



RIGA TECHNICAL
UNIVERSITY

Astrīda Bērziņa

**POLYMER COMPOSITE HEATING ELEMENTS
DESIGNED TO PROVIDE A COMFORTABLE
TEMPERATURE FOR THE HUMAN BODY**

Summary of the Doctoral Thesis



RIGA TECHNICAL UNIVERSITY
Faculty of Materials Science and Applied Chemistry
Institute of Technical Physics

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Doctoral Student of the Study Programme “Materials Science”

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To be granted the scientific degree of Doctor of Science (Ph. D.), the present Doctoral Thesis has been submitted for the defence at the open meeting of RTU Promotion Council on 13 October 2023 at 14:00 at the Faculty of Materials Science and Applied Chemistry of Riga Technical University, 3/7 Paula Valdena Street, Room 445.

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DECLARATION OF ACADEMIC INTEGRITY

I hereby declare that the Doctoral Thesis submitted for the review to Riga Technical University for the promotion to the scientific degree of Doctor of Science (Ph. D.) is my own. I confirm that this Doctoral Thesis had not been submitted to any other university for the promotion to a scientific degree.

Astrīda Bērziņa (signature)

Date:

The Doctoral Thesis has been written in Latvian. It consists of an Introduction, 3 chapters, Conclusions, 59 figures, 9 tables; the total number of pages is 103. The Bibliography contains 101 titles.

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ABBREVIATIONS

2D	two dimensional
3D	three dimensional
CB	electroconductive carbon black nanoparticles
CR	polychloroprene
DKP	dicumyl peroxide
EC-AFM	electroconductive mode of the atomic force microscope
EOK	ethylene-1-octene copolymer
FNT	Fowler–Nordheim tunnelling model
<i>NTC</i>	negative temperature coefficient of resistivity
phr	parts per hundred rubber
<i>PTC</i>	positive temperature coefficient of resistivity
px	pixel
VRH	variable range hopping model
α	coefficient of linear thermal expansion

GENERAL DESCRIPTION OF THE WORK

Introduction

Nowadays, the efficient use of energy is one of the major concerns in the world. Protection from the elements is one of the basic human needs, so efficient heating solutions are very important, especially during the colder months of the year. To increase the efficiency of energy usage for heating, one improvement could be to place the heating element close to the body and heat the body directly, for example, by embedding materials directly in fabrics for clothing. These heating elements need to be flexible, preferably without additional control electronics, and they should be safe in prolonged contact with human skin. The field of soft polymer composites provides the most promising solutions for obtaining such materials.

The electrical resistance (further in text simply “resistance”) of polymer composites can either increase or decrease with increasing temperature. Generally, polymer composites with a percolative structure consisting of conductive particles dispersed in an insulator matrix exhibit a positive temperature coefficient of resistivity (*PTC*). Most commonly, it is explained by the differences in the coefficient of linear thermal expansion between the filler and the matrix material; the filler expands a lot less compared to the matrix, and the thermal expansion of the matrix increases the distance between adjacent filler particles, which in turn reduces the tunnelling currents.

The opposite effect of *PTC* is the negative temperature coefficient resistivity (*NTC*), which is mainly observed at temperatures above the softening or melting temperatures of the polymer matrix, at which point the polymer chains and filler particles are able to rearrange themselves into new electrically conductive channels.

Self-regulating heating materials are useful in areas where the use of bulky electronics is difficult to implement. Self-regulation is provided by materials that have a positive temperature coefficient of resistivity. If electroconductive polymer composites have *PTC*, the resistance of the material increases in the region of a certain temperature. If the resistance increases by several orders of magnitude, then the composite can be used in various commercially important applications, such as self-regulating heating elements [1], over-current [2–4] or over-temperature [3,4] protection devices, in smart homes [5], etc. Polymer composites with *PTC* are easily formed, flexible and lightweight compared to inorganic materials that also exhibit *PTC* but also have considerable disadvantages. Samples made by the same processing technology show quite a wide distribution of electrical properties, and they exhibit a negative temperature coefficient of resistivity if the material is heated above its melting point, resulting in a decrease in electrical resistance as the temperature continues to increase. The *NTC* effect in the field of self-regulating heating elements is undesirable because such materials can easily overheat if the surrounding environment cannot absorb the increasing amount of released heat.

The *PTC* effect in polymer composites filled with conductive nanoparticles was first observed in carbon black (CB) filled low-density polyethylene composites in 1945 by Friedman [6]. Afterwards, this phenomenon was studied further [7–9] and on a much larger scale. Various models that try to explain the *PTC* phenomenon were proposed.

