Effect of the acrylonitrile content in nitrile-butadiene rubber on the relative residual deformation of vulcanizate

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Abstract. The paper presents the results of a study of rubbers based on butadiene-nitrile rubbers (NBR) grades BNKS-40 and BNKS-18. The influence of the content of acrylonitrile (NAC) on the rheological and physico-mechanical properties of vulcanizates has been evaluated. It is shown that the content of NAC in the NBR composition significantly affects the relative residual compression deformation of the vulcanizate both under normal conditions and at elevated temperatures. The dependencies revealed in the work make it possible to make the correct choice of the rubber grade in the development of rubber resistant to compression deformation.

1. Introduction
Modern technology cannot do without rubber-metal products, while they play a very important role in the composition of machines, often determining their performance.
When developing rubber for rubber-metal products, it is necessary to take into account both the conditions of their operation and the type of deformation that rubber undergoes during the operation of these products.
The selection of indicators responsible for the performance of products is usually the most difficult part of the task. For unstressed rubbers, such indicators can be the relative elongation, strength, modulus of elasticity, for stressed rubbers - permanent deformation [1].
Since the geometry of rubber-metal products must remain practically constant throughout the entire service life, the indicator "relative residual compression deformation" becomes one of the most important for rubber, characterizing its ability to maintain elastic properties in the compressed state under specified conditions, and the lower the value of this indicator, the more preferable.
In addition, product specifications often include requirements for this indicator.
It is possible to influence certain properties of rubber by various prescription methods: the introduction of a certain vulcanizing agent, a change in the type and content of fillers and plasticizers, the use of various antioxidants, etc. However, the correct choice of rubbers is half the success in the development of rubber with the required properties, and they are also largely affect the residual compression deformation [2].
The content of acrylonitrile NAC is one of the main criteria for the characteristics of each type of NBR and since the branded range of NBR rubbers is presented in a large assortment, namely with low (17-20 %) medium (27-30 %) high (36-40 %) by the content of acrylonitrile, then when choosing a NBR brand, the question arises - which rubber is preferable to use in order to ensure the required values of the relative residual compression deformation [3, 4].
2. Setting goals
The goal is to develop rubber for rubber-metal products resistant to compressive stress, operated in aggressive environments (oil, alternating temperatures from -5 to +50 °C) and providing a high bond strength with metal, which will avoid delamination from metal reinforcement during static compression under load.

Based on the requirements for operating conditions, namely oil-petrol resistance, it is preferable to use NBR.

In this regard, the following tasks are set in the work:
– to investigate the rheological and physical-mechanical properties of new rubber compositions based on NBR with different NAC content, providing resistance to compressive stress;
– to make a choice of a brand of rubber for use in the development of a rubber recipe for rubber-metal products resistant to compression stress.

3. Objects and research methods
It is known that rubbers based on nitrile butadiene rubber (NBR) are known to be resistant to aggressive media and have a high ability to attach to metal.

Therefore, rubbers based on butadiene-nitrile rubbers of grades BNKS-40 (rubber R-1) and BNKS-18 (rubber R-2) were selected as the objects of study, and the effect of the content of NAC on the relative residual deformation of rubber compression was evaluated.

The characteristics of the rubbers used are presented in table 1.

| Indicator name                      | BNKS-40 | BNKS-18 |
|-------------------------------------|---------|---------|
| Density at 20 °C, g/cm³             | 50-60   | 0,945   |
| Mooney viscosity, 100 °C            | 55      | 40-50   |
| Acrylonitrile content, %            | 36-40   | 17-20   |
| Content of double bonds, %          | 20      | 27      |

The properties of rubber as a structural material are provided not only by the brand of rubber, but also by a number of ingredients (vulcanizing agents, fillers, plasticizers, antioxidants, etc.) in their composition.

For vulcanization of butadiene-nitrile rubbers, a sulfur – containing vulcanizing system (dithiodimorpholine-a sulfur donor) and a dual system of high-activity accelerators (vulcacite CZ/EG-C and vulcacite thiuram/C) were selected.

Stearic acid and zinc oxide were used to activate the vulcanizing group.

As a filler, a combination of medium-active (N550) and high-active (N220) grades of carbon black is used.

Among the plasticizers, dibutylsebacinate is preferred, since it combines well with polar rubbers.

