

ELECTRO-PHYSICAL PROPERTIES OF SUPER-THIN BASALT FIBERS ON THE BASIS OF ARMENIAN BASALT ROCKS BEFORE AND AFTER CHLORHYDRIC ACID TREATMENT

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Abstract: For the first time, electro-physical parameters of super-thin basalt fibers (STBF) on the basis of Armenian basalt rocks are measured before and after chlorhydric acid treatment. It is shown that specific resistance and dielectric parameters of super-thin basalt fibers change essentially after chlorhydric acid treatment. It is revealed from thermogravimetric and other investigations that the probable cause of the change is the increase in total amount of pores and modification of the share of pores of various sizes in STBF followed by the increase of absorption of water molecules from the ambient medium. It is shown, in particular, that the obtained results (in both alternating and constant fields) can be interpreted within the framework of dipole-relaxation mechanism of polarization of water molecules in STBF pores.

1. Introduction

Basalt is a widespread porous material included - along with zeolites - into the class of aluminosilicates. On the basis of basalt rocks, continuous basalt fibers are formed [1-3] widely used for heat- and sound-insulation [4,5]. They are reinforcing materials for improvement of strength characteristics of some composite compounds [6,7]. Besides, due to their high thermal stability, ecological compatibility and inertness in relation to the majority of aggressive materials, basalt fibers are used for clearing of industrial gas emissions without preliminary cooling [8].

Basalt fibers with diameters of the order of microns are 1D crystals and possess all features of nanocrystalline materials (quantum size effect) being of keen scientific and practical interest. According to recent investigations, such systems can present promising materials for highly sensitive gas sensors [9]. However, application of basalt fibers has not received wide recognition because of insufficient examination of their physical and chemical properties [10]. As basalt is dielectric, it is important to study its electrophysical properties depending on various external factors such as the temperature, humidity, chemical modification, etc. In scientific literature there are little or nothing of such works, and available papers only present research of basalt rocks [11]. In particular, measurements of specific electric conductivity ρ in these papers were only carried out using either constant [11] or alternating electric fields [1,12,13]. The values of some physical and chemical parameters, including specific electric conductivity ρ , dielectric constant ε' and dielectric loss coefficient ε'' for basalt fibers in tabulated form are only presented on some Internet sites [1,12,13].

This paper for the first time presents electrophysical characteristics of super-thin basalt fibers

(STBF) from Armenian basalt rocks with average diameter less than 10 microns measured using both constant and alternating electric fields before and after chlorhydric acid treatment.

2. Experimental materials and procedures

STBFs were obtained using standard technology [1-3] on the basis of Armenian basalt rocks (Zolakar village). For technical applications STBFs are manufactured in the form of layered wool with bulk density $D = 0.25 \text{ g/cm}^3$ that is considerable below the real fiber density ($D_R=2.7-2.8 \text{ g/cm}^3$) [1-3,14]. For measurements, pieces of the wool were cut in the form of flat rectangular felt with area S from 0.7 cm^2 to 1.5 cm^2 . Then these samples were placed between two copper-plated laminated bakelite slabs. The same slabs were used as electric probes, to which alternating or constant electric fields were applied. Probes with the samples were attached on a fluoroplastic holder, whose specific resistance ($> 10^{17} \Omega \cdot \text{cm}$) was much more than that of the measured materials.

Treatment of STBFs in acids solution can result in change of their structural and, hence, many physical properties. The treatment technique is known in literature under the name “industrial leaching”. After such treatment, alkaline metals move off the material. This treatment is carried out in two stages. At the first stage STBF is treated at temperature of $(92-93)^\circ\text{C}$ in the chlorhydric acid solution with concentration 5N during 30 minutes, and at the second one in the solution with concentration 1.5N during 3 hours. After the first stage, STBF sample was washed out by distilled water to the absence of traces of Fe^{+3} ions, and after the second stage to the absence of traces of Cl^{-1} ions. The samples were dried to constant weight during 8 hr at temperature of $115-120^\circ\text{C}$. Initial sample after leaching and drying loses 51.5 % of its weight. According to the results of chemical analysis, the end-product has the following structure: SiO_2 - 95.56 %, Al_2O_3 - 2.25 %, Fe_2O_3 - 0.8 % (amounting to 98.61 %). In what follows initial and chemically modified samples will be referred as samples 1 and 2, correspondingly. For these samples, specific electric resistance for direct ρ_{dc} and alternating ρ_{ac} current were measured, ε' and ε'' were determined as well. The specified parameters were measured at the temperature from 15°C to 25°C and relative humidity of air not more than 50%. The parameters ε' , ε'' and ρ_{ac} for basalt fibers were measured by means of a precise bridge for measurement of capacities (TESLA BM 400 G). This bridge enables to measure loss tangent $\tan \delta$ to 0.1 and capacity accurate to $\pm 1 \%$ at a fixed frequency of 800 Hz. To measure higher ε'' , another transformer bridge circuit was developed and fabricated enabled to measure $\tan \delta$ to 50 at frequencies from 200 Hz to 1 MHz. Using this device, it is possible to measure active and reactive components of signals from the investigated samples accurate to $\Delta G=10^{-8} \Omega^{-1}$ and $\Delta C=0.05 \text{ pF}$, correspondingly. Calibration of the device and accuracy testing of the measured