To obtain a flexible heating material which is safe for prolonged contact with human skin, two polymer matrices were chosen – polychloroprene (CR), better known as neoprene, and ethylene-1-octene copolymer (EOK), whose melting point varies from as early as 45 °C to 100 °C. Neoprene is widely used as the material from which diving suits are fabricated and has been acknowledged to be safe for prolonged contact with human skin. EOK melting point, which is also the region of the most intense *PTC*, is at the desired range for the application as a self-regulating heating element to maintain a comfortable temperature for the human body. One matrix is chosen to be polar, but the other is chosen as non-polar to evaluate the influence of the matrix properties. Polychloroprene has double bonds and electronegative chlorine atoms attached to the macromolecule, while ethylene-octene copolymer consists of a branched aliphatic chain of hydrocarbons. The effects of the electrical properties of the matrix material on the overall electrical conductivity are compared, as this is usually left out from considerations in other studies, since the conductivity of the matrix is so many times lower than the conductivity of the filler particles. Also, the materials are considered under working conditions, which means that a voltage is applied to the material heating it internally, and the electrical conductivity dependence on temperature and voltage is considered. Considering this aspect is essential to accurately assess the real situation while the element is in operation.

Aim of the Thesis

The aim is to develop flexible composite materials which would work as self-regulating heating elements in the temperature range of 45–60 °C, which is a comfortable temperature for the human body heating elements and would be safe for prolonged contact with the skin. A related objective is to investigate the mechanism of electrical conductivity in polar and non-polar matrix composites and evaluate the influence of the matrix electrical properties on the overall electroconductivity mechanism, considering both the effects of temperature and applied voltage. As a result, we want to develop guidelines according to which heating elements of different shapes and heating properties for various applications can be modelled.

Main tasks

1. Develop CR-CB and EOK-CB composites with different degrees of filler in the range from 10 phr to 30 phr with CB.
2. Determine the dependence of the electrical resistance of the obtained composites on temperature if the material is heated in external-heating mode.
3. Evaluate the dependence of electrical resistance on temperature and applied voltage if the material is heated in self-heating mode – by applying a voltage.
4. Evaluate the temperature coefficients of resistivity of the composites and compare their nature between external heating and self-heating.
5. Evaluate the impact of the matrix electrical properties on the overall conductivity of the composite.
6. Analyse the possible conduction mechanisms and processes that take place in the composite when it heats up or a voltage is applied.

7. Evaluate the effect of linear thermal expansion on electrical conductivity and determine the coefficient of linear thermal expansion of the composites.
8. Analyse the EC-AFM images and mathematically characterise the dispersion of the filler, propose improvements to the method so that the characteristic indices can be compared with each other for composites with largely different degrees of filling.
9. Evaluate the influence of filler content, composite design, electrode material and placing, and the applied voltage needed to obtain heating elements for practical use.

Scientific novelty

- Until now, the influence of the electrical properties of the matrix on the overall electrical conductivity of the composite in the scientific literature has not been described. There is also very little information on the changes in electrical resistance under the influence of temperature and/or voltage, specifically for CR and EOK composites, so the general novelty is the study of these factors.
- In the self-heating mode, CR-CB composites show a negative temperature coefficient of resistivity and, depending on the applied voltage, 4 dominant mechanisms can be distinguished for the overall conductivity of the composite. It is shown that the electrical properties of the polymer matrix have a significant effect on the overall electrical conductivity of the composite.
- EOK-CB composites with 20 phr and more of CB in the self-heating mode have a positive temperature coefficient of resistivity, and the conductivity mechanism of it is determined.
- By analysing the EC-AFM images also by means of current strength, a particle dispersion characterising method is obtained, which can characterise composites with very different filler concentrations.

Practical significance

New polymer-carbon nanoparticle composites have been developed, which are flexible, easy and inexpensive to manufacture, and they work as heating elements of a comfortable temperature for the human body (45–60 °C) and would be safe for prolonged contact with human skin. The obtained composite CR-CB has *NTC* and can work as a relatively powerful heating element, while EOK-CB has *PTC* and can be used as a self-regulating heating element.

Approbation of the research

The results of the Doctoral Thesis were published in four journal articles and conference proceedings, all indexed in SCOPUS and Web of Science. The results were presented at 8 local and international conferences.

