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Studies of electrical and thermophysical properties of basalt plastics

Orlov Maksim Andreevich,
Head of Laboratory, IEC CM, Bauman MSTU;

Zolotarenko Ivan Dmitrievich,
Leading engineer-designer, IEC CM, Bauman MSTU;

Povolokin Oleg Valerievich,
Head of Laboratory, IEC CM, Bauman MSTU;

Boyarchuk Mikhail Viktorovich,
Assistant engineer, IEC CM, Bauman MSTU;

Alyakshin Oleg Ivanovich,
Assistant engineer, IEC CM, Bauman MSTU;

Gorbunov Alexander Borisovich,
Leading engineer, IEC CM, Bauman MSTU

Bauman Moscow State Technical University (MSTU),
Moskva-105005, Russia.

Abstract

This article presents studies of the principal electrical and thermophysical properties of basalt plastics determined by the unique chemical composition and technological properties of the natural basalt raw material used, such as electrical conductivity, dielectric permittivity, and electrical resistivity.

Keywords: Basalt fiber, bundles, basalt composite materials, electrical conductivity, dielectric permittivity, electrical resistivity, chemical composition of basalt raw material.

INTRODUCTION

Application of basalt fiber reinforcing elements refers to the future-oriented segments in technology of composite materials. Basalt fibers are characterized by improved performance characteristics in wide-range cyclically varying temperature conditions under heavy dynamic loads, providing for their prospective applications in the composite design solutions of modern jet engines, aerospace vehicles, shipbuilding and construction. Other important advantages of basalt fiber include extremely low moisture retaining property, vibration stability and resistance to aggressive media, manufacturability and relatively low production cost [1-10].

It should be noted that the basalt fiber production is based on melts of natural raw materials coming from various deposits, differing significantly in chemical composition and therefore, in their technological characteristics and impact on the quality of the final product. Table 1 presents the chemical composition of basalts originating from different deposits [6].

Table 1. Chemical composition of basalts from different deposits

Oxide	**Basalt from Berestovets deposit (Ukraine)**	**Basalt from Novoturinsky site (Middle Urals)**	**Diabase from Pekhtysh site (Middle Urals)**	**Basalt from “Myandukha” deposit (Arkhangelsk oblast)**	**Basalts of Ukraine**
SiO_2	49.5	47.09-47.59	48.38	51.18	35.9-59.8
TiO_2	2.7	1.08-1.23	0.95	Н/д	0.3-5.3
Al_2O_3	14.49	14.48-14.96	15.45	12.35	11.0-19.3
Fe_2O_3	7.58	6.26-6.84	5.9	3.34	0.9-9.4
FeO	7.51	5.17-6.18	5.89	9.77	0.7-12.9
CaO	8.26	9.26-11.32	10.49	9.83	1.4-14.5
MgO	5.27	6.47-7.09	3.72	7.83	1.5-15.5
MnO	0.2	0.20-0.23	0.18	0.19	N/A
Na_2O	2.56	2.21-2.42	4.5	1.36	1.2-5.1
K_2O	0.6	1.23-2.11	1.02	0.36	0.1-3.3
P_2O_5	0.44	0.20-0.27	0.27	Н/д	N/A
SO_3	0.05	0.01-0.27	0.02	0.84	N/A

Considering these features of raw material sources, periodic studies (controlled testing) of the main technological and operational characteristics of the fiber produced from natural basalt raw materials (specific deposit, delivery batch) is greatly important.

The subject of research presented in this article is the development of practice-oriented methods for testing the basic properties of basalt monofilaments and bundles that largely determine the performance characteristics of derived composite products.

This research involves the following physical characteristics:

1) Electrical conductivity of basalt plastics;
2) Dielectric permittivity;
3) Electrical resistivity.

MATERIALS AND METHODS

Unidirectional basalt plastics shaped as cylindrical rods were prepared for studying the electrical properties and thermal conductivity. Samples were obtained by pultrusion from pre-prepared material – prepregs. Prepregs (impregnated basalt fiber bundles) were made on a winding machine; its structure is shown in Fig. 1.