objects were carried out for known values R and C , which were previously measured using impedance meter BM 507 and capacity meter BM 400 G, accordingly. ε' value was determined from expression $\varepsilon' = C/C_0$, where C is the capacity of a flat capacitor with dielectric and C_0 capacity of this capacitor without dielectric. The parameter ε'' was calculated from formula $\varepsilon'' = \varepsilon' \tan \delta$. ρ_{ac} was determined by formula $\rho_{ac} = (\varepsilon_0 \varepsilon'' \omega)^{-1}$, where ε_0 is the electric constant, $\omega = 2\pi f$ is angular frequency of the electric field [15,16]. Specific resistance of the sample for direct current ρ_{dc} was determined by dual probe method using formula $\rho_{dc} = US/Id$, where U is a constant voltage applied to the sample, I is a current passed through it, S is the effective area of the sample, and d is the effective thickness of the sample in the current direction. For our samples $d \leq 1$ mm. Resistance measurements ($R = U/I$) of the sample for direct current were carried out using electrometric voltmeter V7-30 which allows measurements of R up to $10^{18} \Omega$.

Before and after chemical treatment, the samples were heated at temperature 150°C during 1 hour, then quickly cooled to room temperature; restoration of their weight with time was tracked (in sorption mode) by weighing on electric scales VLR-200 accurate to 0.05 mg (absolute accuracy). The parameter $(m - m_0) \times 100\% / m_0$ (where m_0 is the initial weight of the sample immediately after its rapid cooling to room temperature, and m is its current weight at time point t) determined with time, characterizes relative change of the sample weight. Weight of investigated samples varied in the range from 25 to 40 mg. Relative error in all types of the measurements did not exceed 5%.

3. Results and discussion

Figure 1 presents ρ_{dc} dependences on duration of the applied constant field for samples 1 and 2. It follows from the curves that chemical treatment results in decrease of ρ_{dc} almost by 4 orders of magnitude (Fig. 1, curve 2). It is particularly remarkable that for both samples, curves $\rho_{dc}(t)$ show rapid initial growth followed by their slow subsequent increase. Moreover, if in the case of sample 1 ρ_{dc} reaches its constant value in two minutes after activation of the field, in the case of sample 2 it takes place 2 hours after field activation (this part of the results is not presented in Fig. 1). Actually, considerably long-term relaxation processes take place in sample 2. It is known that dielectric resistance grows, depending on the activation period of constant electric field due to generation of polarization currents caused by delayed displacement currents [15,16]. We assume that the region of rapid growth of ρ_{dc} with time (Fig. 1) is caused by polarization of water molecules presenting in large fiber pores under the effect of constant electric field, whereas relatively slow increase is caused by polarization of water molecules presenting in smaller pores. Also, water in large pores is supposedly connected with the frame relatively weak and is more mobile than in small pores.

