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The influence of hydrochloric acid treatment and temperature on the electro-physical properties of super-thin basalt fibers

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Abstract: Electro-physical parameters of super-thin basalt fiber (STBF) from Armenian basalt rocks are measured before and after hydrochloric acid treatment. It is shown that specific resistance and dielectric parameters of super-thin basalt fiber change essentially after hydrochloric acid treatment. The temperature dependence of these parameters was studied too. The probable cause of the change is an increase in the total amount of pores and modification of the share of pores of various sizes in STBF, followed by an increase of absorption of water molecules from the ambient medium. The results (in both alternating and direct electric fields) are interpreted within the framework of the dipole-relaxation mechanism of the polarization of water molecules in STBF pores.

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1. Introduction

As a porous and hard aluminosilicate material, basalt has wide industrial applications. From basalt rocks, conti–

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nuous basalt fibers are formed[1,2,3], which are used for heat- and sound-insulation[4] [1]. They are reinforcing materials for strengthening some composite compounds[5] [2]. Besides, due to their high thermal stability, ecological compatibility, and inertness to the majority of aggressive materials, basalt fibers are used for clearing industrial gas emissions without preliminary cooling [3].

Low-dimension basalt fibers with diameters of the order of microns are 1D crystals and possess all features of single crystal materials (quantum dimensional effect), being of keen scientific and practical interest. According to recent investigations, such systems are promising materials for highly sensitive gas sensors [4]. However application of basalt fibers has not received wide recognition because of insufficient examination of their physical and chemical properties [5]. Since basalt is dielectric, it is important to study its electro-physical properties under various conditions of temperature, humidity, chemical modification, etc. In the scientific literature there is a scarcity of such works, and the available papers only present research on basalt rocks [6]. 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 in a few papers[1,6,7].

This paper for the first time presents electro-physical and thermal characteristics of super-thin basalt fibers (STBF), with an average diameter less than 10 microns, from Armenian basalt rocks, measured using both direct current (dc) and alternating current (ac) fields before and after hydrochloric acid treatment.

2. Experimental materials and procedures

STBFs were prepared using standard technology[1,2,3] using Armenian basalt rocks (from Abovyan city). For technical applications STBFs are manufactured in the form of layered wool with spurious bulk density $D = 0.25$ g/cm^3, which is considerably lower than the real fiber density

$(D_R = 2.7 - 2.8$ g/cm$^3)$[1,2,3] [7]. 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 ac or dc fields were applied. Probes with the samples were attached to a fluoroplastic holder, with a specific resistance ($> 10^{17}$ $\Omega \cdot$cm) higher than that of the measured materials.

Treatment of STBFs in acids solution can result in a change in their structural and, hence, many physical properties. The treatment technique is known in the literature as "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 temperatures of 92-93°C in the hydrochloric acid solution with concentration 5 N for 30 minutes, and at the second one in the solution with concentration 1.5 N for 3 hours. After the first stage, the STBF sample was washed by distilled water to remove traces of Fe^{+3} ions and after the second stage to remove traces of Cl^{-1} ions. The samples were dried to a constant weight for 8 hrs at a temperature of 115-120°C. The initial sample, after leaching and drying, loses 51.5% of its weight. According to a chemical analysis, the end-product has the following structure: SiO$_2$ – 95.56%, Al$_2$O$_3$ – 2.25%, Fe$_2$O$_3$ – 0.8% (amounting to 98.61%).

Initial and chemically modified samples will be referred as samples 1 and 2, respectively. For these samples, specific electric resistance for direct ρ_{dc} and alternating ρ_{ac} current fields was measured; ε' and ε'' were determined as well. The specified parameters were measured at temperatures from 15°C to 25°C and the relative humidity of air not more than 50%. Parameters ε', ε'' and ρ_{ac} for basalt fibers were measured by means of a precise bridge for measurement of capacitances (TESLA BM 400 G). This bridge can measure the loss tangent tanδ to 0.1 and capacitance accurate to $\pm1\%$ at a fixed frequency of 800 Hz. To measure higher ε'', another transformer bridge circuit was developed and fabricated to measure tanδ 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 samples accurate to $\Delta G = 10^{-8}$ Ω^{-1} and $\Delta C = 0.05$ pF, respectively. 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.

