Effect of modification of nonwoven textiles with biochar and multi-walled carbon nanotubes on their dielectric properties

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Abstract. Dielectric properties of native nonwoven textile as well as textile with bound biochar and multi-walled carbon nanotubes in the frequency range of 10 to $5\cdot10^5$ Hz and at the temperatures of 30 to 60 °C have been investigated. The capacity of native nonwoven textile has been shown to decrease with the temperature according to the Arrhenius law. The activation energy of the temperature dependence of the capacity has been estimated to be 0.09 eV. It has been demonstrated that regardless of the temperature, the frequency dependence of the resistance of the nonwoven textile can be described by two exponential functions. In the presence of bound biochar and multi-walled carbon nanotubes in the nonwoven textile, the conductivity current was 4 orders of magnitude greater than the bias current and increased with the temperature according to the Arrhenius law. The activation energy of the temperature dependence of the inverse resistance (an analogue of the conductivity for homogeneous samples with the same dimensions) has been estimated to be 0.19 eV for the samples with multi-walled carbon nanotubes and 0.62 eV for the samples with bound biochar.

Keywords: nonwoven textile, bound biochar, multi-walled carbon nanotubes, dielectric properties, scanning electron microscopy, activation energy of conductivity, semi-conducting character of conductivity.

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1. Introduction

Different physical methods can be employed for detailed characterization of various textiles [1–7]. To our opinion, one of the main methods of these studies is dielectric spectroscopy [8], since the vast majority of textiles are dielectrics rather than conductors.

As follows from the analysis of the data published in the last five years, the dielectric properties of textiles were theoretically analyzed and studied in detail only in a small number of works (see *e.g.* [9–14]). The most detailed analysis of possible processes in native and modified textiles was performed in the review [9] and dissertation [10]. In [10], the results of the experimental studies are also provided, but mainly for the gigahertz range of the dielectric spectrum. The interest to this range is primarily caused by military tasks as it corresponds to the operation frequencies of thermal imagers. Studies of textiles in the GHz region of the dielectric spectrum were also carried out in [11, 12]. Since the present work concerns the dielectric measurements below 1 MHz as will be shown below, we will not analyze these literature results here.

The results of the studies of dielectric properties of textiles in the frequency range below 1 MHz are presented only in the works [13, 14]. In [13], in addition to the dielectric properties, other properties of the textiles were investigated. At this, the obtained data on the dielectric properties were not properly analyzed. In [14], mainly the dielectric properties were investigated, but the reasons for their changes induced by introduction of various impurities into the textiles were not analyzed. We believe that the reason for such a limited analysis of the obtained results was that the experimental studies were performed only at room temperatures.

The aim of this work is to study the dielectric properties of native and modified with carbon-based particles nonwoven textile (color catcher sheets) in the frequency range up to 1 MHz at the temperatures of 30 °C to 60 °C.

2. Devices and materials

Color catcher sheets (CCS) by Heitmann Farb- & Schmutzfangtücher (Brauns-Heitmann, Germany), developed to prevent color runs during washing, were used as a model nonwoven textile. The studied materials are soft and stable in water solutions for a long time. These materials can be efficiently used for immobilization of various molecules or nano- and microparticles [15]. Biochar produced by Biouhel.cz (Czech Republic) was prepared by pyrolysis of soft wood at 750 °C for 40 min. Prior to use, the biochar was ground using a knife laboratory mixer (Microtron Kinematika 550, Kinematica GmbH, Germany). The samples were sieved using 100 µm sieves. A fraction of the biochar below 100 µm was used for the modification of the nonwoven textile. Laboratory prepared multi-walled carbon nanotubes (MWCNT-COOH-Mn ferrite) containing 70 wt.% of Mn ferrite were provided by one of the authors of this article (SB).

Nonwoven textile (color catcher sheets 1×1 cm in size) with biochar and MWCNT was modified by immersing the textile squares in excess of particles suspension in methanol (10 mg/ml) overnight under mixing. The modified textile squares were subsequently dried at room temperature. Scanning electron microscopy images of both native and modified CCS are presented in Fig. 1.

