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V. V. Myadelets¹, A. V. Kasperovich¹, A. G. Mozyrev²¹Belarusian State Technological University²Tymen State Oil and Gas University**INVESTIGATION OF RELAXATION PROCESS IN ELASTOMERS
FILLED WITH GROUND VULCANIZATE**

In the paper, the relaxation processes in the elastomeric compositions based on nitrile rubber and filled with ground vulcanizate are studied. The ground vulcanizate is obtained from waste products of molded rubber products. The particle size is 0.63–1.00 mm. The main elastic and stress-strain properties of elastomeric compositions under research are determined.

The dependence of the properties on the ground vulcanizate dosage is considered. It is shown that the growth of ground vulcanizate dosage increases the viscosity of the rubber compounds. At the same time the stress relaxation rate was practically not changed. The processes of compression and tension stress relaxation in vulcanizates are studied. It is revealed that the nature of the process of physical relaxation does not change with increasing the dosage of the ground vulcanizate. There is the growth of the modulus with the increasing of the filler dosage. It is determined that the degree of stress relaxation in tensile strain is practically independent on the dosage of the filler and it has an extreme character for the compressed samples.

It is shown that the use of ground vulcanizate as a filler for elastomeric compositions based on NBR can slow processes of the chemical stress relaxation in the elastomeric matrix, as well as it can improve the physical and mechanical properties of vulcanizates. The results of studies suggest that ground vulcanizate can be used as a filler for sealing rubber.

Key words: butadiene-nitrile rubber, ground vulcanizate elastomer composition, filler, viscosity, relaxation, relaxation ratio, tensile strength, residual strain.

Introduction. Relaxation processes in elastomeric materials are essential; they determine the flow of physical and chemical processes in the material. In elastomers they determine their viscoelastic and strength properties and are associated with various forms of molecular mobility.

The course of these processes will be influenced by the nature and strength of the structural units' interaction in the elastomeric composition. As structural elements in this case can be segments of macromolecules, macromolecules in general, supramolecular structures, filler particles etc.

In presence of a filler the relaxation processes in elastomers will be complicated by stress relaxation at polymer – filler interfaces, and rearrangement of the filler particles [1].

Today as rubber fillers substances of different nature and origin are used: carbon black, silica, chalk, lignin and others. The filler addition to rubber mixtures can be carried out to improve the performance properties of vulcanizates, facilitate rubber mixture processing or reduce the rubber compounds cost [2].

From the standpoint of rational use of natural resources and environmental protection perspective elastomeric compositions' filler is ground vulcanizate – dispersed rubber powder, which is prepared in various ways from the production vulcanized waste and worked out rubber products.

Application of grinded vulcanizate can not only lower the cost of rubber compounds, but also retain the valuable properties of the elastomeric

materials. Rubber stress relaxation consists of primary, mainly due to reversible physical relaxation, i.e. to movement of chain segments, and the secondary of irreversible chemical relaxation, which is the result of a chemical reaction with oxygen and mechanical process of bond jitter breaking under stress.

Stress relaxation leads to irreversible permanent deformation which does not disappear after the load removal. It indicates the reduce of rubbery recoverability defining thickening ability of rubber. Relaxation phenomena may be due to the mobility of kinetic units larger than segments, such macromolecules or their parts including tens of segments "submolecule". With their motion range rheological properties are associated and it determines the viscous flow processes [1].

Main part. The aim of this study was to determine the impact of ground vulcanizate (GV) on the relaxation properties of elastomeric compositions on nitrile rubber (NBR). Vulcanizates based on this rubber have increased oil, benzo resistance, so NBR are widely used for the manufacture of hoses, gaskets, antistatic coatings for fuel equipment, seals, conveyor belts, covers and rolls etc. [3]. Elastomeric compositions based on NBR are widely used for the manufacture of various seals, so it was of interest to investigate the processes of physical and chemical relaxation, because it is more consistent with the actual operational environment. As test objects were used elastomer compositions based on rubber – BNKS 18A, which, as

a filler, contained ground vulcanizate with the particle size of 0.63–1.00 mm. BPI was prepared by grinding on a waste product mill (fin) of mechanical rubber products, which were made of rubber mixtures based on NBR, filled with unfilled elastomer composition, shown in Table 1.