To ensure the resistance of rubber to various types of aging, a combination of vulcanox 4010 NA/ LG and acetonanil H is used, which are also effective anti-fatigue agents, antioxidants and anti-ozonates.

To ensure the induction period during the processing of the rubber mixture, Santogard PVI was introduced [5, 6].

The optimal content of the ingredients is pre-selected.

Rubber mixtures were made in a laboratory rubber mixer 4.5 / 20-140 (stage 1) and on laboratory rollers 320 160/160 (stage 2).

The samples were vulcanized at a temperature of 153 °C for 20 minutes.

Standard test methods were used to determine the properties of rubber compounds and vulcanizates [7-9].
4. Experimental results

The results of the tests are presented in Tables 2, 3 and in Figures 1, 2.

| Indicator name                                                                 | Values         | rubber P-1 (BNKS-40) | rubber R-2 (BNKS-18) |
|--------------------------------------------------------------------------------|----------------|-----------------------|-----------------------|
| **Technological properties**                                                   |                |                       |                       |
| Time before the start of scorching at 130 °C, min                             |                | 21.0                  | 19.7                  |
| **Vulcanization characteristics (rheological properties)**                    |                |                       |                       |
| Maximum torque, dNm (MN)                                                      | 11.17          | 12.50                 |
| Minimum torque, da.Nm (ML)                                                    | 0.82           | 1.30                  |
| Time of onset of vulcanization, ts1, min                                      | 6.44           | 5.56                  |
| Time to reach 90 % cure rate, t90, min                                        | 14.76          | 12.44                 |
| Vulcanization rate, Rh, dNm/s                                                  | 2.32           | 2.22                  |

**Figure 1.** Vulcanization characteristics of rubber compounds R-1 and R-2

Analysis of the test results presented in Table 2 showed that the resistance to premature vulcanization of the studied rubber compounds is practically at the same level and provides sufficient time for safe processing. According to the vulcanization characteristics, one can judge the kinetics of vulcanization of rubber compounds. As can be seen from the presented data, rubbers have the same vulcanization rate. The time to start vulcanization and the time to reach 90 % of vulcanization is shorter for rubber based on BNKS-18 than for rubber based on BNKS-40.
Table 3. Results of physical and mechanical tests of rubber mixtures.

| Indicator name                                           | Values                                      |
|----------------------------------------------------------|---------------------------------------------|
|                                                           | rubber P-1 (BNKS-40)                       | rubber P-2 (BNKS-18)                       |
| Physico-mechanical properties                            |                                             |                                            |
| Conditional stress at 300% elongation, MPa               | 7.67                                        | 8.82                                       |
| Conditional tensile strength, MPa                       | 16.32                                       | 13.99                                      |
| Elongation at break, %                                   | 530                                         | 430                                        |
| Relative residual deformation after rupture, %           | 14                                          | 2                                          |
| Hardness, units Shore A                                  | 56                                          | 57                                         |
| Relative residual compression deformation, %             |                                             |                                            |
| – at a temperature of 70 °C for 24 hours;                | 25                                          | 17                                         |
| – at a temperature of 23 °C for 24 hours                 | 14                                          | 8                                          |

Figure 2. Physical and mechanical properties of rubbers R-1 and R-2

Analysis of the test results showed that the physical and mechanical properties are practically at the same level, regardless of the brand of rubber (differences within the tolerance). However, there are differences in the following indicators:

– relative residual compression deformation at a temperature of 70 °C for 24 hours - decreased from 25 % (rubber R-1 (BNKS-40)) to 17 % (rubber R-2 (BNKS-18));
– relative residual compression deformation at a temperature of 23 °C for 24 hours - decreased from 14 % (rubber R-1 (BNKS-40)) to 8 % (rubber R-2 (BNKS-18));
– relative residual deformation after rupture - decreased from 14 % (rubber R-1 (BNKS-40)) to 2 % (rubber R-2 (BNKS-18)).

Thus, to obtain rubbers with low residual compression deformation, it is advisable to use BNKS rubber with an acrylonitrile content of 18%.

5. Conclusion

The influence of the content of acrylonitrile in butadiene-nitrile rubber on the relative residual compression deformation of the vulcanizate was revealed.

It is shown that with a decrease in the content of acrylonitrile, the relative residual compression deformation by 32-43 %, depending on the test conditions.
It is proposed to choose grades of nitrile butadiene rubber with a reduced acrylonitrile content to reduce the residual compression deformation of the vulcanizate.

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