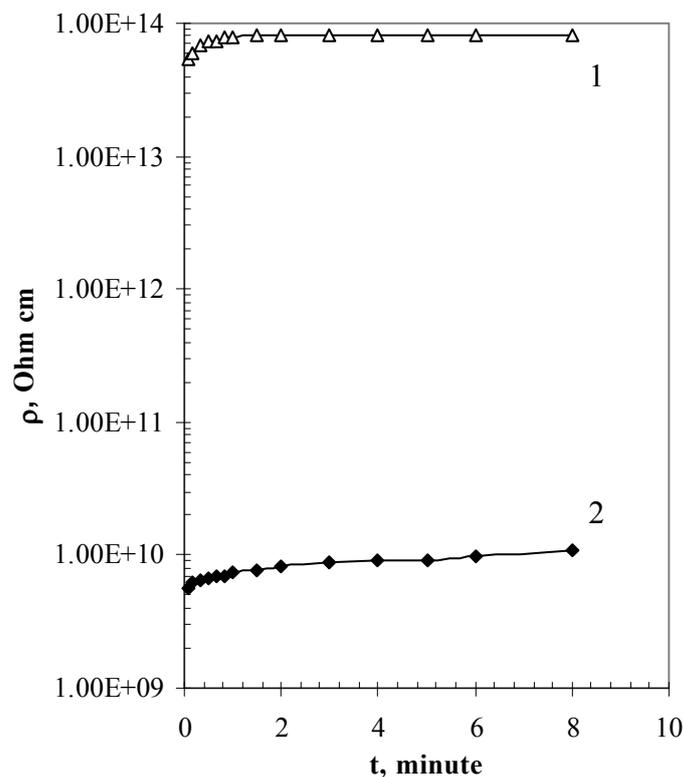


Fig. 1. Dependence of the specific electric resistance on the activation period of constant electric field for sample 1 (curve 1) and sample 2 (curve 2). Curves 1 and 2 were registered at temperature and relative humidity 24.2°C, 44.60 % and 20.4°C, 49.9 %, correspondingly. Bulk density of both samples was 0.4 g/cm³.

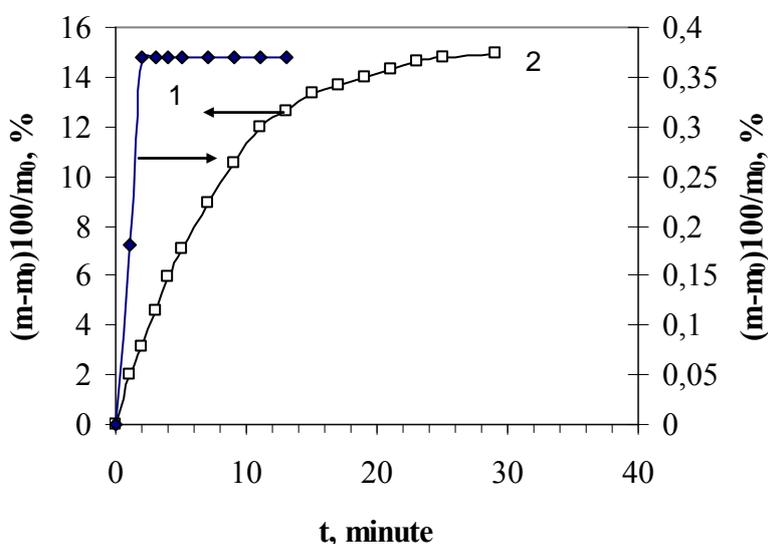


Fig. 2. Restoration of relative weight for samples 1 (curve 1) and 2 (curve 2) in time t after heating at temperature 150°C during 1 hour. Weighing was carried out in the air at 18°C. Both samples have almost identical bulk density of approximately 0.25 g/cm³.

Hence, after activation of constant electric field, at first water molecules in large pores and later water molecules in small pores are polarized. Therefore after activation of constant field, rapid growth of ρ_{dc} with time t is followed by the region of its slow increase. To find correlation between the water content and behavior of ρ_{dc} within the specified parts of $\rho_{dc}(t)$ curve, both samples were heated at 150°C during 1 hour; restoration of their weight with time was tracked. Figure 2 shows

the results of gravimetric measurements of the samples. It is seen that the untreated sample (curve 1) loses at heating less than 0.4% of its weight and comes to its stable weight maximum in 2 minutes after keeping at room temperature, while the leached sample (curve 2) loses 15% of the initial weight and only comes to its stable weight in 30 minutes. The obtained results correlate with the results of study of adsorption properties of various leached STBF samples obtained using thermogravimetric and differential thermal analysis [14]. It is possible to explain many observed phenomena within the framework of the results of this research. It is established that STBF contains three types (in size) of pores: macro-pores with diameter over 50 nm, meso-pores with diameter within a range from 2 to 50 nm, and micro-pores with diameter less than 2 nm [14]. In particular, it is shown in [14] that the fiber of initial sample has the following size distribution of pores: 2% of macro-pores, 1% of micro-pores and 97% of meso-pores. Industrial leaching of STBF modifies size distribution of the pores as follows: 9% of macro-pores, 4% of micro-pores and 87% of meso-pores. Here, increase in total amount of pores from $0.027 \text{ cm}^3/\text{g}$ to $0.1341 \text{ cm}^3/\text{g}$ also takes place [14]. The volume of pores (formed or released from various impurities and salt formations) is filled basically with water resulting in reduction of ρ_{dc} and ρ_{ac} by 3-4 orders of magnitude as well as increase of ε' by a factor of 4.5 and ε'' more than 500 times (see Figs. 1 and 3, as well as Table 1).