Dielectric properties of the samples were measured using the oscilloscope method [16] in the frequency range of 10 to $5\cdot10^5$ Hz and at the temperatures of 30 °C to 60 °C. For the research, we used sandwich-type samples with a protective electrode. The sample area was 1.0 cm^2 and their thickness was 0.25 mm.

A time-varying sinusoidal voltage with the amplitude of 4 V was applied to the sample using a G3-112 generator. A resistance store, acting as a load resistance for a C1-93 oscilloscope, was connected in series to the sample. The voltage from the load resistance was applied to the Y coordinate of the oscilloscope. The X coordinate was supplied with voltage directly from the generator. For most frequencies, the oscillograms differed during the voltage rise and fall (the oscillograms had a shape close to elliptical). In particular, the voltage at the load resistance during the rise of the signal from the generator U_n was greater than the voltage during the fall U_s. Using the analysis carried out in [16], the values of the resistance and capacity were calculated as follows based on the obtained oscillograms.

The expression for calculating the sample resistance is

$$R = 2R_n \frac{U_x}{U_n + U_s}, \quad (1)$$

where R_n is the value of the load resistance, and U_x is the voltage, at which the capacity and resistance are calculated, respectively.

The expression for calculating the capacity is

$$C = \frac{U_n - U_s}{4\pi f \sqrt{U_0^2 - U_x^2}}, \quad (2)$$

where f is the frequency of the measuring signal, and U_0 is the amplitude value of the voltage of the measuring signal, respectively.

In our research, U_0 = 4 V and U_x = 2.4 V.

The sample temperature was maintained using a thermostat and a stabilization unit developed by us. A deviation from the set value of the temperature did not exceed 0.1 °C.

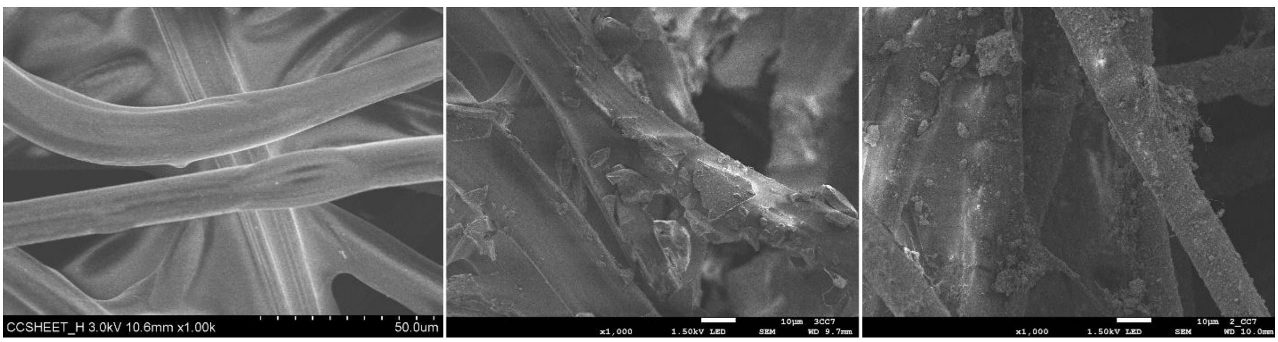

Fig. 1. From left to right: scanning electron microscopy images of native nonwoven textile, textile modified with biochar and textile modified with multi-walled carbon nanotubes. The magnification is 1000×.

3. Experimental results and their analysis

3.1. Dielectric properties of color catcher nonwoven textile

The dielectric properties of the substances homogeneous in bulk are characterized based on the frequency dependences of the components of the dielectric permittivity ε' and ε''. The textiles we studied, which were prepared in the form of nonwoven textile, were not continuous materials. Therefore, their dielectric properties cannot be characterized based on the frequency dependences of ε' and ε''. Since we studied the materials with the same geometric dimensions, we analyzed the frequency dependences of the capacity C and the resistance R or $1/R$ instead of the frequency dependences of ε' and ε''.

Fig. 2 shows the dependence of the capacity of the nonwoven textile on the frequency for the temperatures of 50 °C (curve *1*) and 60 °C (curve *2*) in double logarithmic coordinates. The same dependence was observed at the temperatures of 32 °C and 40 °C.

