The Effect of Temperature on Electric Conductivity of Polyacrylonitrile-Polyaniline Fibers

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ABSTRACT The article presents an analysis of the influence of temperature on the electrical conductivity of composite polyacrylonitrile-polyaniline fibers (PAN/PANI). The fibers are obtained by synthesizing polyaniline directly in the spinning solution of fiber-forming polyacrylonitrile and characterized by X-Ray Diffraction (XRD), Differential Scanning Calorimetry (DSC), Scanning Electron Microscopy (SEM) methods. Electrical characterization of fibers is performed by current-voltage characteristic. The polarizing voltage of the electrodes in the range from -1 V to 1 V with a speed of 100 mV/sec is changed cyclically and linearly while simultaneously the current is measured. The current-voltage characteristic of the fibers is recorded at various temperatures in the range from -15 °C to 100 °C for 30 min. Based on the measurements, temperature changes in the conductance are determined in constant relative humidity. The current-voltage characteristics of the fibers in the ambient atmosphere with a relative humidity of 38 % are linear and symmetrical, which indicates the electron nature of the conductivity and the ohmic contact of the electrode-fiber. The characteristic of temperature conductance changes is not of a typical shape, it is parabolic. The conductance of the developed PAN/PANI fibers at 22 °C is about $1.50 \cdot 10^{-4}$ S (6.7 kΩ) and decreases below and above this temperature. The analysis of research results and literature data enables the determination of individual factors affecting changes in conductance of the tested composite fiber.

INDEX TERMS Composite materials, conductivity measurement, current-voltage characteristics, polymers, textile fibers.

I. INTRODUCTION

The development of electronics and electrical engineering is determined by materials with extremely different electrical properties and good thermal stability. On the one hand, good conductors are necessary and on the other, excellent dielectrics with a strictly defined dependence of their electrical parameters on temperature. Good electricity conductors are metal elements and alloys, most often used to make electrical sockets. Enamel and polymeric materials are excellent dielectrics. The latter, regardless of their form, are typical dielectric materials. For this reason, polymeric materials are commonly used as electrical insulators. Composites such as polymer-silver or polymer-carbon black are used to make conductive layers [1], [2]. Polymers are also used to build humidity sensors, sensors of various gases or biosensors [3]–[8]. In addition, polymeric materials are currently widely researched in connection with the development of the so-called wearable electronics and 3D printing [9]–[11]. In case of these technologies, the possibility of modifying the electrical parameters of the polymers used is being sought for [12], [13]. Introducing electrically conductive fillers into the polymer matrix is one of the ways to increase the conductivity of plastics. Various types of conductive carbon blacks, carbon fibers, carbon nanotubes, graphite, graphene or metal powders are used as electrically conductive admixtures [12], [13]. The resistivity of the obtained composites containing a small amount of conductive filler is almost the same as the polymer matrix resistivity. A significant and distinct decrease in the composite resistivity is observed, only after reaching the so-called critical content of the admixture (after exceeding the percolation threshold). This significant change in composite conductivity is due to the formation of conductive tracks in the non-conductive polymer.

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Electrically conductive polymers characterized by high conductivity are an interesting group of polymers that differ from typical polymers [15], [16]. Among these types of multi-molecular materials, much attention is paid to polyaniline (PANI) because it is a material that is obtained by simple and cheap synthesis methods [17]. In addition, PANI is characterized by good stability in ambient conditions and it is possible to control its electrical conductivity. Despite the afore-mentioned advantages of PANI, it is difficult to obtain conductive layers or fibers from it for applications in flexible electronics. For this reason, one of the research directions is the use of PANI in the process of creating various composite materials [18], [19]. Such materials can be used, for instance, to manufacture:

- anti-corrosive coatings [20],
- electrodes [21],
- supercapacitors [22],
- chemo-resistors for gas detection [23],
- biosensors [24], etc...

Conductive polymer fibers were obtained by depositing PANI on cotton fibers [25] or polyester [26]. Whereas electrically conductive fibers of polyaniline were formed by electrospinning [27], [28]. The mechanical strength of PANI nanofibers and PANI layers deposited on cotton or polyester fibers is not satisfactory. For this reason, despite their high electrical conductivity, these materials cannot be used in the so-called wearable electronics. However, fiber-forming polymers can be doped with electrically conductive polymers to obtain textiles with satisfactory mechanical parameters. Polyacrylonitrile is the example of such a polymer. Polyacrylonitrile fibers (PAN), from the moment they appeared on the world market, have established themselves as one of the best textile raw materials. Their specific properties, specific utility value and cheap raw material base contributed to this.

The advantages of PAN fibers, determining their technical and protective applications, include:

- high resistance to sunlight, long-term insolation causes only a slight deterioration of strength
- resistance to mineral acids, weak bases, most organic solvents and high biological resistance to bacteria, enzymes
- stability of strength properties in a wide temperature range ($-30\,°C$ to $+280\,°C$).

The electrical characterization of each material requires determining not only its resistivity but also the influence of temperature on this parameter. The temperature is the main factor that effects on the concentration and mobility of electric charge. The literature on the subject of polyaniline discusses the mechanisms of electric charge transport in this material rather extensively [15], [16], [29]. There are literature reports regarding the influence of temperature on the conductivity of PANI and blends based on polyaniline [30]–[34], while there is no data on composite fibers in which PANI is an additive.