Microplastic samples were manufactured by winding the epoxy-impregnated bundle of basalt fibers. Blocks for producing microplastics represent a framed construction with laterally fixed grooved drums (Figure 2). The binder-impregnated bundle is placed in grooves. Roving with a linear density of 1,200, 1,600, 1,800, 2,000 and 2,400 g/km was used as bundles. Bundles were treated with an experimental lubricant. ED-22 epoxy resin consolidated by isomethyltetrahydrophthalic anhydride was used as a binder.

Winding was conducted on a winding machine, which does not substantially damage the fiber at all stages of processing, and there is no slippage and abrasion of the fibers, which is very important in basalt fiber applications.

The bundle is fed from the spool 1 located on the spooling frame 2, via the locating ring 3.

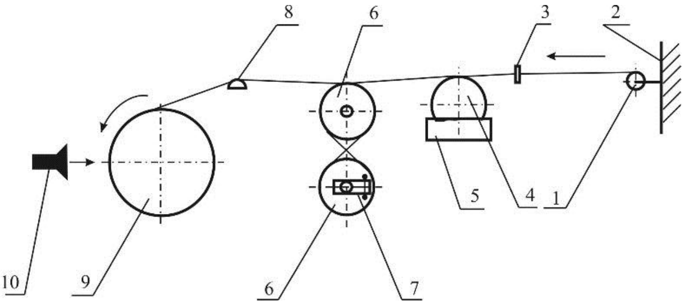


Figure 1. Layout showing the winding of experimental samples of basalt plastics

Figure 2. Frame used to produce microplastics

The spooling frame is equipped with a brake unit that provides pre-tension of the fiber. Further, a binder was applied to the bundle with the impregnating roller 4. The roller is partially immersed in the binder, which is fed from a heated bath 5. It should be noted that the impregnating roller is located slightly upward the supervening mills and the locating ring, which provides a slight bend of the bundle and creates normal stresses at the tangent point, which already at this stage facilitates impregnation of the filler. The final impregnation of the bundle and its tension was performed on tension drums 6 slightly inclined to each other, which enables several turns around the drums and thus a more thorough impregnation. The brake unit 7 provides adjustment of the fiber tension. Further, the impregnated bundle is drawn via the handler 8 placed just beside the frame 9. The impregnating roller 4, bath with the binder 5 and tension drums 6 are heated with hot water of the preset temperature maintained by a thermostat. All elements of the impregnation and tension track were fixed on a vertical plate mounted on the lathe carriage support, which allows winding at a predetermined speed.

To prepare samples of microplastics, after winding the basalt fiber blocks were removed from the winding shaft, cured for 4 hours at 110 °C and cooled to room temperature, both processes in a heating cabinet. Next, the impregnated bundles (prepregs) were cut off from the frames. Table 2 shows the parameters of winding prepregs from basalt fibers.

To measure the electrical and thermal properties of reinforced plastic rods, samples were prepared by molding with spinnerets spinnerets.

After winding the prepreg, the resulting bundles were cut off from the block. Further, the bundles were drawn in spinnerets (Fig. 3) so that the bundle completely filled the channel. Blocks were preheated up to 80 °C and then blocks with prepreg – up to 110 °C, for 4 hours. As a result, basalt plastic rods with a diameter of 9 and 15.5 mm and a length of 120 mm were produced.

Table 2. Technological parameters of winding prepregs from basalt fibers

Parameter Linear density, g/km	Thread tension force, H	Winding speed, m/min	Winding time of one sample, min	
			Diameter 9mm	Diameter 15.5 mm
1,200	5	11.7	2.4	7
1,600	5	11.7	1.8	5.2
1,800	5	11.7	1.6	4.6
2,000	5	11.7	1.4	4.1
2,400	5	11.7	1.2	3.5

Figure 3. Structure of the compound spinneret for manufacturing reinforced plastic rods

Further, samples for measuring electrical properties and thermal conductivity were cut from the rods; their size and number are presented in Tables 3 and 4.