As can be seen from Fig. 2, the dependence of the capacity on the frequency for 32 °C and 60 °C can be described by the following relationship:

$$C = af^{-m}, \tag{3}$$

where a is the parameter (its value, depending on the temperature, practically did not change within the experimental error limits), and m is the exponent (its value is given in Table 1), respectively.

As can be seen from Table 1, the value of the capacity of the nonwoven textile decreases with the frequency according to the power law, and the value of the exponent slightly increases with the temperature.

As is known [8], electric polarization of matter mainly includes dipole and electronic components. For a measuring signal of 10 to $5\cdot10^5$ Hz, the electronic component practically does not change in magnitude. Therefore, the decrease in the capacitance with increasing the frequency means that the dipole component of polarization makes a significant contribution to the dielectric permittivity of the nonwoven textile. That is, the structural elements of the nonwoven textile are polar. This is confirmed by the temperature dependence of the capacity shown in Fig. 3.

Table 1. Parameters of Eqs. (5) and (6) characterizing the electrical properties of the nonwoven textile.

t, °C	n_1	n_2	*m*
32	0.35	1.14	0.13
40	0.39	1.16	0.15
50	0.36	0.91	0.16
60	0.37	0.86	0.19

It can be seen from Fig. 3 that the dependence of the capacity on the temperature for the nonwoven textile can be described by a straight line in the Arrhenius coordinates, which is equivalent to the following relationship:

$$C = C_\infty \exp\left(\frac{W(C)}{kT}\right), \tag{4}$$

where C_∞ is the capacity at the temperature $T = \infty$, $W(C)$ is the activation energy of the temperature dependence of the capacity, k is the Boltzmann constant, and T is the absolute temperature, respectively.

The most important parameter in the relation (6) is the activation energy, which is equal to 0.09 eV according to our estimates.

The frequency dependences of the resistance of the nonwoven textile for the temperatures of 50 °C (*1*) and 60 °C (*2*) in the coordinates $\lg R = \varphi(\lg f)$ are shown in Fig. 4.

It may be concluded from the analysis of the presented data that they can be described by the following relationship:

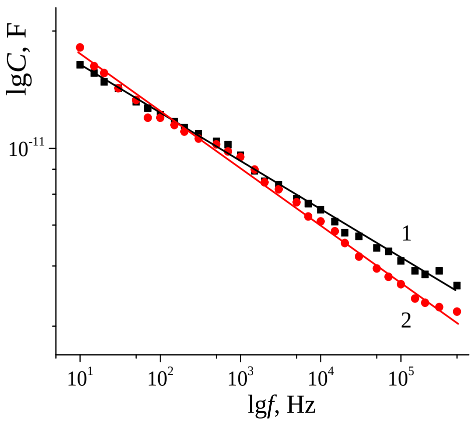

Fig. 2. Dependence of the logarithm of capacity on the logarithm of frequency for the nonwoven textile at the temperatures of 50 °C (*1*) and 60 °C (*2*).

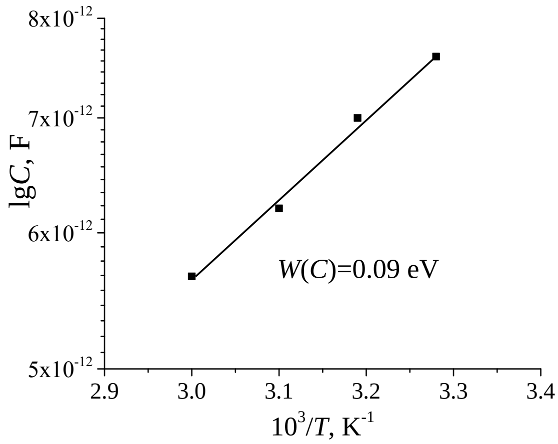

Fig. 3. Temperature dependence of the capacity of the nonwoven textile at the frequency of 10^4 Hz.

