

Received: 28.04.2022

Revised: 30.05.2022

Accepted: 24.06.2022

DOI: 10.17804/2410-9908.2022.3.006-012

INVESTIGATION OF BUTADIENE-ELASTOMER-BASED HIGH MODULUS MATERIALS REINFORCED BY BASALT, GLASS, AND CARBON FABRICS

M. M. Kopyrin^{1, a), *}, A. E. Markov^{1, b)}, A. A. Dyakonov^{1, 2, c)}, A. G. Tuisov^{1, d)},
A. A. Okhlopkova^{2, e)}, A. K. Kychkin^{3, f)}, and N. N. Lazareva^{2, g)}

¹Federal Research Center YaSC SB RAS, 2 Petrovskogo St., Yakutsk, 677000, Russian Federation

²North-Eastern Federal University, 58 Belinskogo St., Yakutsk, 677029, Russian Federation

³V. P. Laronov Institute of Physical-Technical Problems of the North, SB RAS,
1 Oktyabrskaya St., 677980, Yakutsk, Russian Federation

- a)  <https://orcid.org/0000-0002-6018-6391>  mkopyrin91@gmail.com;
b)  <https://orcid.org/0000-0001-6853-6758>  aital.markov@gmail.com;
c)  <https://orcid.org/0000-0002-6959-368X>  afonya71185@mail.ru;
d)  <https://orcid.org/0000-0002-6819-1937>  tagg@rambler.ru;
e)  <https://orcid.org/0000-0003-0691-7066>  okhlopkova@yandex.ru;
f)  <https://orcid.org/0000-0002-5276-5713>  kychkinplasma@mail.ru;
g)  <https://orcid.org/0000-0001-5090-0793>  lazareva-nadia92@mail.ru

*Corresponding author. E-mail: mkopyrin91@gmail.com

Address for correspondence: Office 20, Avtodorozhnaya St., Yakutsk, 5677021, Russian Federation

Tel.: +7 984 101 19 12

A relevant task in improving the properties of elastomers is to increase their strength and stiffness, which affect the reliability and durability of rubber products. The paper presents a technology for manufacturing high-modulus materials based on SKD-V butadiene rubber and reinforcing layers of fabrics from basalt, glass, and carbon fibers. The results of studying elastic strength properties reveal a significant increase in the ultimate strength of reinforced samples in comparison with an unmodified elastomer. The increase in tensile strength varies from 1.7 to 2.8 times. The addition of reinforcing layers reduced the elongation value by 25 to 47 times compared to rubber without reinforcement. High tensile strength and low elongation increase shear resistance. The wear resistance testing of elastomers coated with reinforcing fabrics shows a decrease in abrasion resistance reduced by a factor of 5.8. Abrasion wear and interaction between the reinforcing filler and the polymer are studied by electron microscopy. The study of the microstructure shows a weak contact between the fiber and the elastomeric matrix. Lack of contact during the abrasion process causes destruction of the fibers on the abrasive surface and their further separation. Due to the combination of high tensile strength and low elongation, the reinforced materials obtain high modulus properties combined with lateral mobility.

Keywords: elastomer, basalt fiber, carbon fiber, glass fiber, high modulus material, microstructure.

1. Introduction

In connection with the intensive development of various industries, the task is to search for and create new polymer composite materials (PCM) that meet technical requirements and have high performance. Polymeric materials have a number of advantages and a wide range of applications. The potential for improvement is almost limitless due to the possibility of modifying them by introducing fillers into the volume, applying coatings, joining with other materials, or reinforcing with

various types of fibers and fabrics [1, 2]. One of the areas of polymer materials science is development of high-modulus PCMs based on a combination of elastomers and reinforcing fabrics.

