liquids. It can result in swelling that can cause softening of rubber.

The analysis of table 2 showed that the exposure to high temperatures (110 °C for 72 hours) changed pH of the antifreeze medium: pH of G-energy SNF decreased from 8.127 to 7.901. It can be assumed...
that more prolonged exposure can lead to a critical decrease in pH, i.e., it can have a negative influence on the properties of rubbers.

**Table 2. pH of the medium before and after 72-hour exposure at 110 °C**

| Name                | pH before | pH after |
|---------------------|-----------|----------|
| Fleet Charge        | not available | 8.451    |
| G-energy Si-OAT     | 8.202     | 7.994    |
| G-energy SNF        | 8.127     | 7.901    |

The study of the influence of elevated temperatures on the properties of coolants revealed that the exposure to high temperatures (110 °C for 72 hours) changed pH of the coolant medium: pH of G-energy SNF decreased from 8.127 to 7.901. It is illustrative of the formation of acidic structures, and the volume changed in the antifreezes by 2.0-3.5 % for sample 1, and by maximum 3 % for sample 2 (table 3).

**Table 3. Change in the volume of the samples exposed to the antifreezes at 110 °C for 72 hours**

| Medium           | Change in volume (%) |
|------------------|----------------------|
|                  | Sample 1  | Sample 2  |
| Fleet Charge     | 2.4       | 2.7       |
| G-energy Si-OAT  | 3.5       | 1.7       |
| G-energy SNF     | 2.0       | 2.9       |

The residual compression should not be considered as the satisfactory indication of sealing ability of rubber seals. It is better to assess the sealing performance by the results of compressive strain relaxation tests [8].

When an O-ring cannot provide an elastic contact with a sealing face its sealing effect wears away. The main reason for this might be rubber and operating conditions. The elastic properties of a material depend on the composition of rubber and operating temperature, as well as type and duration of deformation, ageing behavior and chemical stability. The sealing effect of an O-ring depends on low compression set. The compression set defines the elastic behavior under operating conditions and during the service life of a sealing. In view of this, the compression set in various media was studied, and the compressive strain relaxation was assessed. The measurements were conducted 2 hours and 24 hours after deformation relief.

The comparative analysis of tables 4 and 5 showed that sample 2 had a high compression set both in the coolant medium and in air. Thus, it is equal to 34-36 % in the antifreezes at 110 °C, and 56 % in air at 200 °C, sample 1 features better characteristics both in antifreezes (a compressive set of 19-20 %) and in air at 200 °C (39 %). Hence, sample 2 is inferior in this property to sample 1.

**Table 4. Relative compression set with 30 % compression in different media at 110 °C for 72 hours**

| Sample  | Relative compression set after being held at the room temperature (%) |
|---------|---------------------------------------------------------------------|
|         | Fleet Charge | G-energy Si-OAT |
| Sample 1| 2 hours      | 24 hours       | 2 hours | 24 hours |
| 25      | 26           | 19             |
| Sample 2| 51           | 36             | 46      | 34       |
Table 5. Relative compression set with 30 % compression in air at 200 °С for 72 hours

| Sample  | Relative compression set after being held at the room temperature (%) |
|---------|---------------------------------------------------------------|
|         | 2 hours | 24 hours |
| Sample 1 | 42      | 39       |
| Sample 2 | 65      | 56       |

The high compression set and subsequent loss of the sealing effect can be caused by low quality of the rubber and inadequate formulation of the rubber mixture. The fluoroelastomers by different manufacturers have notably different filler components and fluoroelastomer chemistry. Lower elastic properties can be explained by the loss of groups of cross links between the chains of rubber or the formation of new groups (curing).

Therefore, the compressive strain tests showed that sample 1 (imported O-ring) had higher properties than sample 2 (domestic O-ring) both in air and in the antifreezes at elevated temperatures. Sample 1 (imported O-ring) has the lowest relative compression set with 30 % compression in air at 200 °С (39 %), sample 2 (domestic O-ring) is inferior in this property (56 %).

4. Conclusions
The studies of the domestic and imported fluoroelastomer O-rings showed that the imported O-rings for cylinders with antifreeze cooling were more efficient.

The comparative analysis showed that the domestic and imported fluoroelastomer O-rings had notably different filler components and fluoroelastomer chemistry.

The study of the influence of elevated temperatures on the properties of coolants revealed that the exposure to high temperatures (110 °С for 72 hours) changed pH of the coolant medium: pH of G-energy SNF decreased from 8.127 to 7.901, which was illustrative of the formation of acidic structures.

The comparative analysis showed that the domestic O-rings had a higher compression set both in the coolant medium and in air. Thus, it is equal to 34-36 % in the antifreezes at 110 °C, and 56 % in air at 200 °C. The high compression set and subsequent loss of the sealing effect can be caused by low quality of the rubber and inadequate formulation of the rubber mixture.

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