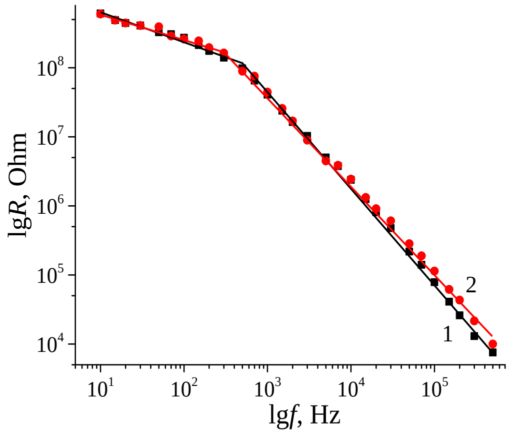

Fig. 4. Frequency dependences of the resistance of the nonwoven textile in the coordinates lg$R$ = φ(lg$f$) for the temperatures of 50 °C (*1*) and 60 °C (*2*).

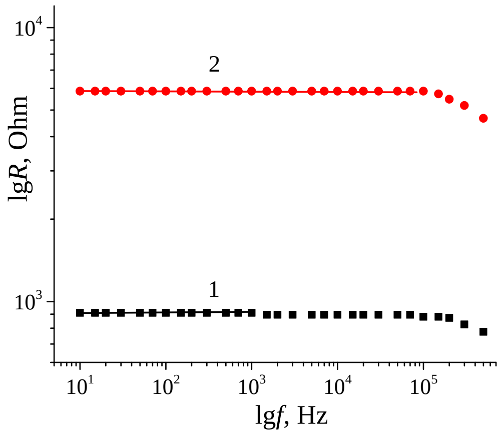

Fig. 5. Frequency dependences of the resistance of the nonwoven textile with biochar (*1*) and MWCNTs (*2*) at the temperature of 60 °C.

$$R = b_1 f^{-n_1} + b_2 f^{-n_2}, \qquad (5)$$

where b_1 and b_2 are the constants, n_1 and n_2 are the power exponents for the dependence of the resistance on the frequency, respectively.

As in the case of the capacity dependence on the frequency, we did not analyze the temperature dependences of the parameters b_1 and b_2, but only the temperature dependences of the parameters n_1 and n_2. The values of n_1 and n_2 for different temperatures are listed in Table 1. From the analysis of the obtained data, a more unambiguous conclusion may be drawn regarding the ratio between n_1 and n_2 (the value of n_1 is almost 3 times smaller than n_2). No clear dependence of the parameters n_1 and n_2 on the temperature can be ascertained.

It was shown above that the capacity of the nonwoven textile changes exponentially with the temperature. Unlike the capacity, it was not possible to ascertain a clear functional dependence of the resistance of the nonwoven textile on the temperature.

3.2. Dielectric properties of nonwoven textile modified with biochar and MWCNTs

When biochar or MWCNTs was introduced into the nonwoven textile, the resistance of the latter decreased by more than 4 orders of magnitude, which led to an increase in the active component of the current. At the sufficiently high values of 1/R, it was not possible to determine the reactive component with sufficient accuracy for analysis by using the oscilloscope method. Therefore, the changes caused by introduction of biochar or MWCNTs into the nonwoven textile will be further analyzed based on the change in the resistance R or 1/R (analogue of the conductivity for homogeneous samples).

It may be concluded from the analysis of the data presented that at low frequencies, the resistance (and

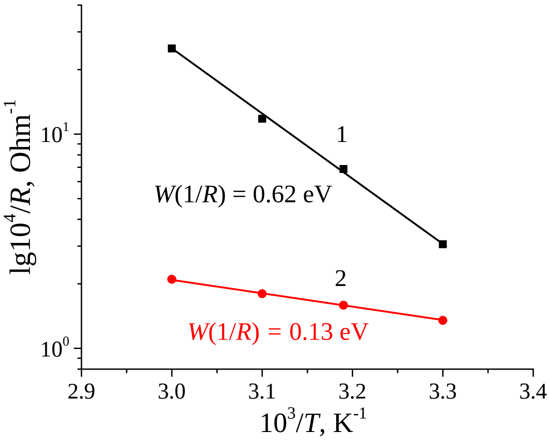

Fig. 6. Temperature dependence of the logarithm of the inverse resistance on the inverse absolute temperature for the nonwoven textile with biochar (*1*) and MWCNTs (*2*).

hence the conductivity for homogeneous samples) does not depend on the frequency. In this case, the inverse value of the resistance for the samples with the same geometric parameters may be considered as an analogue of conductivity.