When developing composites based on elastomers, one must consider the possibility of their operation at low negative ambient temperatures. Winter temperature in some regions can drop below $-40\text{ }^{\circ}\text{C}$, sometimes even below $-50\text{ }^{\circ}\text{C}$, resulting in the failure of rubber products. To improve the reliability of products operating in these conditions, it is necessary to use materials with high frost resistance. Rubber is the main ingredient of the rubber compound responsible for the ability to operate elastomers at low temperatures [3]. It is known [4] that elastomers based on siloxane, butadiene, and isoprene rubbers have a high frost resistance. To create high-modulus frost-resistant PCMs, reinforcing basalt, glass, and carbon fabrics can be used, which retain the stability of properties over a wide temperature range [5, 6, 7, 8]. The advantage of reinforcing fabrics is their physical and mechanical properties; namely, the tensile strength of basalt fiber varies from 4.8 GPa and its elastic modulus is 89 GPa [9], the strength of glass fiber ranges from 1.5 to 5.0 GPa and its elastic modulus ranges from 50 to 90 GPa [10], the strength of carbon fiber is as high as 6–7 GPa and its elastic modulus reaches 600 GPa [11]. Another advantage of these fibers is their chemical resistance. Thus, basalt fiber forms a protective film on the surface due to partial dissolution of the fiber [12]; carbon fiber is chemically inert under normal conditions and in the absence of catalysts [13, 14]; when dissolving, glass fiber adsorbs water and an aggressive medium, with simultaneously slowly dissolving oxide components turning into highly porous silica [15]. The combination of a frost-resistant elastomer with high-modulus fibers will make it possible to obtain a PCM with the properties of two different materials.

The purpose of this research is to study the physical and mechanical properties and structure of high-modulus elastomers based on frost-resistant SKD-V butadiene rubber [16] and reinforcing basalt, carbon, and glass fabrics.

2. Materials and Methods

The objects of the study are elastomeric materials reinforced with fabrics by the layer-by-layer method. Fabrics made of basalt fiber brand BT-11 (100) (Factory of technical fabrics, Russia) with a surface density of 351 g/m^2 and a 5/3 twill weave, fiberglass brand TR-560-30A (100) (PolotskSteklovolokno, Belarus) with a surface density of 560 g/m^2 and a 2/2 twill weave, carbon fiber brand 2/2-1000-12K-400 (Prepreg-SKM, Russia) with a density of 407 g/m^2 and a 2/2 twill weave were used as a reinforcing layer. A rubber compound based on frost-resistant butadiene rubber of the SKD-V brand (Sibur, Russia) was used as an elastomeric matrix. The ingredients were mixed in a PL-2200 closed rubber mixer (Brabender, Germany) for 20 min. The recipe and the time of introducing the ingredients into the rubber compound are shown in Table 1.

TABLE 1. Recipe and time of introduction of rubber compound ingredients

No.	Ingredients	MF	Introduction time, min
1	SKD-V	100.0	0
2	Stearic acid	2.0	0
3	Technical Carbon N550	50.0	2
4	Zinc oxide	3.0	5
5	Sulfenamide C	0.9	10
6	Sulfur	1.5	12

The prototypes were produced by the layer-by-layer method, i.e. rubber mixture – reinforcing fabric layer – rubber mixture. A schematic representation of the stacking of the samples is shown in Fig. 1.

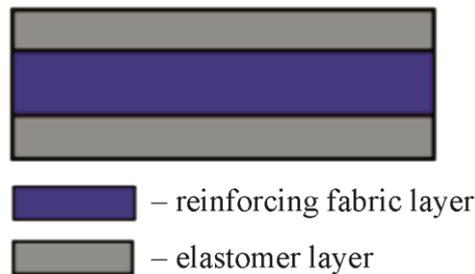


FIGURE 1. Reinforced material: elastomer layer – reinforcing fabric layer – elastomer

Vulcanization of rubber compounds and hybrid elastomeric composites was carried out in a PKMV-100 hydraulic press (Impulse, Russia) at 155 °C for 20 min under a pressure of 10 MPa.

The elastic-strength properties of the reinforced elastomers were determined by means of an Auto-graph AGS-JSTD testing machine (Shimadzu, Japan) according to ISO 37-2020; wear resistance was determined on an MI-2 friction machine (Polymermash group, Russia) using an abrasive surface with a grain size of 150 according to ISO 4649-85, the test time was 5 min; hardness was determined by the Shore A method according to ISO 7619-1-2009. The microstructure of low-temperature cleavages and the friction surface was studied in a JSM-7800F scanning electron microscope (JEOL, Japan) at a low accelerating voltage in the secondary electron mode.