In this article, we present the results of the research on the effect of temperature on the electrical properties of these fibers obtained by the standard wet method from a spinning solution of polyacrylonitrile (PAN). The tests were carried out in the range from $-15\,°C$ to $100\,°C$ by the DC method. A two-electrode system was used because the fibers cannot be measured in a four-electrode system. The conductivity of these fibers at ambient temperature is about $150\,\mu S$ ($6.7\,k\Omega$) while pure PAN fibers have a resistance of around $100\,G\Omega$. Below the ambient temperature, their conductance decreases, but it also decreases when the temperature rises to $100\,°C$. The conductance of fibers exposed to low temperature changes in a fully reversible way, while the conductance of fibers exposed to a temperature above $60\,°C$ changes irreversibly. The initial characterization of the obtained PAN/PANI composite fibers was presented in our earlier article [35].

II. MATERIALS AND METHODES

A. MATERIALS

Polyacrylonitrile (PAN) (Good-Fellow Co.) was used as a fiber-forming polymer, which contained 99.5 wt.%. polyacrylonitrile and 0.5 wt.%. methyl polyacrylate. Polyaniline was prepared from aniline chloride $C_6H_7N \cdot HCl$ (Sigma-Aldrich Co.) and ammonium persulfate $(NH_4)_2S_2O_8$ (POCH, Poland). Dimethylformamide (DMF) (Chempur, Poland) was used as a solvent in the processes.

B. SYNTHESIS METHOD

Two polyacrylonitrile solutions in dimethylformamide containing 1 wt.%. of PAN were prepared. 0.5 mole of aniline hydrochloride was added to one and 0.6 mole of ammonium persulfate to the other. Then the two solutions were mixed together. The reaction was carried out at a temperature not exceeding $4\,°C$, mixing the solution for 4 hours. The reaction mixture was filtered to remove large colourless crystals formed (Figure 1a). On the other hand, the SEM observations showed that the filtrate contained cube-shaped PANI particles (Figure 1b).

13.5 wt.% polyacrylonitrile was added to this solution, heated to $40\,°C$ and stirred for 2 hours. The obtained spinning solution was cooled. The average masses of polyacrylonitrile and polyaniline were determined by gel permeation chromatography (GPC). The weight average molecular weight of polyacrylonitrile (Mw) and the number average molecular weight (Mn) of polyacrylonitrile were $Mw = 6.446 \cdot 10^5$ and $Mn = 1.774 \cdot 10^5$, respectively. The PAN polydispersity index was 3.634. The weight average molecular weight determined by this method and the number average molecular weight of the polyaniline formed in DMF were: $Mw = 1.292 \cdot 10^4$ and $Mn = 4.263 \cdot 10^3$, and the polydispersity index was about 3.031. Thus, the average molecular weights of PAN were higher than those of PANI.

C. FORMATION OF FIBRES

Composite polyacrylonitrile-polyaniline (PAN/PANI) fibers were obtained by wet method [35], [36]. This method is
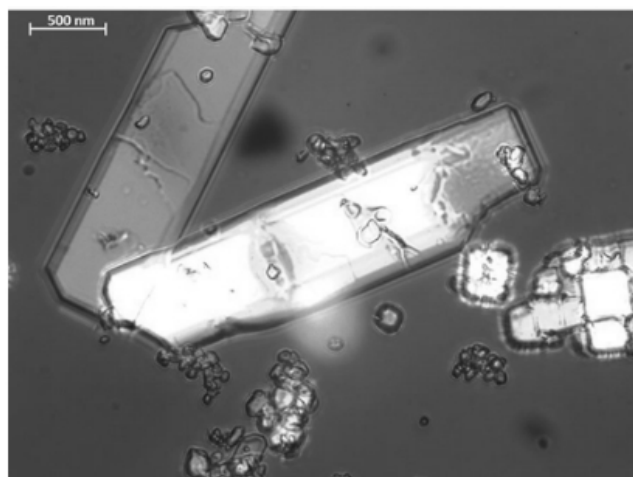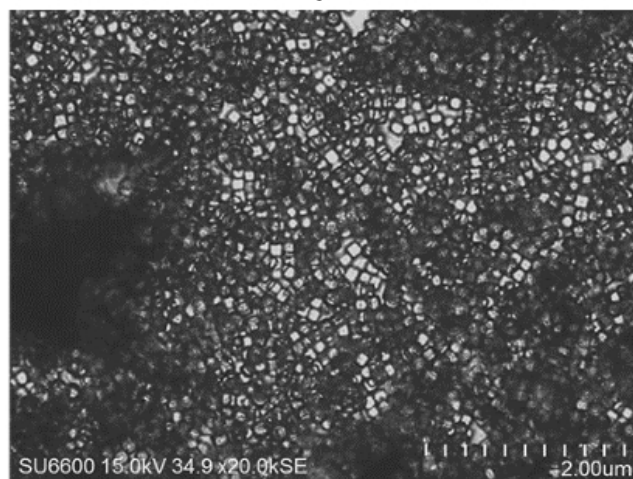
FIGURE 1. Precipitation in solution after synthesis reaction PANI in DMF with 1% PAN, a) large colourless crystals, b) cube-shaped PANI particles.