Fig. 6 shows the temperature dependence of 1/R on the inverse temperature in the Arrhenius coordinates for the nonwoven textile with biochar (curve *1*) and MWCNTs (curve *2*). It is clearly seen from this figure that both for biochar and MWCNTs modification, a linear dependence of the logarithm of 1/R on 1/T is observed. As in the case of the dependence of the capacity of the nonwoven textile on the temperature, such a dependence of 1/R on 1/T can be described by the relation

$$1/R = B\exp\left(-\frac{W(1/R)}{kT}\right), \qquad (6)$$

where the coefficient B is equal to the inverse resistance at the temperature $T = \infty$, and $W(1/R)$ is the activation energy of the temperature dependence of $1/R$, respectively.

It has been found from the analysis of the temperature dependences shown in Fig. 6 that the $W(1/R)$ is equal to 0.19 eV in the case of the presence of MWCNTs in the nonwoven textile, while it is equal to 0.62 eV in the presence of biochar impurities.

4. Conclusions

1. Since the investigated nonwoven textile samples without/with modification with biochar and multilayered carbon nanotubes had the same geometric dimensions and were heterogeneous in bulk, their dielectric properties were proposed to study based on the analysis of the frequency dependences of the resistance R (or $1/R$) and capacity C instead of analyzing the components of the complex dielectric permittivity.

2. It was shown that the capacity of the native nonwoven textile decreases with the frequency according to the power law regardless of the temperature. This dependence may be explained by the significant contribution of the dipole component of polarization of the nonwoven textile.

3. It was found that the temperature dependence of the capacity of the nonwoven textile can be described by a linear dependence in the Arrhenius coordinates. The activation energy for such a temperature dependence was estimated to be 0.09 eV.

4. It was shown that in the presence of biochar and MWCNTs in the nonwoven textile, the resistance value decreases by more than 4 orders of magnitude. At the same time, as in the case of the temperature dependence of the capacity, the logarithm of the inverse resistance is a linear function of the inverse temperature.

5. The value of the activation energy of the temperature dependence of the inverse resistance of the samples as a function of the inverse absolute temperature was estimated. It was shown that in the case of MWCNTs modification, the activation energy of the temperature dependence of the logarithm of $1/R$ on $1/T$ is 0.19 eV, while it is equal to 0.62 eV in the presence of biochar in the nonwoven textile.

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Kolanowska A.: investigation.
Boncel S.: conceptualization, resources, project administration.
Mariano J.: investigation.
Zolochevska K.: sample preparation technology.
Kovalchuk T.M.: project administration, writing – review & editing.
Kopčanský P.: resources, investigation, visualization, writing – review & editing.
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Вплив модифікації нетканого текстиля біовугіллям та багатошаровими вуглецевими нанотрубками на його діелектричні властивості

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Анотація. У діапазоні частот 10…5·10^5 Гц і температур 30…60 °С досліджено діелектричні властивості нетканого текстиля, немодифікованого та модифікованого біовугіллям та багатошаровими вуглецевими нанотрубками. Показано, що ємність немодифікованого текстиля зменшується з ростом температури за законом Арреніуса. Оцінено енергію активації для температурної залежності ємності. Її величина становить 0,09 еВ. Показано, що незалежно від температури частотну залежність опору текстиля можна описати за допомогою двох експоненціальних залежностей. При наявності у текстилі біовугілля та багатошарових вуглецевих нанотрубок струм провідності був на 4 порядки більшим, ніж струм зміщення, і збільшувався з ростом температури за законом Арреніуса. Оцінено енергію активації для температурної залежності величини, оберненої опору (аналог провідності для зразків з однаковими розмірами). Для зразків з багатошаровими вуглецевими нанотрубками вона дорівнює 0,19 еВ, а для зразків з біовугіллям – 0,62 еВ.

Ключові слова: нетканий текстиль, біовугілля, багатошарові вуглецеві нанотрубки, діелектричні властивості, скануюча електронна мікроскопія, енергія активації провідності, напівпровідниковий характер провідності.