3. Results

Fig. 2 shows the microstructures of the basalt fabric (BF), the glass fabric (GF), and the carbon fabric (CF).

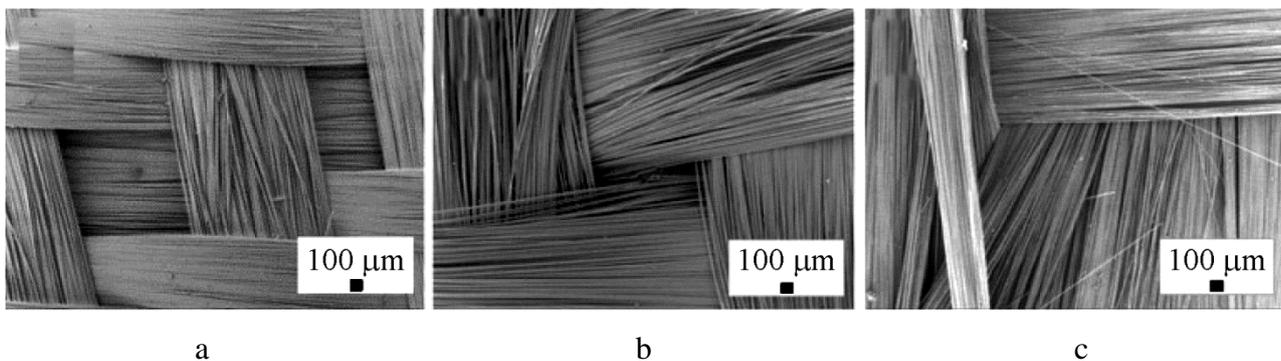


FIGURE 2. Micrographs of the fabrics: BF (a); GF(b); CF (c)

The microphotographs show that the basalt fabric has a denser weave between fiber bundles relative to the fiberglass and carbon fabrics. Presumably, this is due to the fact that the ratio of the number of interlacing fibers of the basalt fabric is 5 to 3, while it is 2 to 2 for the fiberglass and carbon fabrics.

Figure 3 shows the comparison diagrams of relative elongation and ultimate strength for the original elastomer and the elastomers reinforced with BF, GF and CF layers.

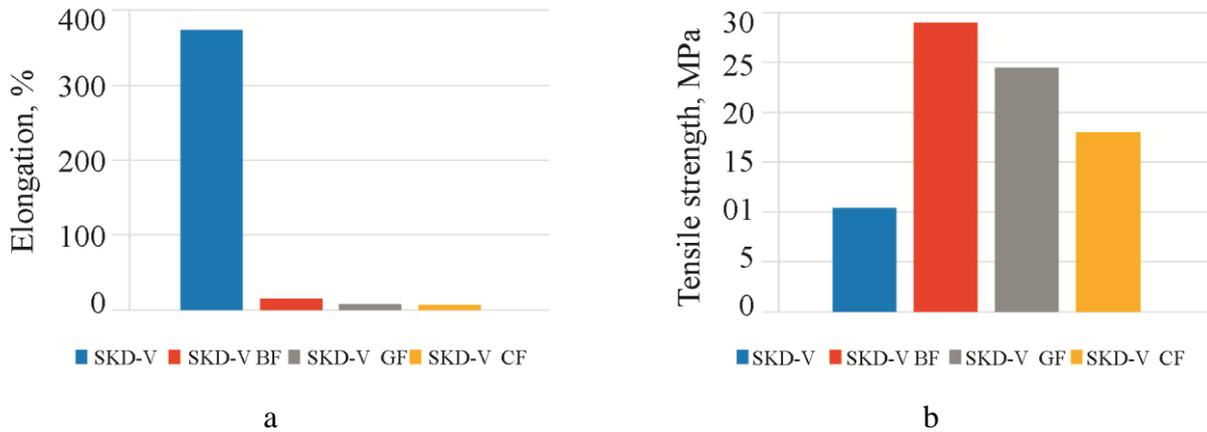


FIGURE 3. Diagrams of the physical and mechanical properties (a – elongation; b – tensile strength) of the elastomers based on rubber SKD-V, SKD-V with BF, SKD-V with GF, SKD-V with CF