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Publications:

1. **A. Berzina**, V. Tupureina, I. Klemenoks, and M. Knite, “A Method for Dispersion Degree Characterization Using Electro Conductive Mode of Atomic Force Microscopy”, *Procedia Comput. Sci.*, vol. 104, pp. 338–345, 2017. (SCOPUS, WOS, SNIP 0.885)
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3. **A. Berzina**, I. Klemenoks, V. Tupureina, and M. Knite, “Ethylene-octene copolymer and carbon black composite electro-thermal properties for self-regulating heating”, *IOP Conf. Ser. Mater. Sci. Eng.*, vol. 500, no. 1, p. 012012, Apr. 2019. (SCOPUS, WOS, SNIP 0.517)
4. **A. Berzina**, I. Klemenoks, and M. Knite, “The influence of DC voltage on the conductivity of chloroprene rubber-carbon black composites for flexible resistive heating elements”, *RSC Adv.*, vol. 13, no. 26, pp. 17678–17684, Jun. 2023. (SCOPUS, WOS, SNIP 0.866)

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7. Bērziņa, A., Eglīte, S., Klemenoks, I., Tupureina, V., Knite, M. The effect of crosslinking on the electro-thermal properties of carbon black (CB) and ethylene-octene

copolymer (EOC) composites. In: *Materials Science and Applied Chemistry 2019 Programme and Abstract book*, Latvia, Riga, 24 October 2019. online: 2019, p. 16.

8. Bērziņa, A., Klemenoks, I., Knite, M. Neoprene and ethylene-octene copolymer composites for temperature self-regulating heating elements. In: *Joint International Conference Functional Materials and Nanotechnologies and Nanotechnology and Innovation in the Baltic Sea Region 2022 Book of abstracts*, Latvia, Riga, 3–6 July 2022. online: 2022, p. 177. e-ISBN 978-9934-23-645-7.

THESES TO DEFEND

1. Polychloroprene (CR) – carbon black (CB) composite shows a negative temperature coefficient of resistivity because the overall electrical conductivity consists of zinc and chloride ion conductivity, electron and hole conductivity, and charge carrier tunnelling conductivity.
2. The ethylene-octene copolymer (EOK) composites exhibit a positive temperature coefficient of resistivity, which is determined by matrix thermal expansion-induced decrease in tunnelling conductivity.
3. For applied voltages – CR up to 20 V, but EOK up to 10 V – the tunnelling current dependence on the electric field can be well described by the Simmons model for intermediate voltage range ($V < \phi_0/e$, where e is the charge of an electron and ϕ_0 is the height of rectangular barrier).
4. Although polychloroprene composites exhibit negative temperature coefficient of resistivity, the power output for the same applied voltage is higher compared to EOK composites, and they are better suited for applications as heating elements.
5. EOK-CB composites can be used as self-regulating heating elements because of their positive temperature coefficient of resistivity.

MAIN RESULTS OF THE THESIS

Literature overview

In general, several mechanisms of electrical conductivity are possible, which consider the influence of temperature or voltage. They are divided into electron tunnelling and electron hopping models. Tunnelling models related to temperature effects fall into two types. The first type is the electrical tunnelling effect observed between similar electrodes separated by a thin insulating layer [10]. The second type is fluctuation-induced tunnelling [11], discovered by Sheng. This model describes the temperature-dependent electrical conductivity using a fluctuation probability function when the field generated by the thermal fluctuations is stronger than the applied field. Unfortunately, this model describes electrical conductivity below the boiling point of liquid nitrogen.

Tunnelling effects, which consider the influence of the electric field, are described by Fowler–Nordheim tunnelling (FNT) [12]. This model assumes that electrons can overcome a barrier of a certain height because it is bent under the influence of an intense electric field.

Electron hopping under the influence of temperature can occur by 2 mechanisms. The first mechanism dominates at high temperatures when the thermal energy is large enough to excite electrons from the valence band to the conduction band, thus increasing the electrical conductivity. Processes of this type can be described by the Arrhenius equation [13]. The other type is known as variable range hopping (VRH) [14] for low temperatures. This theory describes the temperature dependence of conductivity in disordered systems when a charge jumps between two localised sites with similar energies, which are spatially separated by an insulator layer.

The *PTC* effect of polymer nanocomposites is most intense in the region of the percolation threshold. The aggregates forming the agglomerate network are weakly connected and are easily disrupted, for example, due to the thermal expansion of the matrix, which results in the composite becoming an insulator. Therefore, the greatest *PTC* effect can be observed for filler concentrations directly in the region of percolation threshold or slightly above it, where the amount of the filler is still low.

Although no specific mechanism describes the effects of *PTC* and *NTC*, all models, to a greater or lesser degree, accept volume expansion as an influencing factor. The explanation based on the tunnelling effect is the most widely accepted. According to this, electrons can overcome a thin layer of the insulating matrix formed between adjacent conductive particles, aggregates or agglomerates as a result of electron tunnelling. Rapid expansion at temperatures close to the melting temperature of the matrix increases these gaps between the filler particles, thereby reducing the probability of electron tunnelling. Accordingly, the *NTC* effect is explained by the reagglomeration of electrically conductive particles in the polymer melt, thus restoring part of the electrically conductive channels. To reduce the *NTC* effect, which is undesirable, the polymer composite can be cross-linked, or a multi-layer system can be formed with each layer having different temperature coefficients of resistivity.