Table 1
Formulation of unfilled elastomeric composition

Ingredient	Dosage, pts. wt
NBR brand BNKS-18A	100.0
Zinc oxide	3.0
Sulfur	1.5
Stearic acid	1.0
Accelerator TBBS	0.7
<i>Total</i>	106.2

The pulverized vulcanizate at dosages of 10, 20, 30, 50, 100, 150, 200 pts. wt was introduced into composition of the given content. The vulcanization was carried out in samples within the time at the optimum vulcanization at 153°C.

Relaxation processes may occur not only at the stage of the product finished use, but also when processing of the rubber composition. Mooney viscosity is a comprehensive measure of the viscoelastic properties of the uncured elastomer composition.

This indicator has been widely used to assess the rheological properties of the rubber compounds. It should be noted that the deformation of the polymer systems in the fluid state leads to changes in their internal structure, which is accompanied by the development of viscosity anomalies, high elastic deformations, normal stresses [4].

All this is a consequence of changes in the relaxation properties of the system under the influence of external loads. To facilitate steady flow the most “long-living”, i.e. slowly relaxing, structure elements, constraining achievement of steady state flow regime should be subjected to destruction [4].

With mechanical treatment of elastomeric composition, for example during the processing, deformation energy is accumulated, and it makes the process implementation more difficult – increases energy consumption, leads to blanks’ shrinkage etc. In this regard, studies were conducted according to the stress relaxation of unvulcanized elastomeric compositions filled with shredded vulcanizate.

Test of stress relaxation in the elastomeric composition is carried out with viscometer MV2000 produced by the company Alpha Technologies, immediately after completion of the viscosity measurement. Thus, after the test of the rubber composition sample (1 min preheating, 4 min test) the stress relaxation data were recorded within

1 min before the end of the test. The total test time was 6 min. Mathematically, this fall by a power law is described in the equation [5, 6]:

$$M = k \cdot t^{-\alpha},$$

wherein M is the amount in the torque, conv. u. Mooney; k is the amount of torque in the first second after the rotor stopping, conv. u. Mooney; t is time, s; α is relaxation rate (slope of the relaxation).

Results of the rheological properties’ study of the uncured elastomeric compositions are given in Table 2.

Table 2
Results of the study of the rheological properties of the elastomeric compositions

GV dosage, pts. wt	Mooney viscosity ML (1 + 4), conv. u.	α	k , conv. u. Mooney
0	66.00	-0.330	38.2
10	70.26	-0.337	40.1
20	74.52	-0.344	42.0
30	78.78	-0.351	43.9
50	87.30	-0.365	47.8
100	102.5	-0.356	56.8
150	118.9	-0.335	66.4
200	128.8	-0.330	72.0

The results show that increasing the content of pulverized vulcanizate results in an increase in the Mooney viscosity (ML (1 + 4)) in comparison with the unfilled composition to 19.4% at 30 pts. wt GV, 55.3 to 100 wt %, and 95.2% for 200 pts. wt GV. The dependence of parameter k on the number of pulverized vulcanizate has the same character. It should be noted that the dependence of the relaxation processes rate in the investigated uncured compositions of the GV dosage is extreme.

So, at 20 phr GV it increases by 4.2% compared to unfilled composition at a dosage of 100 pts. wt – by 10.6%, and at 200 pts. wt – it is equal to α for the elastomeric composition without filler.

Thus, by increasing the dosage of pulverized vulcanizate only viscous component of the Mooney viscosity index, which conforms to the Newton law, and the elastic component, which is characterized by the relaxation rate, takes the lowest values at doses of 30–100 pts. wt, i. e. GV introduction allows to reduce deformation energy accumulation in comparison with the unfilled elastomeric composition.

Elastic-strength indicators of vulcanizates were determined on a tensile testing machine Tensometer T 2020 DC by the company Alpha Technologies in accordance with GOST 270–75. The test results are shown in Table 3.

Table 3
**Basic elastic-strength characteristics
of investigated elastomeric compositions**

GV dosage, pts. wt	Relative tensile strength, MPa	Elongation at break, %
0	1.42	413
10	1.56	396
20	1.93	369
30	2.13	332
50	2.61	278
100	3.07	247
150	3.05	208
200	3.12	204

The results show that with increasing dosage of the pulverized vulcanizate there is an increase in relative tensile strength. Thus, at a dosage of 50 pts. wt the increase in strength is 83.8%, at 200 pts. wt – 119.7% compared with unfilled elastomeric composition. It should be noted that at increasing of the GV content more than 100 pts. wt the index of relative tensile strength doesn't change and hardly varies in the range 3.05–3.12 MPa.