It can be seen from the relative elongation diagram that the introduction of a reinforcing layer into the elastomer matrix leads to a significant decrease in elasticity, that the relative elongation decreases by a factor of ~25–47 compared to the original rubber, and that it is 15.5 % for the elastomer with BF, 8.4 % for the elastomer with GF, and 7.1 % for the elastomer with CF. The decrease in the elastic properties is due to the inability of the reinforcing layers to suffer large strain-induced changes. Thus, the reinforcement of the elastomer reduces its deformability.

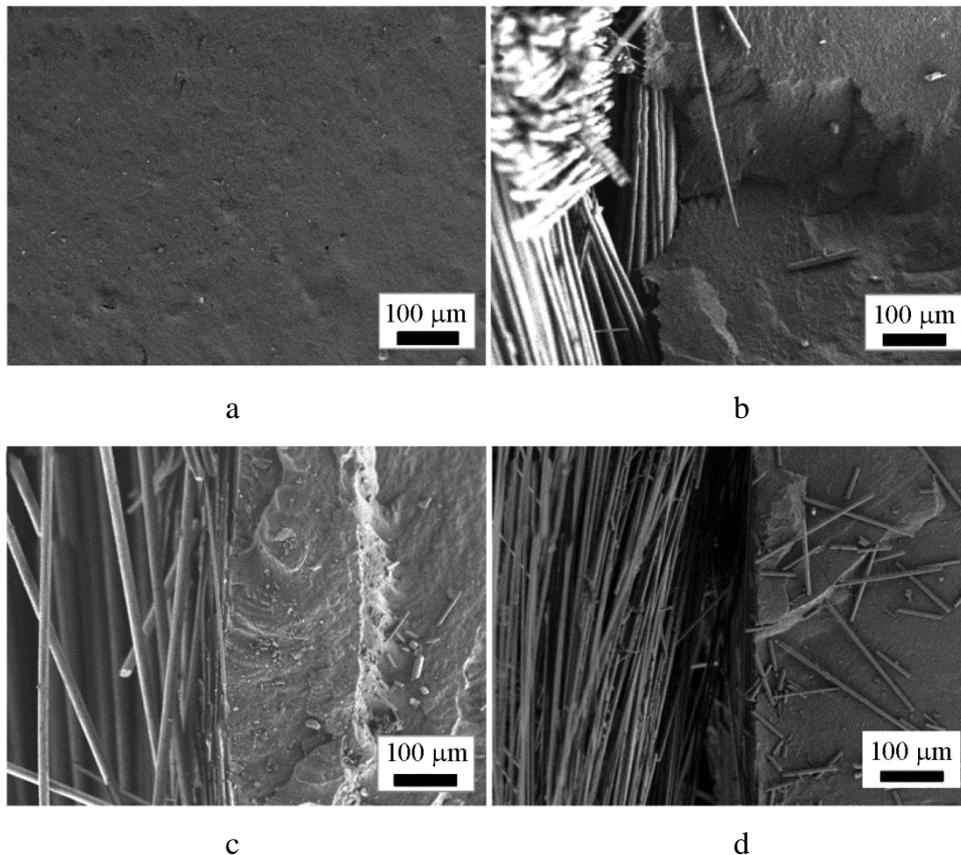


FIGURE 4. Microphotographs of specimen cleavages: SKD-V (a); SKD-V with BF (b); SKD-V with GF (c); SKD-V with CF (d)

The introduction of a reinforcing layer into the rubber compound significantly increases the strength properties of the elastomers (Fig. 3b). The strength increases 1.7 to 2.8 times from that of the original rubber. The specimen reinforced with BF has the highest strength properties (~29 MPa). The introduction of a reinforcing layer of BF, CF, and GF into the rubber compound imparts high-modulus properties to the elastomeric composites by increasing the strength properties and significantly reducing elasticity.

Figure 4 shows micrographs of brittle fractures for the SKD-V elastomers and the composite elastomers with the addition of a reinforcing layer.