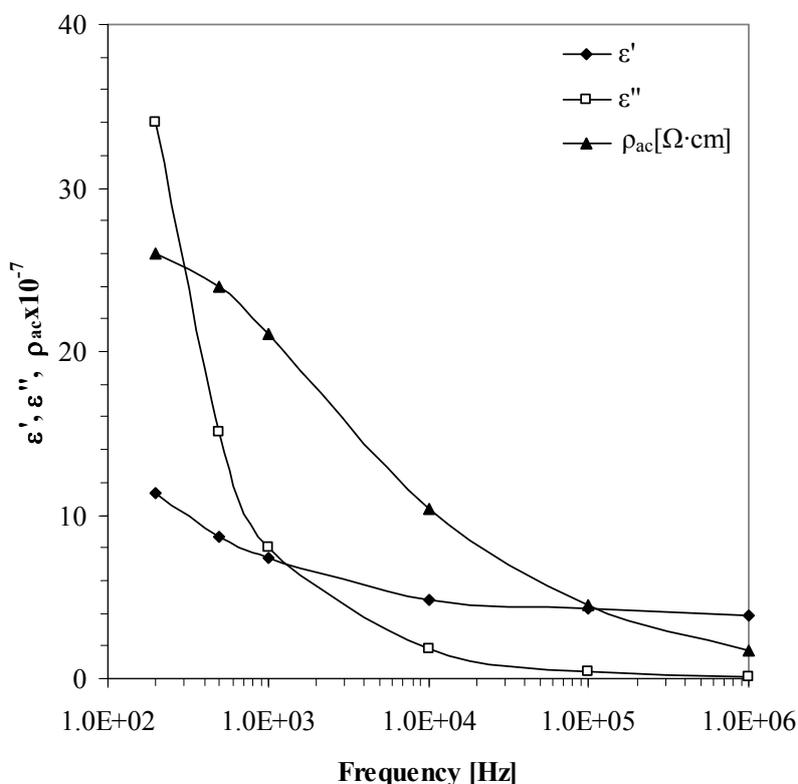


Fig. 3. Frequency dependence of dielectric constant (ε'), dielectric loss coefficient (ε'') and specific electric resistivity for alternating current (ρ_{ac}) at $T = 15^\circ\text{C}$ for sample 2.

Table 1. Electrophysical parameters of samples 1 and 2 measured at 15°C using alternating electric field with frequency of 800 Hz.

Sample	Parameters		
	ε'	ε''	ρ_{ac} [$\Omega \cdot \text{cm}$]
1	1.735	$1.6 \cdot 10^{-2}$	$1.4 \cdot 10^{11}$
2	7.8	9	$2.2 \cdot 10^8$

Increase in percentage of micro-pores is really - as we have supposed - one of the principal causes of occurrence of long-term processes of ρ_{dc} stabilization in sample 2 after activation of constant electric field.