The value of ε' was determined from the expression $\varepsilon' = C/C_0$, where C is the capacitance of a flat capacitor with a dielectric, and C_0 the capacitance without a dielectric. Parameter ε'' was calculated from the formula $\varepsilon'' = \varepsilon'$ tanδ

1 http://www.junantai.com/en/products/basalt/basalt_fiber.htm
2 http://www.bvolokno.ru/index.php
3 http://naftaros.ru/kompozitsionnye/bazaltovyetehno/
4 http://www.izhstroy.ru/catalog/articles/9/
5 http://naftaros.ru/articles/2/
6 http://naftaros.ru/articles/3/
7 http://naftaros.ru/articles/21/

and ρ_{ac} was determined by the formula $\rho_{ac} = (\varepsilon_0 \varepsilon'' \omega)^{-1}$, where ε_0 is the dielectric constant, and $\omega = 2\pi f$ is the angular frequency of the electric field [8, 9]. Specific resistance of the sample for direct current ρ_{dc} was determined by the dual-probe method using the formula $\rho_{dc} = US/Id$, where U is a direct-current voltage applied to the sample, I is a current passed through it, S is an effective area of the sample, and d is an 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 an electrometric voltmeter V7-30 that allows measurements of R up to $10^{18}\Omega$.

Before and after chemical treatment, the samples were heated to 150°C for 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). Parameter $(m-m_0) \cdot 100\%/m_0$ (where m_0 is 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 the relative change of the sample weight. The weight of the samples varied from 25 to 40 mg. Relative error in all types of the fulfilled measurements did not exceed 5%.

3. Results and their discussion

Fig. 1 presents ρ_{dc} dependences on duration of the applied dc field for samples 1 and 2. It is obvious from the curves that chemical treatment results in a decrease of ρ_{dc} by almost four orders of magnitude (Fig. 1, curve 2). For both samples, curves $\rho_{dc}(t)$ show rapid initial growth followed by a slow increase. Moreover, if in the case of sample 1, ρ_{dc} reaches its constant value in two minutes after switch-on 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, long-term relaxation processes takes place in sample 2. It is known that dielectric resistance grows depending on the activation period of the dc field, due to generation of polarization currents [8, 9]. We assume that the region of rapid growth of ρ_{dc} with time (Fig. 1) is caused by polarization of water molecules present in large fiber pores under the effect of the dc field, whereas the relatively slow increase is caused by polarization of water molecules present in smaller pores. Also, water in large pores is more weakly connected with the frame and is more mobile than in small pores. Hence, after activation of the dc field, at first, water molecules in large pores and later, water molecules in small pores are polarized. Therefore, after activation of the dc field,
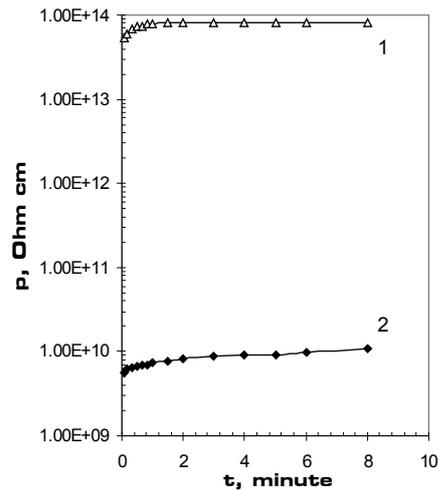