Pristine CR matrix shows an *NTC*, and the conductivity is ionic, while in the case of CR-CB composites, the observed temperature dependence in one case is *PTC* for concentrations

lower than 25 wt% of CB; but increasing the concentration, the *PTC* effect decreases. In another article, the relationship observed is thermally activated for the concentrations of 10 phr and 20 phr of CB – as the temperature increases, the conductivity also increases (*NTC*). Composites with 30 phr of CB is a transition, where the conductivity increases at first but then decreases with further increase in temperature. Starting with 40 phr and 50 phr of CB, the trend is similar to metals – conductivity decreases as temperature increases (*PTC*).

From this, we can conclude that the influence of the matrix on the general conductivity of the composite is so significant that it is comparable to purely temperature-induced effects – the thermal expansion of the matrix as there are transitional stages described in the literature, where the material switches from one type of thermal dependence to another type just by changing the amount of filler.

The dependence of conductivity on temperature and/or applied voltage is very little studied for ethylene-octene copolymer. For the pure matrix, we found no research describing this, most likely because the electrical resistivity of the matrix is very high $>10^{16} \Omega \cdot \text{cm}$. The temperature dependence of the conductivity of EOK-CB composites, if a voltage is applied, showed *NTC* properties which is very unusual. It should be mentioned that this research obtains this relationship indirectly since the main objective was to increase the recovery of the original shape for a shape memory material with the help of Joule heating.

CR and EOK are very thermally stable; according to the literature, they start to noticeably decompose only at temperatures greater than 300 °C. For CR, this temperature range is from 290 °C to 480 °C, but for EOK, it is from 300 °C to 400 °C for it to fully decompose. Adding a certain amount of filler can inhibit decomposition, and shift it to occur at higher temperatures, but too much filler content can promote thermal conductivity, and heat can reach the middle of the sample faster.

In general, the data on both polymers and their composites regarding the effect of temperature and/or voltage on the conductivity are ambiguous, if they have been examined at all. For the most part, such studies have not been carried out, so in this work, a strong emphasis is placed on the effect of temperature on the resistance, and the effect of the applied voltage and the subsequent temperature increase on the electrical resistance of the composites. We determined the possible conductivity mechanisms and tried to explain the electrical processes occurring in the structure of the composite, which affect the macro-resistance.

From the review of the literature, it can be concluded that in order to obtain a heating element of a comfortable temperature for the human body, which would be safe for prolonged contact with human skin, the possible matrix materials are polychloroprene, which is widely used as a diving suit material, and ethylene-octene copolymer, which has a melting point of 60–80 °C, which is very close to the operating temperature of the heating element of a comfortable temperature for the human body and could show the greatest *PTC* effect precisely in this temperature region.

Materials and methods

In this work, two matrix materials are discussed and compared – polychloroprene (CR) Baypren 611 M43 (*Arlanxeo*) and ethylene-octene copolymer (EOK) Engage 8200 (*Dow*

Chemical) with the cross-linking agent dicumyl peroxide (DKP). Graphitised carbon black nanoparticles (CB) Printex XE2 with a primary particle size of 30 nm and a specific surface area of 950 m²/g are used as the filler.

For each matrix material, samples with different CB concentrations from 10 phr to 30 phr (parts per hundred rubber) have been made. Sample designations are formed by matrix abbreviation-filler abbreviation XX, where XX is the amount of filler in the composite expressed in phr. For example, the designation of a polychloroprene carbon black composite with a 20 phr of CB composition is CR-CB20. To distinguish the cross-linked EOK from the non-cross-linked nEOK, the small letter “n” is added before the non-cross-linked nEOK, but the rest is formed analogously.

The CR-CB composites are made by dissolving CR in chloroform, dispersing CB in chloroform by ultra-sonification, and pouring the two mixtures together and letting the solvent evaporate. The individual components of EOK-CB composites are mixed on a two-roll mill. Afterwards, both composites are prepared in a similar way – roll-formed, pressed and shaped (cross-linked) to create samples of size 20 mm × 10 mm × 1 mm. Samples of pristine matrix material are made in the same way as with the filler, except that the CB filler is not added. The dimensions of the formed cylinder are 50 mm in diameter and 5 mm in thickness.