Table 3. Geometric dimensions and number of samples for studying electrical properties

Linear density of basalt roving, g/km	Dielectric loss tangent, electrical conductivity			Volume resistivity		
	Diameter, mm	Thickness, mm	Number, pcs.	Diameter, mm	Thickness, mm	Number, pcs.
1,200	9	1	5	9	2	5
1,600	9	1	5	9	2	5
1,800	9	1	5	9	2	5
2,000	9	1	5	9	2	5
2,400	9	1	5	9	2	5

Table 4. Geometric dimensions and number of samples for measuring thermal conductivity

Linear density of basalt roving, g/km	Diameter, mm	Thickness, mm	Number, pcs
1,200	15.5	3	5
1,600	15.5	3	5
1,800	15.5	3	5
2,000	15.5	3	5
2,400	15.5	3	5

Selected samples for testing had a smooth surface without blisters, chips, irregularities, notches, scratches, cracks, and delaminations.

Manufactured samples were marked on the outside.

Determination of basalt fiber content in microplastics

The volume fraction of basalt fibers in microplastics is determined by the experimental method that consists in measuring the mass (analytical scales GOST 24104-88, index error ≤ ±1% of the measured value) and length (measuring metal ruler GOST 427-75) of microplastics.

Test results are processed in the following sequence:

- determine the total length of all samples in the batch:

$$L = \sum_{i=1}^{10} l_i,$$

where l_i is the length of one sample;

- calculate the mass of basalt fiber in microplastics:

$$M_F = T \cdot L,$$

where T is the linear density of the basalt bundle;

- determine the mass of the matrix:

$$M_M = M - M_F,$$

where M is the total mass of the sample batch.

The volume fractions of binder and fiber in microplastics is calculated upon the data obtained:

$$V_M\% = (M_M/\rho_M)/V \cdot 100\%$$

$$V_F\% = (M_F/\rho_F)/V \cdot 100\%$$

where ρ_M, ρ_F is the density of the matrix and fiber, respectively.

For calculations, the matrix density is taken as 1,200 kg/m^3, the basalt fiber density – 2,650 kg/m^3.

Determination of volume resistivity, dielectric loss tangent and electrical conductivity of basalt plastics

The test procedure is developed upon the following documents: GOST Russia 50499-93 "Solid electrical insulating materials. Methods of test for volume resistivity and surface resistivity" and ASTM D 150-11" Standard Test Methods for AC Loss Characteristics and Permittivity (Dielectric Constant) of Solid Electrical Insulation".

Measuring the volume resistivity is based on the scheme shown in Figure 4. The voltage applied to the sample is measured with a DC voltmeter. Current is measured by a current measuring device, such as an electronic amplifier or an electrometer.

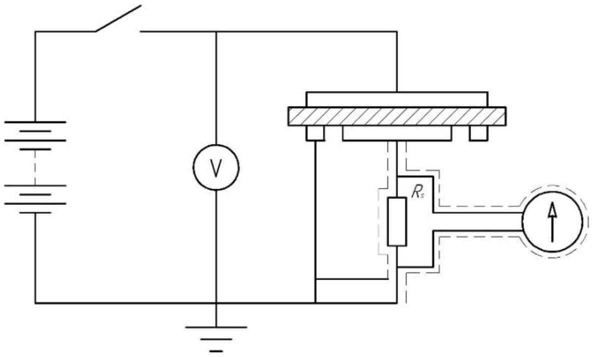


Figure 4. Schematic diagram of volume resistivity measurement

The dielectric loss tangent and electrical conductivity are measured by the parallel-plate test method, see diagram in Figure 5.

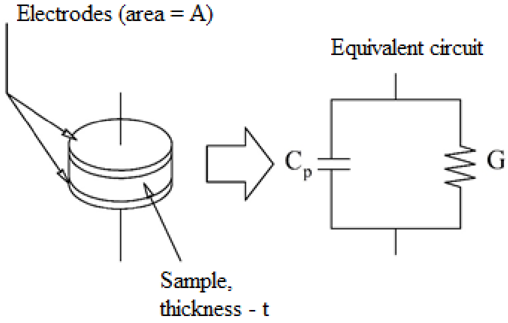


Figure 5. Schematic diagram illustrating the parallel-plate method

Electrodes (area = A); Equivalent circuit; Sample, thickness – t

The method is based on the following equations:

$$\mathrm{tg}\delta = \frac{G}{\omega \cdot C_p},$$

where tgδ is the dielectric loss tangent, G – the electrical conductivity, C_p – the electrical capacitance of the sample, ω – the circular frequency.