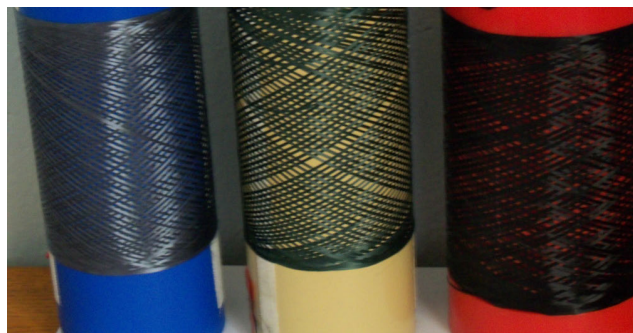very good repeatability and the possibility of obtaining fibers of any length.

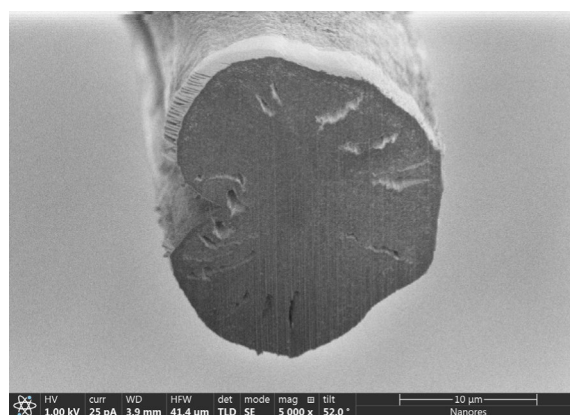**FIGURE 2.** The polyacrylonitrile-polyaniline (PAN/PANI) fibers on the coils.

FIGURE 3. Cross-section of PAN/PANI composite fiber.

commonly used to obtain polyacrylonitrile fibers (PAN). A typical fiber spinning solution PAN was prepared by dissolving polyacrylonitryle (13.5 wt. %) in dimethylformamide (DMF) at 40°C. The spinning solution, after passing through the nozzle, was introduced into a solidifying bath in which PAN coagulates in the form of fibers. Then the fibers underwent a coagulation bath. In a solidifying bath (60 % aqueous DMF solution) at 20 °C and in a plasticizing bath (50 % aqueous solution of DMF) at a temperature of 70 °C, the solvent and other substances from the formed fibers were removed intensively. The composite fibers underwent stretching process only in a plasticizing bath. During this process the orientation of macromolecules takes place and the fiber structure is ordered, which improves the mechanical properties of the fibers. The resulting composite fibers PAN/PANI did not undergo stretching in the steam because they cracked. The formed and stretched fibers were wound on coils (Figure 2). The obtained fibers are characterized by

As shown in Figure 3, composite fibers obtained by the standard wet method contain numerous of pores. For that reason, their strength is lower than polyacrylonitrile fibers.

The formed PAN/PANI composite fibers were initially characterized and the obtained test results are presented in the article [35]. Based on the research presented in this article, it was found that:

- PAN/PANI fibers diffraction patterns have distinct peaks corresponding to the pseudo orthorhombic phase of PANI (Figure 4) [37]–[39]. These results also reveal that PANI has interactions including hydrogen-bonding and electrostatic attraction with the PAN chains.
- The degree of crystallinity of PAN/PANI fibers determined by the Hinrichen method was 0.32 and was much smaller than in the PAN fibers, which was 0.53. The reason for the lower degree of crystallization is the occurrence of interactions between nitrile (PAN) and amino (PANI) groups, which is also indicated by data in the literature [40].
- The mean crystallite dimension, determined by the Debye-Scherrer equation, in PAN was 5.7 nm, and in the polyaniline it was bigger and amounted to17.9 nm.
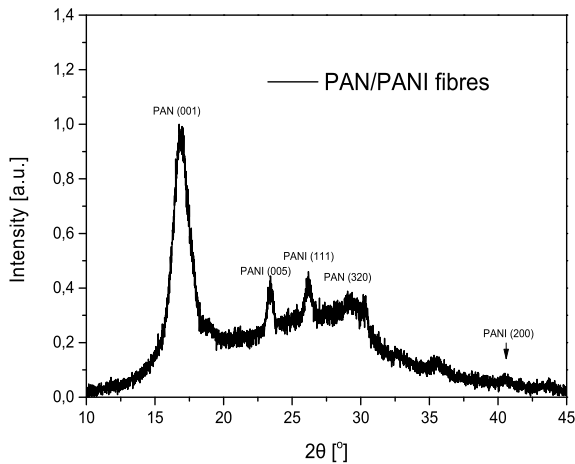- Three mass losses were found on the basis of the DTG (differential thermal analysis curve): the first between

FIGURE 4. Diffractometer of the composite PAN/PANI fibers.

25 and 100 °C, the second between 200 and 300 °C and the third one around 420 °C.