Figure 1. Dependence of specific electric resistance on duration of dc field for sample 1 (curve 1) and sample 2 (curve 2). Curves 1 and 2 were registered at temperature and relative humidity 24.2°C, 44.60% and 20.4°C, 49.9%, respectively. Spurious bulk density of both samples was 0.4 g/cm³.

rapid growth of ρ_{dc} with time t is followed by its slow increase. To find a correlation between the water content and behavior of ρ_{dc} within the specified parts of the $\rho_{dc}(t)$ curve, both samples were heated at 150°C for 1 hour; restoration of their weight with time was tracked. Fig. 2 shows the results of gravimetric measurements of the samples. The untreated sample (curve 1) loses less than 0.4% of its weight after heating and comes to its stable weight maximum in 2 minutes at room temperature, while the leached sample (curve 2) losses 15% of the initial weight and only comes to its stable weight in 30 minutes.

The results correlate with the results of the study of adsorption properties of various leached STBF samples obtained using thermo-gravimetric and differential thermal analysis [7].

Figs. 3 and 4 show the results obtained for a temperature dependence from 100 to 365 K of ε', ε'' and ρ_{ac} parameters for the chemically modified samples. It is seen from the graphs that electro-physical parameters of the initial and chemically processed samples are different depending on temperature. If ε' for the initial samples is constant within the whole investigated temperature interval, ε'' and ρ_{ac} show another behavior. Here, with an increase of temperature up to 300 K the ε'' increases (and ρ_{ac} decreases) and comes to saturation. However growth of ε'' within a range from 100 to 200 K occurs at a much lower rate than in the range from 200 to 300 K.

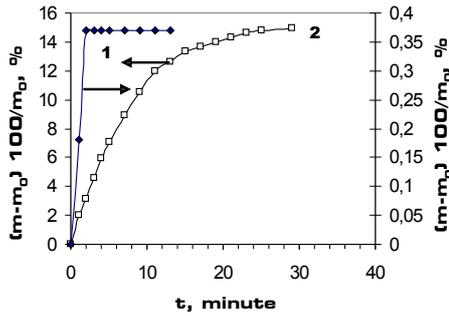The result is explained by the dipole-relaxation polariza-

Figure 2. Restoration of relative weight for samples 1 (curve 1) and 2 (curve 2) in time t after heating at temperature 150°C for 1 hour. Weighing was carried out in the air at 18°C. Both samples have almost identical bulk density of approximately 0.25 g/cm^3.
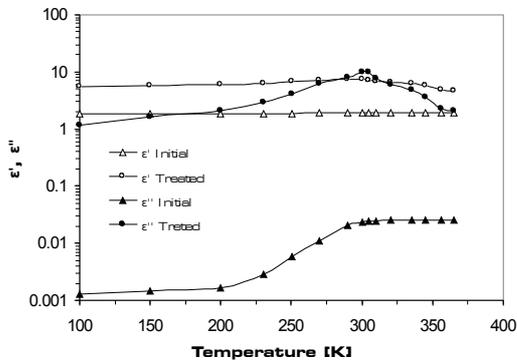

Figure 4. Temperature dependence of ρ_{ac} for the initial (1) and treated (2) STBF samples at the fixed density $D = 0.4$ g/cm^3. Relative humidity of air was 50%.

Figure 3. Temperature dependence of dielectric permeability ε' and dielectric losses ε'' for initial (1) and treated (2) sample of STBF at the fixed density $D = 0.4 g$/cm^3. Relative humidity of air was 50%.

Figure 5. Frequency dependence of dielectric constant ε', dielectric loss coefficient ε'' and specific electric resistance for alternating current ρ_{ac} at $T = 15$°C for sample 2.

tion mechanism of water existing in the basalt fibers. With increase of temperature, molecular forces between water dipoles are weakened, which should strengthen dipole–relaxation polarization. However, at the same time the energy of thermal movement of molecules increases, reducing the orienting effect of the field. With the increase of temperature, water evaporation also takes place and reduces the effect of polarization, too. Due to competition among these mechanisms, a behavior presented in Figs. 3 and 4 is observed. It is established that after acid processing, the water content in basalt fibers grows from 0.4% to 18% of its initial weight. This fact leads to a reduction of ρ_{ac} by three orders of magnitude and a reduction of ρ_{dc} by more than 3–4 orders (Figs. 1 and 4).