Elongation at break (Table 3) reduces in comparison with the unfilled elastomeric composition. Thus, with the GV content of 30 pts. wt the decrease in this indicator is 19.6% towards vulcanizate without GV at 100 pts. wt – 40.2%, and at 200 pts. wt – 50.6%. Perhaps this is due to re-

striction of molecular mobility and increase of mechanical losses during deformation owing to the filler introduction. The characteristics of vulcanizates' properties based on NBR led to their widespread use for the manufacture of various seals. The permanent deformation mode is the most preferred for seal operation. When operating in this mode a continuous process flows to reduce the stress to its equilibrium value – stress relaxation. In this regard, studies were conducted to determine the effect of pulverized vulcanizate on the process of physical stress relaxation at tensile strain and compressive strain. Physical tensile stress relaxation was examined with tensometer at a relatively – samples' deformation $\varepsilon_t = 100\%$, the sample stretching rate was 500 mm/min, the observation length – 30 min. Stress versus time is shown in Fig. 1.

The graphic dependences of stress relaxation in tension show that the increase of ground vulcanizate does not change the nature of relaxation processes. It should be noted that increasing of GV dosage leads to the increase of investigated vulcanizates' modules. Physical compressive stress relaxation was examined at relative samples' deformation $\varepsilon_{\text{comp}} = 25\%$, the sample compression rate was 500 mm/min, the observation length – 30 min. Dependence of compressive stress on the time is shown in Fig. 2.

It reveals that the dependence of the compressive stress on time does not vary with increasing of filling degree of the elastomeric composition GV, and is accompanied by modules increase.

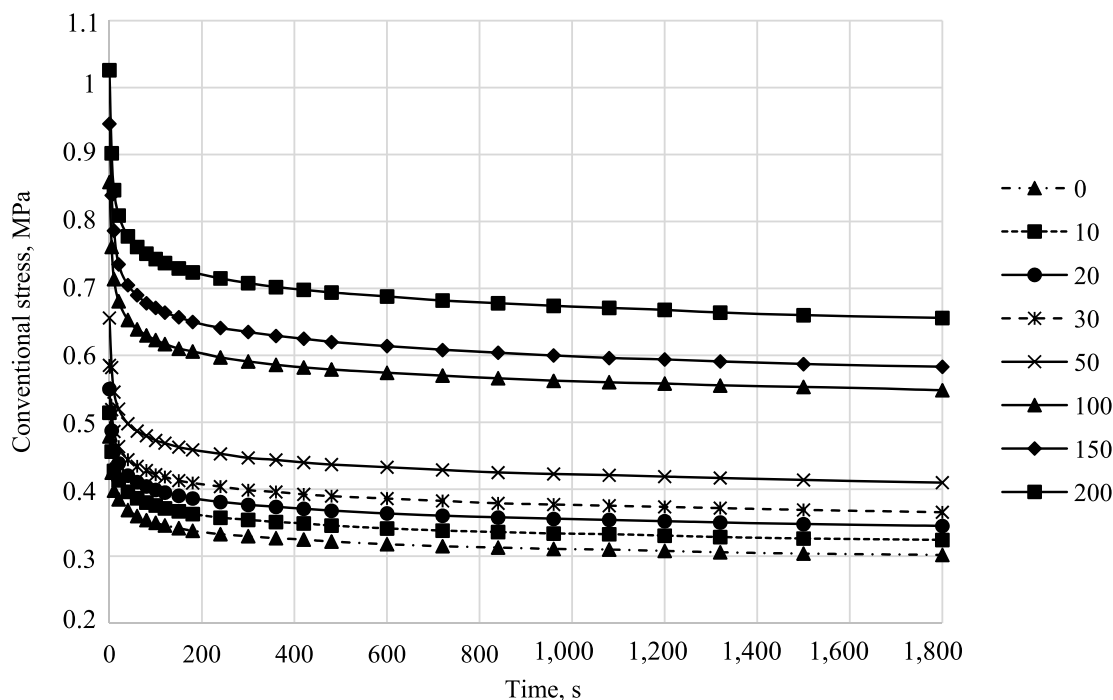


Fig. 1. Curves of samples' physical relaxation of investigated tensile compositions