- The first peak is caused by the removal of water absorbed in fibers. As is known, polyaniline has a high water absorption capacity, which binds strongly or weakly. Water molecules weakly bound are connected to the PANI chain with one hydrogen bond. If they are connected with two hydrogen bonds, most often connecting two neighbouring PANI chains, then they are bound tightly.
- DSC analysis of fibers test results showed that below 100 °C there is an endothermic peak associated with water desorption. The intensity of water desorption decreases above 60 °C, while the decrease rate of this peak intensity is higher for PAN/PANI fibers than for PAN fibers (Figure 5).
- Polyacrylonitrile fibers are characterized by a much more homogeneous structure and lower porosity in comparison to composite PAN/PANI fibers [35], [41].
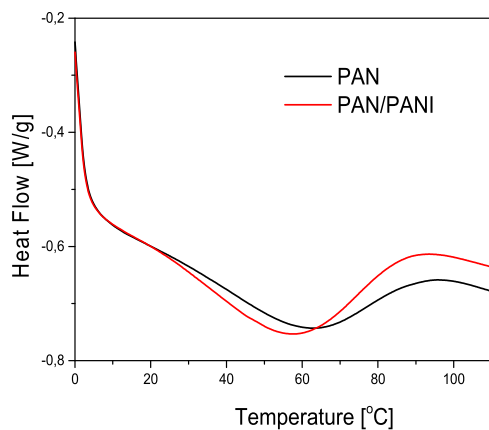

FIGURE 5. Differential scanning calorimetry (DSC) curve of PAN/PANI and PAN fibers during heating.

III. RESULTS OF ELECTRICAL INVESTIGATION AND DISCUSSION

Electrical characterization of composite PAN/PANI fibers was performed by current-voltage characteristics in a

two-electrode system because there was no possibility of electrical characterization of the fibers in a four-electrode system. The I-V characteristics of the fibers at various temperatures were recorded by means of the SI 1287 potentiostat-galvanostat (enabling measurement up to 0.4 nA) from Solartron using CorrWare and CorrView software from Scribner. During the measurements with this method, the polarizing voltage of the electrodes was changed cyclically and linearly, and at the same time the electric current was measured. The rate of voltage change was 100 mV/sec. The voltage was varied in the range 1 V to −1 V. At each temperature, measurements were made continuously over a period of 30 min.

Tests of electrical conductivity were performed along the fibers (along the long axis of fibers). Before measurements, the samples were stored in an atmosphere with a temperature of 22 ± 1 °C and a relative humidity of 38 %.

In order to perform the electrical characterization, the fibers were fastened between two substrates made of alundum ceramics. Gold electrodes made by screen printing were located on one of the substrates. The distance between the electrodes was 5mm (Figure 6).
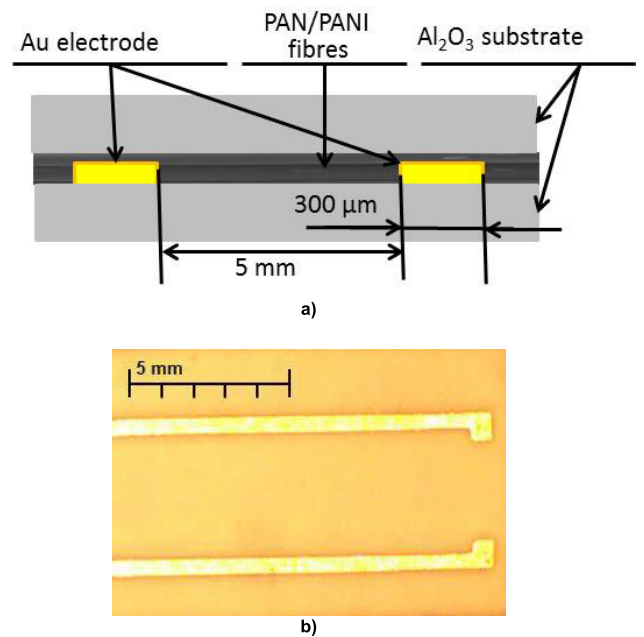

FIGURE 6. a) The scheme; b) electrodes of the measuring system for the electrical characterization of fibers.

The current-voltage characteristics of fibers in an ambient atmosphere with low relative humidity of 38 % were linear and symmetrical in the temperature range from 25 °C to −15 °C and again to 25 °C (Figure 7).

This indicates the electron nature of conductivity and the ohmic contact of the electrode - fiber. The slope of these characteristics I = f(U) increases with the rise of measurement temperature, and therefore the increase in temperature causes an increase in the conductivity of fibers. Such conductance changes are characteristic of semiconductors. At a
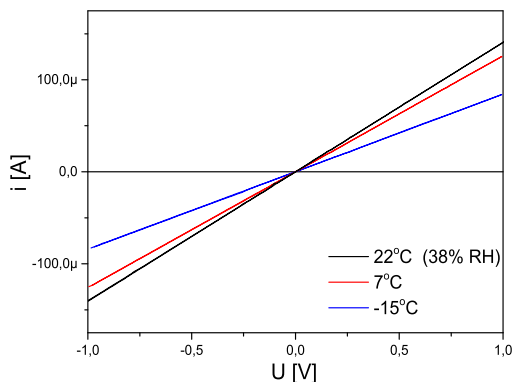
FIGURE 7. Current-voltage characteristics of PAN/PANI composite fibers during cooling.

temperature below the ambient temperature, the conductance of the fibers was setting fast at a stable level (Figure 8).

After measurements at −15 °C, the conductance of fibers returned to the initial value, characteristics of the ambient temperature, and did not change over time (Figure 9).

During the temperature rise, the current-voltage characteristics of the composite fibers also showed a linear character (Figure 10), and their slope was also smaller than of that measured at ambient temperature. This indicates that the conductance of fibers decreases as the temperature rises.

In contrast to the conductance changes at temperatures below ambient temperature, the conductance value decreased when the measurement temperature was above the ambient temperature (Figure 11). The most significant changes in conductance value over time were found when the measurement was carried out at a temperature of 50 °C (Figure 11).