It is seen from Fig. 3 that all three parameters ρ_{ac} , ε' and ε'' decrease with increase in the electric field frequency, which testifies according to known publications [15,16] that in sample 2 dipole-relaxation polarization mechanism functions caused by water molecules. The reason of decrease in the parameters ρ_{ac} , ε' and ε'' with the increase in frequency lies in the fact that water dipoles have no time to orient in the field direction [15,16], which means reduction of polarization. The increase in water sorption capacity of the sample causes strong growth of ε' and ε'' (polarization phenomenon) and conductivity (decrease of ρ) in sample 2. It is interesting to note that at room temperature sample 1 (Fig. 1, curve 1) reaches its maximum value ρ_{dc} of approximately $10^{14} \Omega \cdot \text{cm}$, that is by two orders of magnitude more than ρ_{dc} of hard Egyptian basalt [11]. In our opinion, there are two reasons of the observed high ρ_{dc} of STBF. First, when obtaining STBF firm basalt by melting, concentration of some ions (Al^{3+} , Fe^{3+} , Ti^{4+} , Ca^{2+} , Na^{1+} , K^{1+}) decreases. Second, increase in the role of current carrier scattering at numerous interface regions (surface of fibers) occurs. A similar effect takes place in the case of basalt rock, which in solid has smaller ρ_{dc} than in form of fine powder [11]. Comparison of our results with those known from other works [1, 4, 12, 13] has shown that untreated STBFs [1, 4, 13] present the following values: $\varepsilon'=2.2$ and $\rho_{ac}=10^{14} \Omega \cdot \text{cm}$ at $f=1\text{MHz}$, whereas [12] gives at the same frequency $\rho_{ac}=10^{15} \Omega \cdot \text{cm}$. If this ε' exceeds our results by not more than 30%, ρ_{ac} exceeds our results (see Table 1) by several orders of magnitude. In case of static measurements our maximum value $\rho_{dc}=9 \cdot 10^{13} \Omega \cdot \text{cm}$ is close to one of those obtained in [1, 4, 13]: $\rho_{ac}=10^{14} \Omega \cdot \text{cm}$. One of the possible reasons of the observed difference between our results and ρ_{ac} from other sources can be different behavior of frequency dependence of the parameter for untreated STBF samples. Unlike the sample 2, ρ_{ac} of sample 1 should increase with frequency growth. Since in the case of dipole-relaxation mechanism ε'' dependence on the electric field frequency reveals a peak, position of which strongly depends on

experimental conditions (air temperature, humidity and pressure) and structures of the sample (density and impurity content), research of the influence of these factors is an important problem [16]. No details concerning experimental conditions were given in [1,4,12,13]. Let us note that low humidity and pressure can cause high ρ_{ac} value. Our preliminary results show that the consideration of these factors (humidity, temperature and packing density of basalt felt) can really explain the reason of discrepancy between the values of electrophysical parameters.

4. Conclusions

Using alternating and constant electric field, for the first time electrophysical parameters (ε' , ε'' , ρ_{ac} and ρ_{dc}) of STBF samples on the basis of Armenian basalt rocks are measured at room temperature before and after leaching in chlorhydric acid. The following main results are obtained:

1. It is determined that after activation of constant electric field, both samples reveal first fast increase in ρ_{dc} with time and then relatively slow approaching its maximum value. Moreover, if sample 1 ρ_{dc} achieves the maximum value (approximately $10^{14} \Omega \cdot \text{cm}$) in 2 minutes, sample 2 achieves it in more than 2 hours. Gravimetric measurements have shown that in both STBF samples two distinct slopes are caused by the presence of water in large and relatively small pores. It is determined that high concentration of water molecules in sample 2 leads to strong growth of its ε' and ε'' parameters and to reduction of ρ_{ac} and ρ_{dc} by 3-4 orders of magnitude. This reduction for ρ_{dc} is 10 times more than for ρ_{ac} .
2. It is revealed that in STBF dipole-relaxation polarization mechanism functions caused by dipoles of water molecules. Moreover, slowing of relaxation processes is manifested stronger in sample 2. Water molecules are located in macro-, micro- and meso-pores. It is supposed that in micro-pores they are connected relatively stronger than in other pores. Hence, initial growth of ρ_{dc} is caused by fast displacement of dipoles in larger pores, and slow increase by dipoles in micro-pores. However, after leaching of STBF, percentage of micro- and a macro-pores increases several times at the expense of meso-pores time; hence, the role of delayed processes for ρ_{dc} increases strongly too (sample 2).
3. Comparison has shown that the values of ε' and ρ_{ac} parameters in the initial STBF obtained by us, are lower by 30% and 3–4 orders of magnitude, correspondingly, than the results from available publications. It is revealed that our value of $\rho_{dc} \sim 10^{14} \Omega \cdot \text{cm}$ coincides with the lower boundary of measurement interval of ρ_{ac} (10^{14} - $10^{15} \Omega \cdot \text{cm}$) known from other works. In comparison with hard Egyptian basalt, STBF felt made of Armenian basalt rock has doubled ρ_{dc} value. The possible reason of this difference is connected with low

concentration of various ions (current carriers) in STBF and high concentration of interfaces in the form of fiber surfaces which are strong scattering centers for the current carriers.

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