It is established that STBF contains three types (in size) of pores: macro–pores with diameter over 50 nm, meso–pores with diameters from 2 to 50 nm, and micro–pores
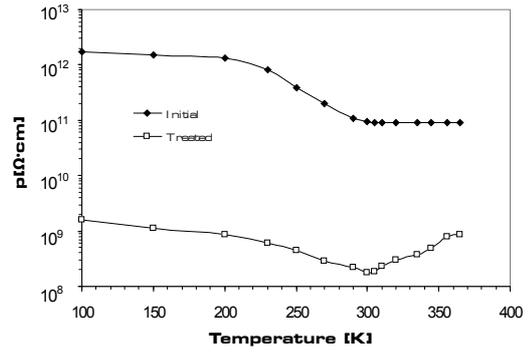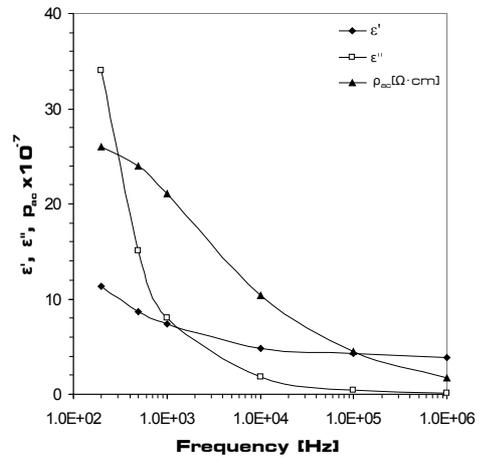
with diameter less than 2 nm. The fiber of the initial sample has the following size distribution of pores: 2% of macro–pores, 1% of micro–pores, and 97% of meso–pores [7]. Industrial leaching of STBF modifies the size distribution of the pores as follows: 9% of macro–pores, 4% of micro–pores, and 87% of meso–pores. Here, the increase in total concentration of pores and their average volume from 0.027 cm^3/g to 0.1341 cm^3/g also takes place [7]. The volume of pores (formed or released from various impurities and salt formations) is filled basically with water, resulting in a reduction of ρ_{dc} and ρ_{ac} by 3–4 orders of magnitude, as well as increases of ε' by a factor of 4.5 and ε'' by more than 500 times (see Table 1).

Increase in the percentage of micro–pores is one of the principal causes of long-term processes of ρ_{dc} stabiliza-

Table 1. Electro-physical parameters of samples 1 and 2 measured at 15°C using ac field with frequency of 800 Hz.

sample	ε'	ε''	$\rho_{ac}\,[\Omega\cdot\text{cm}]$
1	1.735	$1.6\cdot10^{-2}$	$1.4\cdot10^{-11}$
2	7.8	9	$2.2\cdot10^{8}$

tion in sample 2 in a dc field (Fig. 1).

It is seen from Fig. 5 that all three parameters ρ_{ac}, ε' and ε'' decrease with increase of the ac field frequency caused by the dipole–relaxation polarization mechanism of water molecules, which agrees with other researchers' results [8, 9]. The reason for the decrease of parameters ρ_{ac}, ε' and ε'' with the increase of frequency is that water dipoles have no time to orient in the field direction [8, 9], which means a 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 of ρ_{dc} at approximately 10^{14} Ω·cm, that is, by two order of magnitude more than the ρ_{dc} of hard Egyptian basalt rock [6].