Unfortunately, the slope of the current-voltage characteristics was much smaller than the initial one after the fibers were cooled to 22 °C (Figure 12). The value of fibers conductance decreased threefold.

The conductance of these fibers did not change significantly even after 72 hours from the end of measurements at 100 °C. It still did not reach the set value and increased very slowly (Figure 13). The measurements were made at ambient temperature, i.e. at 22 °C. This slow increase in conductance over time may be due to the absorption of water vapor from the surroundings.

Based on the current-voltage characteristics of these fibers (Figure 7 and 10), temperature changes of conductance in the atmosphere with constant relative humidity were determined (Figure 14). The temperature range was selected based on the DSC and DTG (differential thermal analysis curve) results of studies which were presented in the article [35].

This characteristic has a unique, rare, almost parabolic shape.

Conductivity as a function of temperature of various materials usually decreases linearly (metals) or increases exponentially (semiconductors). However, materials with almost parabolic characteristics of temperature resistance changes are also known. An example of such materials are thick
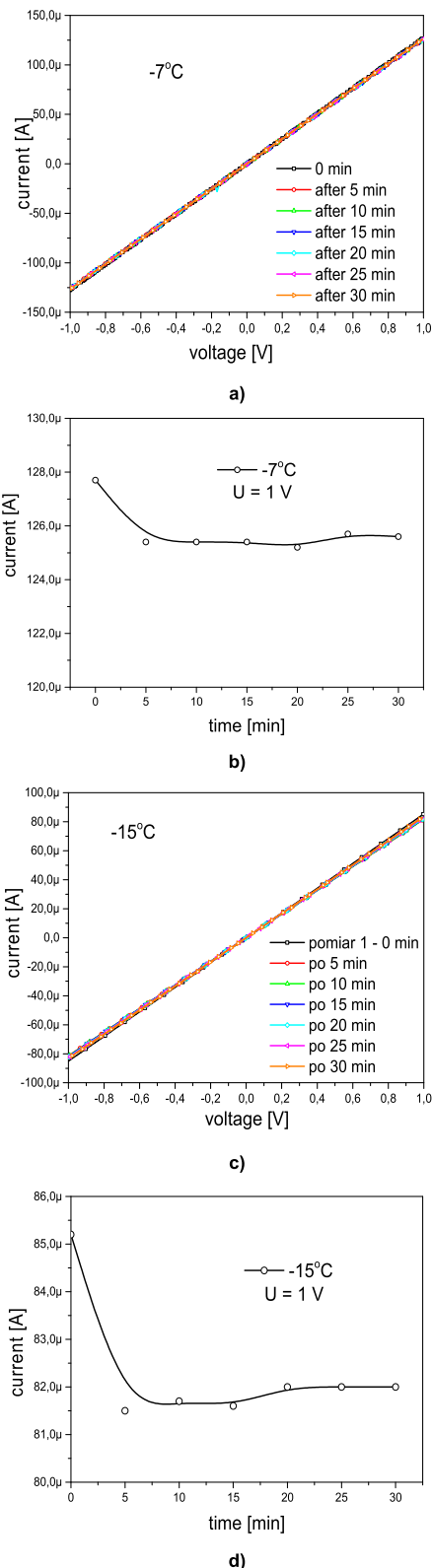

a)

b)

c)

d)

FIGURE 8. Current-voltage (a, c) and current (b, d) characteristics as a function of measurement time at a), b) 7 °C; c), d) −15 °C.

film composite resistors that contain conductive particles, for example ruthenium dioxide, and an amorphous glass matrix [42].
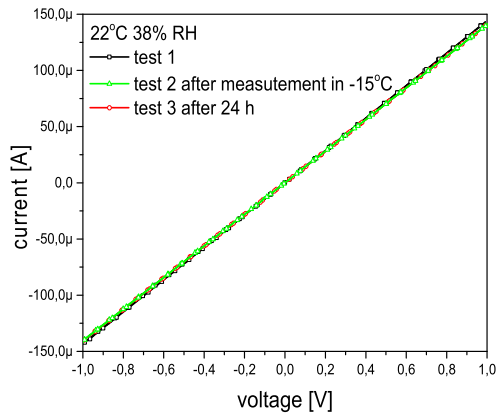
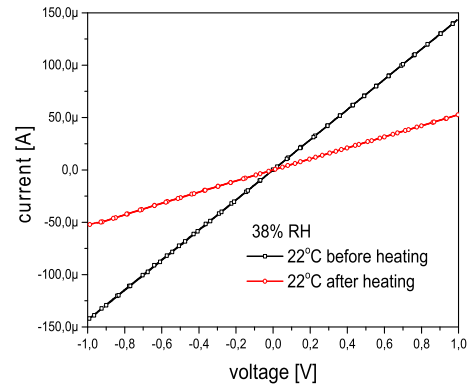**FIGURE 9.** Current-voltage characteristics as a function of measurement time taken at ambient temperature.
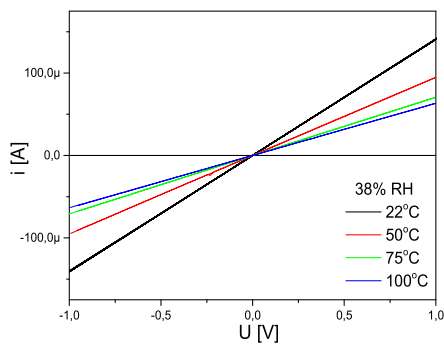