Figure 4 b-d shows the contact points of two different layers: reinforcing fabric and rubber. For example, in Fig. 4b one can see areas of tight contact of the basalt fibers *pressed* into the rubber mass. The fibers on the samples with GF and CF (Fig. 4c, d) adhere less closely to the rubber. These samples showed lower strength during testing. It follows from the analysis of the microstructure that the adhesion of BF, GF, and CF to the rubber is weak due to the chemical inertness of the fibers.

Figure 5 shows diagrams of Shore A hardness and wear resistance of the rubber samples based on the SKD-V rubber and the rubbers with reinforcing layers.

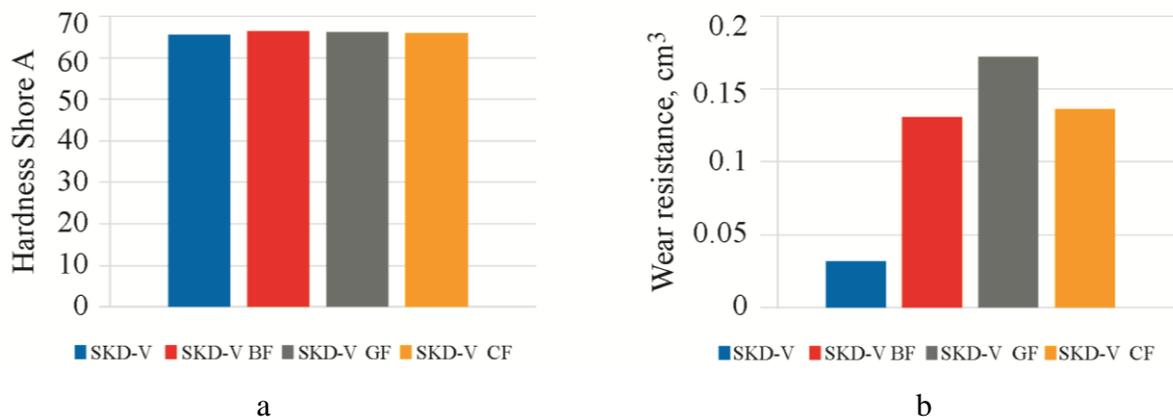


FIGURE 5. Diagrams of Shore A hardness (a) and wear resistance (b) for the elastomers based on the rubbers SKD-V, SKD-V with BF, SKD-V with GF, and SKD-V with CF

The hardness numbers of the elastomers with reinforcing layers (Fig. 5a) are on the same level with the original rubber, the variation being 1 arb. unit. Presumably, this is due to the fact that the reinforcing fabrics are soft materials, and thus they do not increase the hardness of the composites.

According to the results of studying the abrasive abrasion of the samples (Fig. 5b) coated with reinforcing surface layers of BF, GF, and CF, there is a tendency of a decrease in the wear resistance of the composites coated with fabrics. The volumetric abrasion of the specimens increases 4.1 to 5.8 times compared to the original elastomer, and it amounts to 0.131 cm³ for BF, 0.172 cm³ for GF, and 0.136 cm³ for CF. Reinforcing fabrics have inert properties when interacting with other materials and high hardness; this reduces the resistance to the abrasive action of large particles. Presumably, in the process of friction of the reinforcing fabrics on the abrasive surface, they become destroyed and peeled off from the elastomer surface.

Figure 6 shows micrographs of the surface of the samples after testing for abrasion resistance.