$$\mathrm{tg}\,\delta = \frac{\varepsilon_r''}{\varepsilon_r'},$$

where ε'_r is the real part of the dielectric constant, ε''_r– the imaginary part of the dielectric constant.

$$\varepsilon_r' = \frac{t \cdot C_p}{A \cdot \varepsilon_0},$$

$$\varepsilon_r'' = \frac{t}{\omega \cdot R_p \cdot A \cdot \varepsilon_0},$$

where R_p is the equivalent series resistance; A– the contact area, t– the sample thickness; ε_0– the dielectric constant.

The following equipment is required: impedance meter and tester for material parameters with the measurement range 1 MHz-1 GHz, teraommeter, and caliper, according to GOST 166, with a measurement error of ≤ 0.1 mm.

To measure the electrical resistivity, conductive paste is applied on the sample surface and it is fixed in the measuring cell (Figure 6).

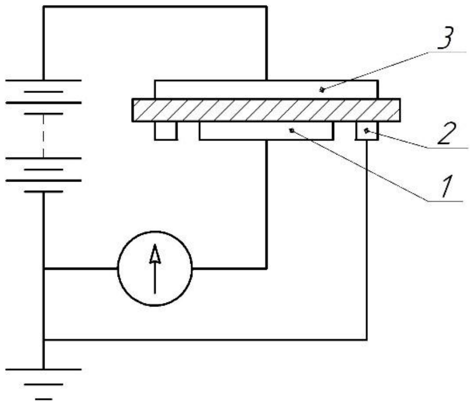


Figure 6. Measuring cell for testing the volume resistivity. 1 – protected (measuring) electrode, 2 – protective (guard) electrode, unprotected electrode (voltage electrode)

Constant voltage of 100 V was used for measurements.

The electrical conductivity and dielectric loss tangent were measured with the impedance analyzer. For this purpose, conductive paste was applied to the sample and then the sample was placed into the measuring cell. Further, the change in conductivity and the dielectric loss tangent depending on the frequency were recorded using the impedance analyzer software. The operating frequency range was 1-700 MHz.

The volume resistivity was calculated by the formula:

$$R_v = R\frac{S}{h},$$

where R is the measured resistance, S – the contact area, h – the sample thickness.

Determination of thermal conductivity of basalt plastics

The test procedure is developed upon the following documents: GOST 23630.2-79 “Plastics. Method for the determination of thermal conductivity” and ISO 11357-4 “Plastics – Differential scanning calorimetry (DSC) – Part 4: Determination of specific heat capacity”.

The method implies creation of a stationary heat flux passing through a flat sample of a certain thickness and directed perpendicular to the front (largest) faces of the sample, measuring the density of this heat flux, the temperature at the opposite front faces and the sample thickness. To determine the thermal conductivity of basalt, its heat capacity needs to be evaluated. The method for calculating specific heat capacity (C_p) from an experimental DSC signal is based on the following equations:

$$Q = C_p \cdot m \cdot dT$$

or

$$dQ = C_p \cdot m \cdot dT,$$

$$\frac{dQ}{dt} = C_p \cdot m \cdot \frac{dT}{dt},$$

$$\frac{dQ}{dt} \cdot m^{-1} = C_p \cdot \frac{dT}{dt}$$

The heat flux $\frac{dQ}{dt}$ (the amount of heat per unit time per unit mass of the sample) is determined by differential scanning calorimetry.

$$DSC = \dot{Q} = \frac{dQ}{dt},$$

The heat capacity of the test sample is calculated by the formula:

$$C_p = \frac{m_{\mathrm{ref}}}{m_{\mathrm{s}}} \cdot \frac{DSC_s - DSC_{\mathrm{b}}}{DSC_{\mathrm{ref}} - DSC_{\mathrm{b}}} \cdot C_{p\,\mathrm{ref}}\ (\mathrm{J \cdot g^{-1} \cdot K^{-1}})$$

where DSC_{s}, DSC_{b} are experimental signals from the sample and the pot, where the sample is placed, m_{ref} is the mass of the calibration (reference) sample, m_{s}– mass of the sample, $C_{\mathrm{p\,ref}}$ – specific heat capacity of the calibration sample.