In our opinion, there are two reasons for the observed high ρ_{dc} of STBF. First, when obtaining STBF fiber basalt by melting, the concentration of some ions (Al^{3+}, Fe^{3+}, Ti^{4+}, Ca^{2+}, Na^{1+}, and K^{1+}) decreases. Second, an increase of the role of current–carrier scattering at numerous inter-face regions (surface of fibers) occurs. A similar effect takes place in the case of basalt rock, which in a solid has smaller ρ_{dc} than in a fine powder [6]. Comparison of our results with those known from other works[8,9,10,11] has shown that untreated STBFs[8,9,11] present the following values: $\varepsilon' = 2.2$ and $\rho_{ac} = 10^{14}$ Ω·cm at $f = 1$ MHz, whereas[10] gives $\rho_{ac} = 10^{15}$ Ω·cm at the same frequency. If ε' exceeds our results by almost 30%, then ρ_{ac} exceeds our results (see Table 1) by several orders of magnitude. In case of dc field measurements our maximum value $\rho_{dc} = 9\cdot10^{13}$ Ω·cm is close to one of those obtained by others[8,9,11]: $\rho_{ac} = 10^{14}$ Ω·cm. One possible reason for the difference between our results and other sources could be

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[8] *http://www.junantai.com/en/products/basalt/basalt_fiber.htm*

[9] *http://www.izhstroy.ru/catalog/articles/9/*

[10] *http://naftaros.ru/articles/3/*

[11] *http://naftaros.ru/articles/21/*

a different behavior of frequency dependence of the parameter for untreated STBF samples. Unlike sample 2, ρ_{ac} of sample 1 should increase with frequency growth. Since, in the case of the dipole–relaxation mechanism, ε'' dependence on the electric–field frequency reveals a peak, the position of which strongly depends on experimental conditions (air temperature, humidity, and pressure) and structure of the sample (density and impurity content), research on the influence of these factors is an important problem [9]. No details concerning experimental conditions were given in other papers[8,9,10,11]. Low humidity and pressure, however, can cause a high ρ_{ac} value. The above-mentioned 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 electro–physical parameters.

4. Conclusions

Using direct and alternating current measurements, for the first time electro–physical parameters (ε', ε'', ρ_{ac} and ρ_{dc}) of STBF samples using Armenian basalt rocks are measured at room temperature before and after leaching in hydrochloric acid. The following main results are obtained:

1. For direct current measurements, both samples reveal a fast increase of ρ_{dc} with time and then a relatively slow increase approaching its maximum value. Moreover, if sample 1 ρ_{dc} achieves the maximum value (approximately 10^{14} Ω·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 small pores. A high concentration of water molecules in sample 2 leads to strong growth of its ε' and ε'' parameters and to a 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. In STBF, the dipole–relaxation polarization mechanism functions are caused by dipoles of water molecules in electric fields. Moreover, slowing of relaxation processes is manifested more strongly in sample 2. Water molecules are located in macro- micro- and meso-pores. It is supposed that in micro-pores they are connected more strongly 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, the percentage of micro- and macro-pores increases several times at

the expense of meso–pores; hence, the role of slow processes for ρ_{dc} increases strongly, too.

3. The comparison has shown that the values of ε' and ρ_{ac} in the untreated STBF obtained are lower by 30% and 3-4 order of magnitude, respectively, than the results from available publications. The value of $\rho_{dc} \sim 10^{14}$ $\Omega \cdot$cm here coincides with the lower boundary of the measurement interval of ρ_{ac} ($10^{14} - 10^{15}$ $\Omega \cdot$cm) known from other works. Compared with hard Egyptian basalt, STBF felt made of Armenian basalt rock has twice the ρ_{dc} value. The possible reason for this difference is connected to the low concentration of various ions (current carriers) in STBF and the high concentration of interfaces in the form of fiber surfaces that are strong scattering centers for the current carriers.

4. The electro–physical parameters of the initial and chemically processed samples are different depending on temperature. This result is explained by the dipole–relaxation polarization mechanism of water existing in the basalt fibers.

Acknowledgments

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