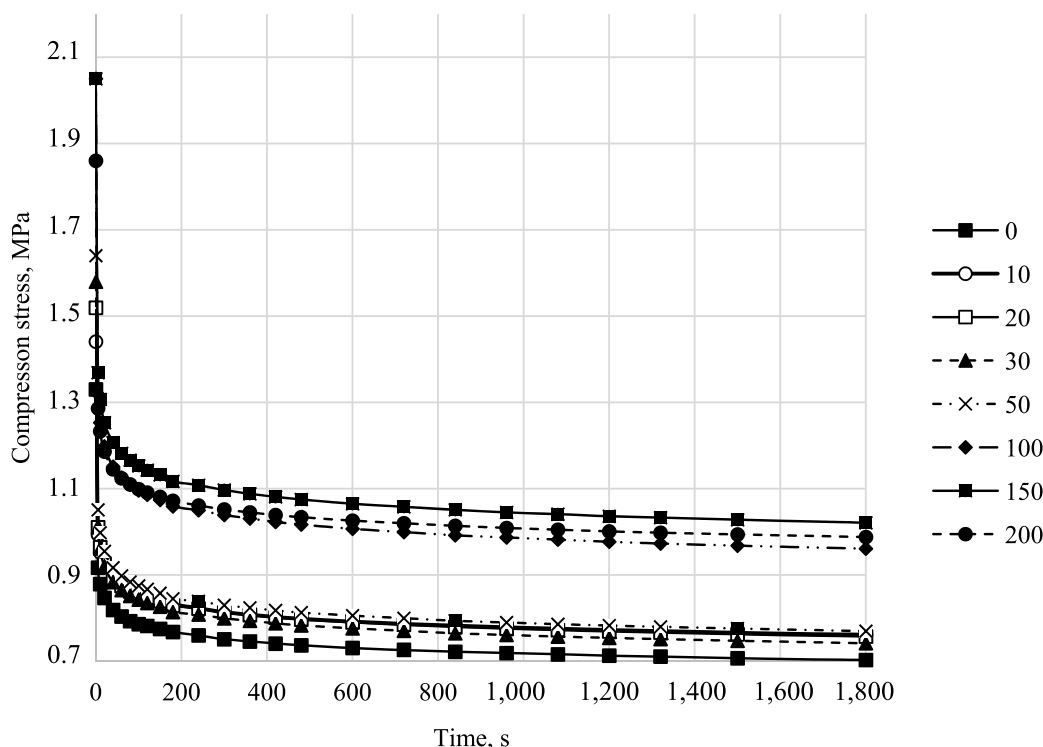


Fig. 2. Physical relaxation curves of investigated elastomeric compositions' samples comprising BPI in various doses (indicated to the right of the chart) at compressive strain (25%)

For quantitative evaluation of physical relaxation process it was determined the degree of stress relaxation. The calculation was made by the formula

$$R_{\sigma}^A = \left(1 - \frac{\sigma_{30}^A}{\sigma_0^A} \right) \cdot 100,$$

wherein σ_0^A and σ_{30}^A mean the compressive stress in the sample at the beginning and at 30 min of the test, respectively, MPa.

Calculation results of the stress relaxation degree are shown in Table 4.

Table 4

The stress relaxation degree in the samples of investigated elastomeric compositions

GV dosage, pts. wt	The stress relaxation degree R_{σ}^A , %	
	At tensile $\varepsilon_t = 100\%$	At compression $\varepsilon_{comp} = 25\%$
0	36.9	47.1
10	37.0	47.1
20	37.2	50.1
30	37.5	53.0
50	37.5	53.1
100	36.2	53.3
150	38.4	50.2
200	36.1	46.9

From these data it is evident that the degree of stress relaxation at tensile is practically independ-

ent of ground vulcanizate dosage and is in the range of 36.9–38.4%. At compressive deformation the dependence R_{σ}^A on the dosage GV has the extreme nature – the highest values R_{σ}^A are observed for samples containing 30, 50 and 100 pts. wt GV.

It can be assumed that at these dosages the compressive strain application leads to a deformation of filler particles which have elastic properties. The increase of GV amount over 100 pts. wt leads to decrease of relaxation degree, which may be due to increase of defect amount in the structure of the elastomeric matrix, which causes deterioration of deformation. An additional feature of the stress relaxation is the static compressive modulus, which is calculated by the formula

$$E_{comp}^A = \frac{\sigma_0^A}{\varepsilon_{comp}},$$

wherein σ_0^A is a compressive stress in the sample after exposure for 30 min, MPa. The dependence of the static modulus in compression on the ground vulcanizate dosage is shown in Fig. 3.