Testing is performed with a device providing measurements of heat capacity with an error ≤ 10%, which consists of the measuring unit, the power supply and regulation unit, which provides steady heating with an average speed of 0.1 °C/min, and automatic temperature regulation of an adiabatic cover;

the Netzsch DSC 204 F1 Phoenix differential scanning calorimeter; analytical scales with an error of ≤ ±1% of the measured value. The sample diameter and thickness are measured with a caliper with a measurement error of ≤ 0.1 mm.

Testing was conducted in the following order: the sample was weighed with an error of ≤ 0.001 g, its height and diameter were measured with an error of ≤ 0.01 mm. The contact surfaces of the sample, the base and the pressure rod were wiped with ethyl alcohol; then a thin layer of organosilicone liquid was applied to them. The test temperature ranged from 50 to 125 °C; the temperature gradient was measured at heating with the interval of 25 °C (base temperature).

The heat capacity is measured with a differential scanning calorimeter.
At least, 3 baseline (with empty pots) measurements were taken. The temperature program and other measurement conditions were selected according to ISO 11357-4.

A calibration (reference) sample for heat capacity (sapphire weighing 49.90 mg) was placed into the sample pot. The sample mass was measured with an accuracy of ± 0.01 mg. Then the calibration heat capacity sample was measured at least 3 times, with subtraction of the baseline.

Further, the sample studied for heat capacity was placed into the pot and measured at least 3 times, with subtraction of the baseline. Further, the measurements results for the calibration and test samples were loded into the device software and the sample heat capacity was calculated.

The thermal conductivity of samples (λ, W/mK), is calculated for each temperature by the formula:

$$\lambda = \frac{h}{P_0}(1 - \sigma_\beta),$$

where h is the sample height, m; P_0– the sample thermal resistance, m•K/W; σ_β is the correction for the sample thermal expansion, which is calculated by the formula:

$$\sigma_\beta = \beta \cdot \Delta t,$$

where β is the reference value of the coefficient of linear thermal expansion, deg^{-1}; Δt – the temperature range in the test, °K.

The thermal resistance of the sample (P_0) was calculated by the formula:

$$P_0 = \frac{n_0 \cdot S}{n_T \cdot K_T}(1 + \sigma_c) - P_k,$$

where S is the cross-section area, m^2; P_k– correction accounting for the thermal resistance of contacts and estimated from calibration of the device; n_0– the temperature gradient on the sample, division count on the galvanometer scale; n_T– the temperature gradient on the heat flowmeter, division count on the galvanometer scale; K_T – the proportionality factor characterizing the effective thermal conductivity of the working layer of the heat flowmeter, determined from the device calibration; σ_c– correction for the sample heat capacity.

Correction for heat capacity (σ_c) was calculated by the formula:

$$\sigma_c = \frac{C_0 m_0}{2 \cdot (C_0 m_0 + C_c m_c)},$$

where C_0 is the specific heat capacity of the sample, J/kg•K; C_c– specific heat capacity of the rod, J/kg•K; m_0–the sample mass, kg; m_c the rod mass, kg.

The Celsius temperature (t), which includes the measured value of thermal conductivity, was calculated by the formula:

$$t = t_c + 0{,}5 A_t K_u \cdot n_0,$$

where t_c– is the rod temperature, °K; A_t– the temperature coefficient of the thermocouple, K/mV; K_u– sensitivity of the galvanometer, mV/divisions; n_0–readings of the galvanometer (scale divisions).