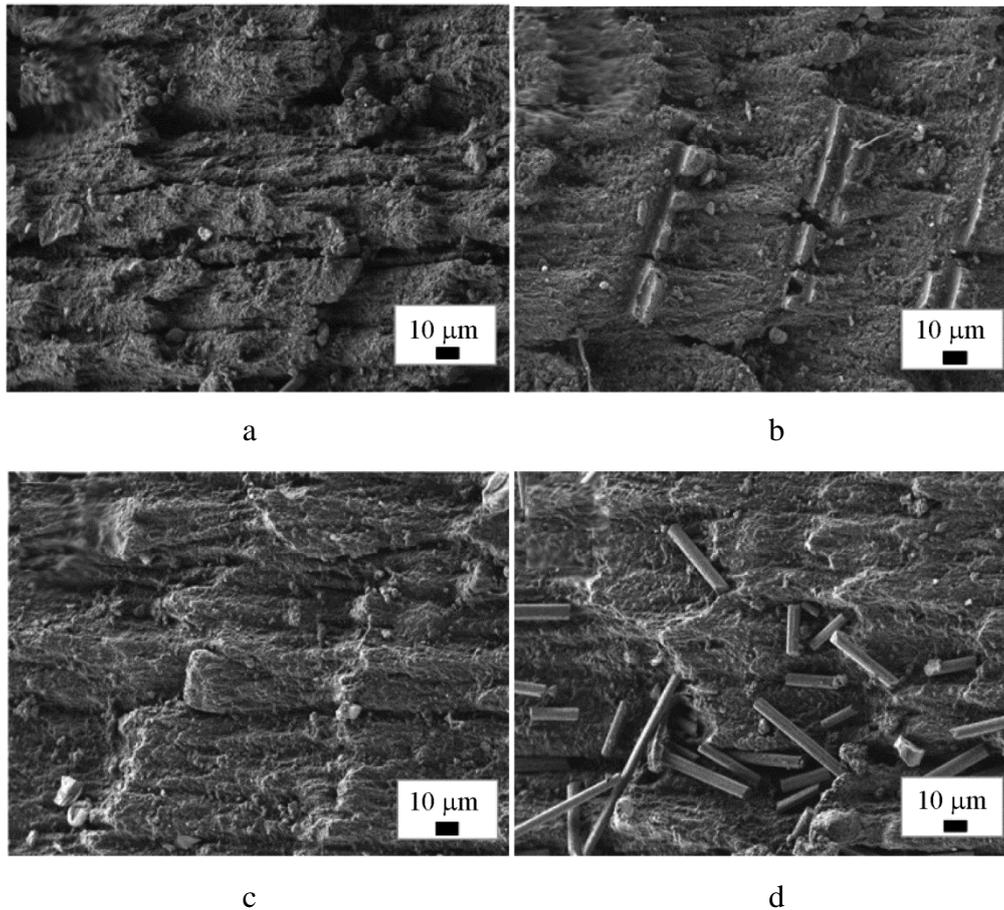


FIGURE 6. Micrographs of the samples tested for wear resistance: SKD-V (a); SKD-V with BF (b); SKD-V with GF (c); SKD-V with CF (d)

When comparing the micrographs of the friction surface of the original and reinforced samples, one can observe a looser surface of the SKD-V sample with traces of grooves from the abrasive and a wavy surface of the reinforced rubbers. In Fig. 6 b–d, fragments of BF, GF, and CF fibers are clearly visible. Conceivably, during abrasion, the fabrics made of carbon, glass, and basalt fibers become destroyed on the abrasive surface and subsequently fall off.

4. Conclusion

The study of the physical and mechanical properties of reinforced elastomers has shown the following results:

- the tensile strength of the reinforced elastomers is 1.7 to 2.8 times that of the original elastomer, the maximum increase in strength of 29 MPa being observed in the sample reinforced with basalt fabric;
- the relative elongation of the reinforced samples decreases significantly, 25 to 47 times, compared to the elastomer without a reinforcing layer, the decrease occurs by 25–47 times;
- the microstructure study shows a weak adhesive interaction of BF, CF, and GF with the elastomeric matrix;
- the formation of a surface layer of BF, CF, and GF on the rubber surface leaves wear resistance unincreased due to the low adhesion of the fibers with the elastomer and the fragility of the reinforcing fabrics.

High strength values in combination with low relative elongation provide reinforced materials with high resistance to shear deformations, i.e. high modulus properties.

Acknowledgment

This work was supported by the Ministry of Education and Science of the Russian Federation under state assignments Nos. FSRG-2020-0017 and FWRS-2022-0001. The research used the scientific equipment of the shared research facilities of the Federal Research Center of the Yakut Scientific Center, SB RAS; it was performed as part of the activities under grant No. 13.TsKP.21.0016.