From the above it is obvious, that the increasing of GV dose leads to an increase of the static modulus values at index compression (Fig. 3). It indicates a reinforcing effect of ground vulcanizate as a filler. It should be noted that at the dosages of 100 pts. wt and more this figure varies slightly and is in the range of 3.84–4.08 MPa.

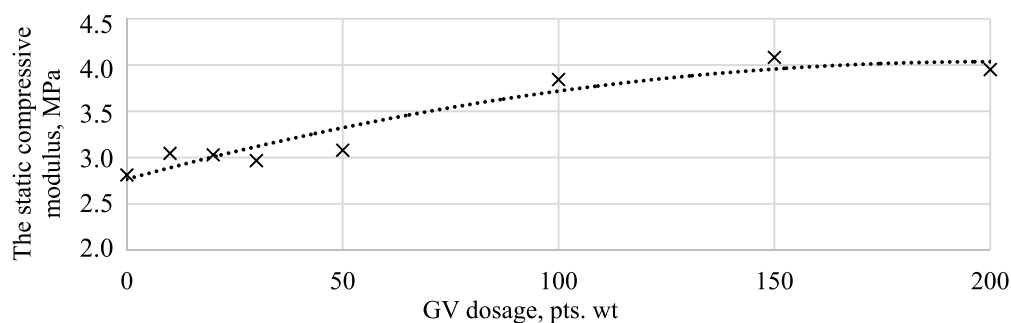


Fig. 3. The dependence of the static modulus in compression ($\epsilon_{\text{comp}} = 25\%$) on the crushed vulcanizate dosage

Chemical stress relaxation was evaluated by the change in the accumulation of residual deformations during thermooxidizing ageing. Tests were conducted at temperature -100°C and a relative compressive strain of 25% within 24 hours. The indicator dependence of the relative compression set (CS) on the dosage of ground vulcanizate is shown in Fig. 4.

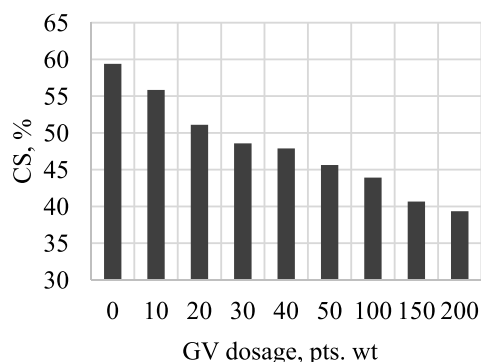


Fig. 4. The dependence of the relative compression set on dosage of ground vulcanizate

With increasing of GV dosage it is observed a CS decrease. Compared with unfilled vulcanizate at GV content of 30 pts. wt CS reduces by 18.2% and 100 pts. wt – 26.1%; at 200 pts. wt – 33.8%. It can be assumed that the GV introduction in the elastomeric compositions causes troubles for implementation of chemical relaxation processes, and therefore contributes to a more complete sample recovery after the load removal, which is confirmed by the data on indicators CS.

Conclusion. Thus, it was found that increasing of the ground vulcanizate dosage causes the increase of Mooney viscosity indicator of unvulcanized elastomeric compositions. The relaxation rate is minimum at dosages of GV 30–100 pts. wt.

It is shown that by increasing the GV content more than 100 pts. wt vulcanizate tensile strength remains practically constant and is in the range of 3.05–3.12 MPa. Relative elongation at break is reduced in comparison with the unfilled elastomeric composition with an increase of the BPI amount in the composition.

The results demonstrated that changing the pulverized vulcanizate dosage does not influence the nature of the physical stress relaxation curves both in tensile deformation and compression. It is established that values of the moduli of the investigated vulcanizates increase with the GV dosage rise.

It is shown that the degree of stress relaxation in tension practically doesn't depend on the crushed vulcanized dosage and is in the range of 36.9–38.4%, but at compressive strain this dependence is not linear with the maximum at BPI content equal to 30, 50 and 100 pts. wt. Perhaps this is due to the elastic properties of BPI that occur during compression of the sample. It was revealed that at GV doses of 100 pts. wt and more a static compressive modulus varies little and is in the range of 3.84–4.08 MPa.

The paper says that with increasing GV dosages, there is a decrease in the CS content at GV equal to 30 pts. wt by 18.2%, when 100 pts. wt by 26.1%; at 200 pts. wt by 33.8% as compared to the unfilled vulcanizate. This allows suggesting retardation of chemical relaxation in the elastomeric matrix.

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