At least, five measurements were taken with the reference standard of quartz optical glass. The thermal conductivity of the heat flowmeter (K_T) was calculated by the formula:

$$K_T = \frac{\lambda}{h} S \frac{n_0}{n_t}(1 + \sigma_c),$$

where h is the height of the reference standard, m; S is the cross-section area of the reference standard, m^2; $\frac{\lambda}{h}$ –the thermal conductivity coefficient of the reference standard measured under the test, W/mK; n_0– the temperature gradient on the sample, the number of divisions of the galvanometer scale; n_T– the temperature gradient on the heat flowmeter, the number of divisions of the galvanometer scale; σ_c– correction for the sample thermal capacity.

Correction for the thermal contact resistance of the sample (P_k) was calculated by the formula:

$$P_k = \frac{S}{K_T}\frac{n_0}{n_T}(1 + \sigma_c) - \frac{h_м}{\lambda_м},$$

where $h_м$ – is the height of the copper sample, m; $\lambda_м$ – coefficient of thermal conductivity of copper, W/mK.

The thermal conductivity of the heat flowmeter (K_T) is verified against the mean value (P_K) and was calculated by the formulas:

$$\sigma_k = P_k \frac{\lambda}{h},$$

$$K_T = \frac{\lambda \cdot S \cdot h_0}{h \cdot n_T (1 + \sigma_k - \sigma_c)},$$

The specific heat capacity of basalt plastics was determined by the specialized software for the Netzsch DSC 204 F1 Phoenix differential scanning calorimeter.

Measurement results were processed statistically by calculating:

Mean value, $\bar{x} = \frac{\sum_{i=1}^{n} x_i}{n}$,

Standard deviation, $S_x = \left(\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n-1}\right)^{\frac{1}{2}}$,

where $\bar{n}$ is the number of measurements.

Test results

Table 5 presents the composition of microplastics based on basalt fiber bundles with varying linear density. Notably that regardless of the bundle linear density, the fiber content in microplastics varies only slightly and makes 50-60 vol. %. The matrix content remains almost unchanged.

Table 5. Content of reinforcing fiber and epoxy matrix in basalt plastics

T, g/km	Type of lubricant	$V_M^{\%}$, vol. %	$V_F^{\%}$, vol. %
1,200	1	47	53
	2	48	52
1,600	1	44	56
	2	46	54
1,800	1	48	52
	2	50	50
2,000	1	47	53
	2	45	55
2,400	1	45	55
	2	44	56

Figures 7-9 and Table 6 demonstrate the results for the electrical properties of unidirectional basalt plastics along the reinforcement direction. The linear density of reinforcing fibers and the type of lubricant practically do not affect the values of dielectric permittivity, electrical conductivity, dielectric loss tangent, and the volume resistivity.

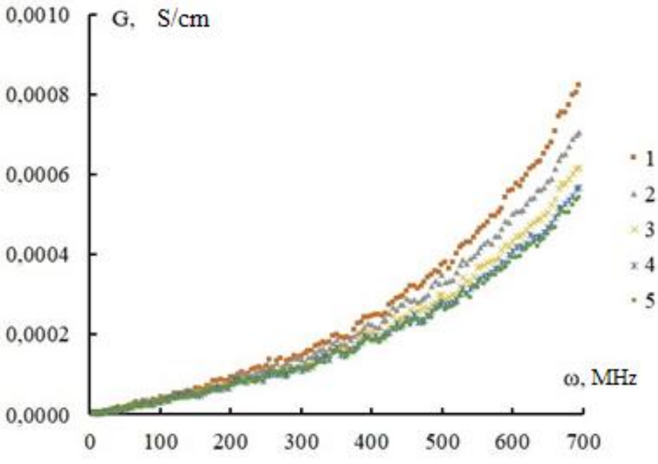
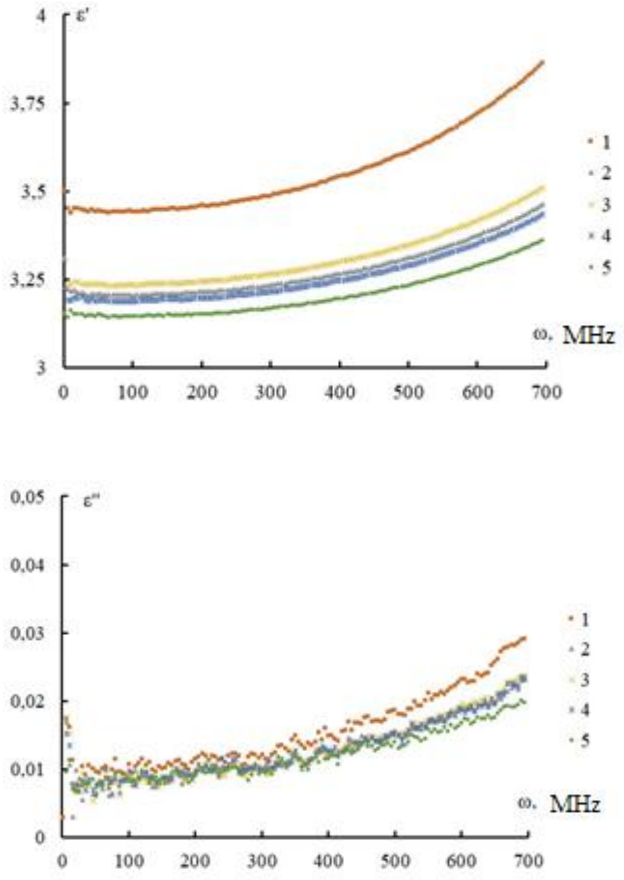