FIGURE 10. Current-voltage characteristics of PAN/PANI composite fibers during heating.
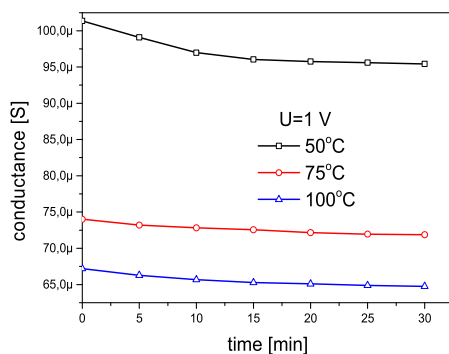
FIGURE 11. Change of conductance of composite PAN/PANI fibers in time at 50, 75 and 100 °C.

FIGURE 12. Current-voltage characteristics of PAN/PANI composite fibers before and after heating.

FIGURE 13. A change in time in: a) conductance; b) current-voltage characteristics of fibers during measurements at ambient temperature.

Many researchers have attempted to explain the causes of parabolic changes in resistance as a function of temperature of such composite materials and they have proposed various theories. Some believe that such behaviour of thick composite layers is a consequence of electron percolation [1], [42], [43]. According to this theory, conductivity is mainly determined by electron jumping as a result of tunnelling electrons through potential barriers formed by thin glass layers separating conductive particles. In addition, they suggest the presence of two competing effects causing a temperature coefficient of resistance of a different sign [43]. It is also believed that the increase in resistance with the rise of temperature is caused
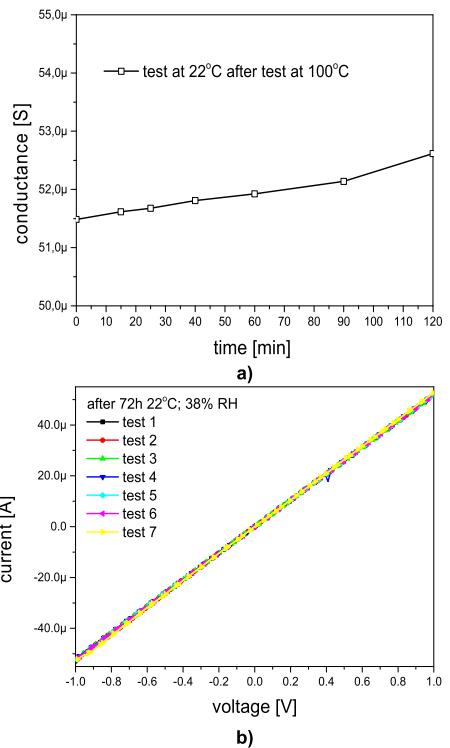
by the growth of the height of the tunnelling potential barrier under the influence of temperature [44].

Other scientists have pointed out that such characteristics may be the result of mechanical stress occurring between the resistor and the substrate due to the difference in the coefficients of thermal expansion of these materials [45]–[47]. The geometrical dimensions of the resistor printed onto the substrate change during heating. Consequently, the distance between the conductive grains changes, causing a change in resistance. In addition to the afore suggested factors, as it is well known, temperature causes a direct change in the concentration and mobility of electric charge carriers.
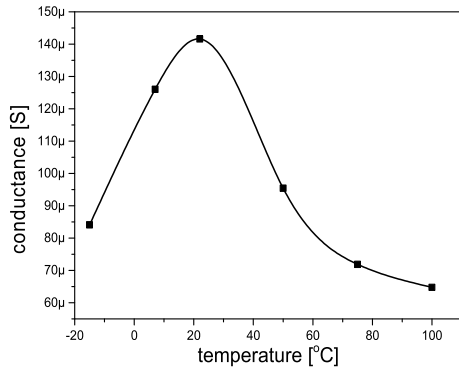
FIGURE 14. Temperature changes of conductance of PAN/PANI composite fibers.

This is also suggested in the case of polyaniline with secondary dopant [33].

In contrast to the theories discussed above regarding two-phase resistors having the form of a composite layer containing an amorphous glass matrix and polycrystalline conductive particles, the tested composite fibers are made of a semicrystalline dielectric matrix of the PAN and semicrystalline conductive PANI [35], [38]. It is well known that amorphous regions are found in crystalline polymers between crystalline regions. Until recently, it was thought that the amorphous areas in fibers were completely disordered. It is currently assumed that there is some degree of order in the amorphous area, but it is definitely smaller than in the crystalline area. Considering the chemical composition of fibers and the fact that PANI does not dissolve in DMF, it should be assumed that PAN/PANI fibers are a polymer/polymer composite. Thus, big polyaniline crystallites (17.9 nm) are located in the amorphous areas of the PAN.