References

1. Hollaway L.C. *Advanced polymer composites and polymers in the civil infrastructure*, Elsevier, 2001, 320 p.
2. Oladele I.O., Omotosho T.F., Adediran A.A. Polymer-Based Composites: An Indispensable Material for Present and Future Applications. *International Journal of Polymer Science*, 2020, vol. 2020, pp. 1–12. DOI: 10.1155/2020/8834518.
3. Bukhina M.F., Kurlyand S.K. *Low-temperature behavior of elastomers*, Leiden, VSP/Brill, 2007, vol. 31, 320 p.
4. Wang H., Yang L., Rempel G.L. Homogeneous Hydrogenation Art of Nitrile Butadiene Rubber: A Review. *Polymer Reviews*, 2013, vol. 53, No. 2, pp. 192–239. DOI: 10.1080/00914039608029377.
5. Balaji K.V., Shirvanimoghaddam K., Rajan G.S., Ellis A.V., Naebe M. Surface treatment of Basalt fiber for use in automotive composites. *Materials Today Chemistry*, 2020, vol. 17, pp. 1–28. DOI: 10.1016/j.mtchem.2020.100334.
6. Ali Z., Gao Y., Tang B., Wu X., Wang Y., Li M., Hou X., Li L., Jiang N., Yu J. Preparation, Properties and Mechanisms of Carbon Fiber/Polymer Composites for Thermal Management Applications. *Polymers*, 2021, vol. 13, No. 169, pp. 1–22. DOI: 10.3390/polym13010169.
7. Newcomb B.A. Processing, structure, and properties of carbon fibers. *Composites Part A: Applied Science and Manufacturing*, 2016, vol. 91, No. 1, pp. 262–282. DOI: 10.1016/j.compositesa.2016.10.018.
8. Tang X., Yan X. A review on the damping properties of fiber reinforced polymer. *Journal of Industrial Textiles*, 2020, vol. 49, No. 6, pp. 693–721. DOI: 10.1177/1528083718795914.
9. Liu Q., Shaw M.T., Parnas R.S., McDonnell A.M. Investigation of basalt fiber composite mechanical properties for applications in transportation. *Polymer Composites*, 2006, vol. 27, No. 1, pp. 41–48. DOI: 10.1002/pc.20162.
10. Lee C., Liu D. Tensile Strength of Stitching Joint in Woven Glass Fabrics. *J. Eng. Mater. Tech.*, 1990, vol. 112, No. 2, pp. 125–130. DOI: 10.1115/1.2903298.
11. Newcomb B.A. Processing, structure, and properties of carbon fibers. *Composites Part A: Applied Science and Manufacturing*, 2016, vol. 91, pp. 262–282. DOI: 10.1016/J.COMPOSITESA.2016.10.018.
12. Dalinkevich A.A., Gumargalieva K.Z., Marakhovskii S.S., Aseev A.V. Temperature–humidity corrosion behavior of basalt epoxy plastics. *Prot. Met. Phys. Chem. Surf.*, 2015, vol. 51, pp. 1176–1184. DOI: 10.1134/S2070205115070060.
13. Liu Y., Kumar S. Recent Progress in Fabrication, Structure, and Properties of Carbon Fibers. *Polymer Reviews*, 2012, vol. 52, No. 3, pp. 234–258. DOI: 10.1080/15583724.2012.705410.
14. Yang S., Cheng Y., Xiao X., Pang H. Development and application of carbon fiber in batteries. *Chemical Engineering Journal*, 2020, vol. 384, pp. 123294. DOI: 10.1016/j.cej.2019.123294.
15. Schutte C.L. Environmental durability of glass-fiber composites. *Materials Science and Engineering: R: Reports*, 1994, vol. 13, No. 7, pp. 265–323. DOI: 10.1016/0927-796x(94)90002-7.
16. Dias M.L., Schoene F.A., Ramirez C., Graciano I.A., Sirelli L., Gonzalves R.P. Thermal and crystallization behaviour of epoxidized high cis-polybutadiene rubber. *Journal of Rubber Research*, 2019, vol. 22, No. 4, pp. 195–201. DOI: 10.1007/s42464-019-00028-5.