Figure 7. Dependence of electrical conductivity of basalt plastics on frequency. Linear density of the bundle: 1 – 1,200 g/km; 2 – 1,600 g/km; 3 – 1,800 g/km; 4 – 2,000 g/km; 5 – 2,400 g/km



(b)

Figure 8. Dependence of the real (a) and imaginary (b) parts of the dielectric constant of basalt plastics on frequency. 1 – 1,200 g/km; 2 – 1,600 g/km; 3 – 1,800 g/km; 4 – 2,000 g/km; 5 – 2,400 g/km

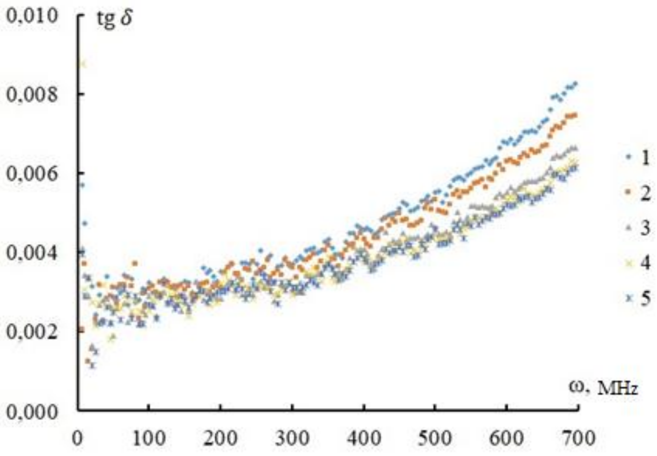


Figure 9. Dependence of the dielectric loss tangent of basalt plastics on frequency. 1 – 1,200 g/km; 2 – 1,600 g/km; 3 – 1,800 g/km; 4 – 2,000 g/km; 5 – 2,400 g/km

Table 6. Volume resistivity of basalt plastics based on bundles with different linear density

T, g/km	R_v, Ohm·cm
1,200	$5 \cdot 10^{16}$
1,600	$5 \cdot 10^{16}$
1,800	$5 \cdot 10^{16}$
2,000	$5 \cdot 10^{16}$
2,400	$5 \cdot 10^{16}$

According to the test results, it can be concluded that the electrical properties and thermal conductivity of basalt plastics measured along the fibers are virtually non-dependent of the bundle linear density.

CONCLUSIONS

The study protocol developed and presented in this article provides the framework for controlled technological product testing and includes practice-oriented studies of the following technical characteristics:

1) Content of reinforcing fiber and epoxy matrix in basalt plastics;
2) Dependences of electrical conductivity of basalt plastics on field frequency;
3) Dependences of the real and imaginary parts of the dielectric constant of basalt plastics on frequency;
4) Dependences of the dielectric loss tangent of basalt plastics on frequency.

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