When analysing the influence of temperature on the conductivity of materials with such composition and structure, it should be taken into account that under the influence of temperature the following change:

- the distance between amorphous regions of polyacrylonitrile in which conductive polyaniline macromolecules are found. This change is triggered by differences in the values of linear expansion coefficients of both polymers. Coefficient of thermal expansion of PAN shows a typical polymer behaviour. The value of coefficient of thermal expansion (CTE) is much higher above Tg ($108 \cdot 10^{-6}$/ °C) than its value below Tg ($57 \cdot 10^{-6}$/ °C) [48].
- PANI linear expansion coefficient, which is the result of the coexistence of classical thermal expansion and contraction due to the release of water [31]. A. Rudajevova *et al.* found that in the first polyaniline heating cycle, the deformation resulting from water desorption is significantly greater than that resulting from classical thermal expansion. As a consequence of these two competitive processes, they observed negative thermal expansion. However, after drying PANI, its thermal expansion coefficient was $20 \cdot 10^{-6}$ K^{-1}.

- water content associated with polyaniline macromolecules. According to literature data, in case of PANI, the conductivity value decreases during heating and in vacuum [31], [49]. This effect is explained by the effect of water on the conductivity of polyaniline. Based on numerical simulations, it was found that water molecules increase the binding of the dopant to the PANI, and thus increase the conductivity [50], [51]. For this reason, water is treated as a secondary admixture. It has been experimentally proven that after removing water from polyaniline, the initial conductivity value is not achieved even after several days of storing this polymer in ambient atmosphere. It may also stem from a change in PANI microstructure due to a contraction resulting from the release of water.
- PANI degree of oxidation. Based on the FTIR test, it was found that partial PANI oxidation occurs when the polymer is exposed to a temperature of 100 °C [52].

Based on the above comments, the conductance of PAN/PANI fibers as a function of temperature G(T) can be expressed by the following relationship:

$$G(T) = G_o - \delta G_\varepsilon(T) - \delta G_{ox}(T) - \delta G_h(T) + \delta G_{DC}(T) \tag{1}$$

where: G_o is conductance at any reference temperature, $\delta G_\varepsilon(T)$ is a change in conductance due to thermal deformation, $\delta G_{ox}(T)$ is a change in conductance as a result of partial oxidation of PANI, and $\delta G_{Rh}(T)$ is a change in conductance due to the release of water molecules from the fibers structure, $\delta G_{DC}(T)$ is a change in conductance as a result of a change in mobility and concentration of electric charge carriers.

It is well known that the conductivity of any material depends on the concentration of electric charge carriers, their charge and mobility (2).

$$\delta = n \cdot e^- \cdot \mu \tag{2}$$

where: δ - electrical conductance; n - concentration of electric charge carriers, e^- - electron charge ($1.6 \cdot 10^{-19}$ C); μ - mobility of electric charge carriers. Depending on the type of material, the mobility always changes under the influence of temperature, but the concentration of electric charge carriers can also change [53].

The tested composite fibers were wet-formed from DMF solution and solidified in aqueous DMF solution. After the forming process, fibers were dried and stored at ambient temperature (22 °C) in an atmosphere with a relative humidity of about 40 %.

The linear conductance of standard polyacrylonitrile fibers is approximately 10^{-11} S [35] and the conductance of the developed PAN/PANI fibers is about $1.50 \cdot 10^{-4}$ S at 22 °C.

During temperature changes from 22 °C to −15 °C and again to 22 °C (Figure 7 and 14), fully reversible changes in conductance of the developed composite fibers were found. During cooling, the conductance decreased, and during heating an increase in conductance was observed. Such conductance changes are typical of semiconductor materials with a

negative temperature coefficient of resistance (TCR). It can be assumed that in this temperature range, the dominant factor causing an increase in the conductance of fibers is $\delta G_{DC}(T)$, i.e. an increase in the concentration and mobility of electric charge carriers caused by an increase in temperature (3).

$$\delta G_{DC}(T) > \delta G_{\varepsilon}(T) + \delta G_{Rh}(T) + \delta G_{ox}(T) \qquad (3)$$

The other three factors, i.e. thermal deformation $\delta G_{\varepsilon}(T)$, release of water molecules from the fibers structure $\delta G_{Rh}(T)$ and thermal oxidation in this temperature range, i.e. below 22 °C, do not significantly affect conductance changes or do not occur at all. The deformation value is too small and water in such conditions is not released from the fiber structure because this temperature is lower than the temperature at which the fibers were stored. The release of water from the fiber structure is an endothermic process (Figure 5), so energy (heating) rather than cooling is required.

When the fiber temperature increased above ambient temperature, the PAN/PANI fiber conductance began to decrease. The conductance changes during heating to a temperature of about 60 °C were greater and then they decreased. The observed decrease in electrical conductance may be the result of water loss, which acts as a secondary admixture [54]. This theory is confirmed by the analysis of the performed tests results using the Differential Scanning Calorimetry (DSC) method (Figure 5). In the initial range of temperature increase, water weakly bound in the fiber structure is released. This process is facilitated by increased fiber porosity (Figure 3, Figure 5). Then there is the release of water more strongly associated with PANI. The release of water causes the fiber to contract, and at the same time an increase in temperature counteracts it because the materials expand under the influence of temperature. It can be assumed that these two effects do not change the geometrical dimensions. Therefore, conductance changes above 22 °C are not caused by thermal deformation $\delta G_{\varepsilon}(T)$, nor by partial oxidation of PANI $\delta G_{ox}(T)$. Thus, in this temperature range, conductance changes are caused by the release of water molecules from the $\delta Rh(T)$ fiber structure causing changes in mobility and concentration of electric charge carriers (4).

$$G(T) = G_o - \delta G_h(T) + \delta G_{DC}(T) \qquad (4)$$

It is widely accepted that under the influence of temperature in semiconductors, the concentration and mobility of electric charge carriers change, the change in their concentration being the dominant one. As a result, the conductance of semiconductors increases with the rise in temperature. However, treating PANI-related water as a secondary dopant [54] it should be stated that it is the loss of water that causes the conductance to decrease despite the temperature increase.

Above 60 °C, the conductance decrease rate decreases with rising temperature (Figure 14). Whereas the course of the endothermic process clearly decreases on the DSC curve (Figure 5). This may indicate a slower release of water or the occurrence of an additional phenomenon. Electrical parameters of PAN/PANI fibers after being subjected to 100 °C

for 0.5 h and then after being cooled to ambient temperature (22 °C, 38 % RH) did not return to their initial values even after 72 hours (Figure 13).

Based on this, it can be assumed that above 60 °C not only does the water release, but also the partial oxidation of PANI occurs, causing irreversible changes in the fiber structure and thus in their conductance. This observation is consistent with the results of tests on polyaniline exposed to a temperature of 100 °C [52].

IV. CONCLUSION

The use of any materials in technology requires the knowledge of not only their parameters at ambient temperature, but also the determination of the influence of a basic factor, i.e. temperature on their properties. It is also important to know the mechanisms of changing parameters under the influence of temperature. For this reason, this article analyses the effect of temperature on the electrical conductance of composite polyacrylonitrile-polyaniline fibers (PAN/PANI). Polyaniline was synthesized by chemical method in dimethylformamide during the preparation of the spinning solution. The content of polyacrylonitrile in the spinning solution was 13.5% by weight, and the PANI content, according to the authors, was supposed to be 1% by weight. Unfortunately, some of the PANI precipitated in the form of large crystals that were removed from the solution so that they would not hinder the process of forming the fibers. The spinning solution was filtered in order to remove these crystals. While spinning, efforts were made to maintain the set, constant concentrations of spinning baths, their temperature and appropriate speeds of feeding and receiving fibers at feeding and receiving points. PAN/PANI composite fibers, obtained after forming in coagulation and solidification baths, were not stretched in steam due to their breaking during too high collection speeds behind the evaporator. According to the authors of the article, improving the strength of composite fibers PAN/PANI requires modification of the fiber formation process.

Despite the unsatisfactory mechanical strength, the obtained PAN/PANI composite fibers have an electrical conductivity of about 150 μS in atmosphere with a relative humidity of about 40% and ambient temperature (22 °C).

The conductivity of these fibers lowered both during the decrease (down to −15 °C) and increase of temperature (up to 100 °C). Characteristics of the temperature changes in the conductivity of composite fibers had a rare, parabolic shape. In the temperature range from 22 °C to −15 °C and back to 22 °C, the conductance changes were fully repeatable. During the temperature increase from −15 °C to 22 °C, the fiber conductance increased. Unfortunately, in the temperature range from 22 °C to 100 °C, the conductance of the fibers first decreased quickly (to about 60 °C), and then continued to decrease but at a much slower rate.

Based on the analysis of test results and of literature data, it was found that the conductance value of the tested fibers,

determined at the reference temperature, changes under the influence of temperature changes as a result of:

- thermal deformations,
- changes in mobility and concentration of electric charge carriers,
- releasing water molecules from the fiber structure,
- partial oxidation of PANI.

Each of these factors determines the conductance in a different temperature range. It seems that the contribution of the factor associated with thermal deformations is the smallest because both PAN and PANI are polymers, and thus materials with low stiffness.

Below ambient temperature, changes in electrical conductivity in the tested material are similar to temperature changes observed in case of semiconductor materials. Therefore, in the studied range of temperature changes, the dominant factor causing an increase in conductance is the change in mobility and concentration of electric charge carriers.

Above the ambient temperature, in the range of 22 °C to about 60 °C, the process of releasing water from the fiber structure seems to be the dominant factor, which reduces conductance. According to literature data, water is treated as a secondary dopant. This conclusion is confirmed by the results of tests performed with the DSC method.

When the temperature of composite fibers is higher than 60 °C, then the rate of change in conductance changes under the influence of temperature, and on the DSC characteristics of the fibers the intensity of the endothermic process decreases. It might be due to two factors, i.e., a slower evaporation rate of water and/or the start of another process, which is the partial oxidation of polyaniline. The occurrence of the second process was demonstrated in the research by Bhadra *et al.* [52]. If the conductance changes above 60 °C were caused only by a slower rate of water release from the fiber structure, they would be fully reversible, as it is known from the research on polymer humidity sensors. Unfortunately, the electrical conductance of the PAN / PANI fibers, after being subjected to 100 °C for 0.5 h, did not return to its initial value even after 72 hours from the moment they were cooled to ambient temperature (22 °C, 38 % RH). Therefore, it should be assumed that at this temperature also partial PANI oxidation occurs, causing irreversible changes in the structure of the fibers, and thus in their conductance.

Bearing in mind the results of the authors' research published earlier [35] and the ones presented in this article, it should be stated that the direction of research on composite fibers, an electrically conductive polymer/fiber-forming polymer is of interest both in scientific and utilitarian terms.

The presented test results show that this type of composite fibers can be used in the construction of humidity sensors working at up to 50 °C or as a resistive material. However, this requires optimization of the process of obtaining composite fibers and accurate determination of the impact of humidity on their conductance as well as response and return times.

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