In order to characterise the thermo-electric properties of the samples, they were measured in the **self-heating mode** – by applying an external voltage – and in the **external-heating mode** – by changing the ambient temperature. Linear thermal expansion measurements were performed with a high-resolution camera (HikVision) and a Linkam high-precision temperature control platform for microscopy (THMSE 600). To characterise the dispersion degree, the NT-MDT atomic force microscope (Smena) in conductive contact mode (EC-AFM) was used to obtain the electroconductive channel images.

The self-heating mode experiment was performed by simultaneously determining four parameters – the current strength, the voltage drop on a known standard resistor, the voltage drop on the standard resistor and the sample, and the temperature at the sample surface. In the beginning, the power supply is set in a constant-current mode – 1 mA for 30 s (only a small voltage needed for measuring is applied), then it is switched to a constant-voltage mode and the corresponding experimental voltage required for the experiment (0.5–30 V) is set for a specific time, which varies from 5 s to 10 min. This applied voltage heats the sample internally, giving off Joule–Lenz heat. Next, the power supply is switched back to constant-current mode – 1 mA to measure the relaxation of the sample for 10 min.

Measurements for the external-heating mode are performed by placing the sample in a precise temperature control cell (Linkam THMSE 600), and the power supply works only in constant-current mode of 1 mA, only a small voltage needed for measuring is applied. During one measurement cycle, at the start, the temperature is held for 1 minute at 20 °C, then it is raised at a rate of 3 °C/min to 60 °C, where it is held for 5 minutes, and then it is lowered at a rate of 3 °C/min to 20 °C.

Formulas for the mathematical processing of the EC-AFM data to characterise particle dispersion are as follows – *d-Index*, which characterises the homogeneity of channel distribution by area:

$$d\text{-Index} = \frac{1}{2} \left[1 - \frac{s(b)}{0.5270} + \frac{\bar{b}}{\max(b)} \right], \quad (1)$$

where

b – the set of values in percentages taken up by electroconductive channels observed for each of the nine segments of the image;

$s(b)$ – standard deviation for the set of values b , calculated by: $s(b) = \frac{\sum(b_i - \bar{b})^2}{8}$;

\bar{b} – the arithmetic mean value of b ;

$\max(b)$ – the largest value of b ;

0.5270 – largest possible standard deviation for 9 numbers that range between 0 and 1.

The formula for calculating *s-Index*, which characterises the homogeneity of the channel size distribution, is as follows:

$$s\text{-Index} = \frac{1}{2} \left[\frac{l}{N} + 1 - \frac{\max(a)}{\sum_{i=1}^N a_i} \right], \quad (2)$$

where

a_i – the size of each conductive channel in pixels;

$\max(a)$ – the largest value of a ;

N – the electroconductive channel count;

l – the number of electroconductive channels whose area is less than a threshold of 5 pixels (px).

c-Index is the arithmetic mean of the previous two indexes *d-Index* and *s-Index*, which characterises the sample overall.

Results and discussion

CR-CB composites

Self-heating and external-heating mode

As seen in Fig. 1, when a voltage of 5 V is applied to the material, the resistance initially drops rapidly, after which for 10 phr and 20 phr of CB samples, the resistance goes to a steady state, while for the 30 phr samples, the resistance begins to increase. On the other hand, the reached temperature for all CR-CB samples increases because of the released Joule heat. The initial drop in resistance can be explained by the increased movement speed of charge carriers ($v \sim U$) and the Maxwell–Wagner interphase polarisation effect. During this effect, charges accumulate on the boundary between two materials with different charge carrier relaxation times when an electric field is applied [15]. In the case of a polar matrix, this effect is much more pronounced than in the case of a non-polar matrix, where the magnitude of the Maxwell–Wagner polarisation effect is relatively small because there are not as many free charge carriers who can accumulate.

Two types of processes take place in the material as the temperature increases, which have mutually opposing effects on the electrical resistance:

- (i) as the temperature increases, the matrix expands more than the filler particles, which increases the distance between the conductive particles and decreases the tunnel currents – the resistance increases;
- (ii) as the temperature of the composite increases, the movement speed of the charge carriers and electrically conductive particles increases, and the charge carriers are able to move faster – the conductivity increases. On the other hand, the particles can rearrange and form new contacts with neighbouring particles, contributing to the increase in conductivity.

The applied voltage can increase the movement speed of charge carriers, which results in higher conductivity for a polar dielectric material than for a non-polar dielectric material. Because polychloroprene has a polar polymer chain which contains electronegative chlorine atoms attached to the macromolecule, which may contain local conjugated double bonds and impurities, which are induced in the matrix during cross-linking, the voltage-induced

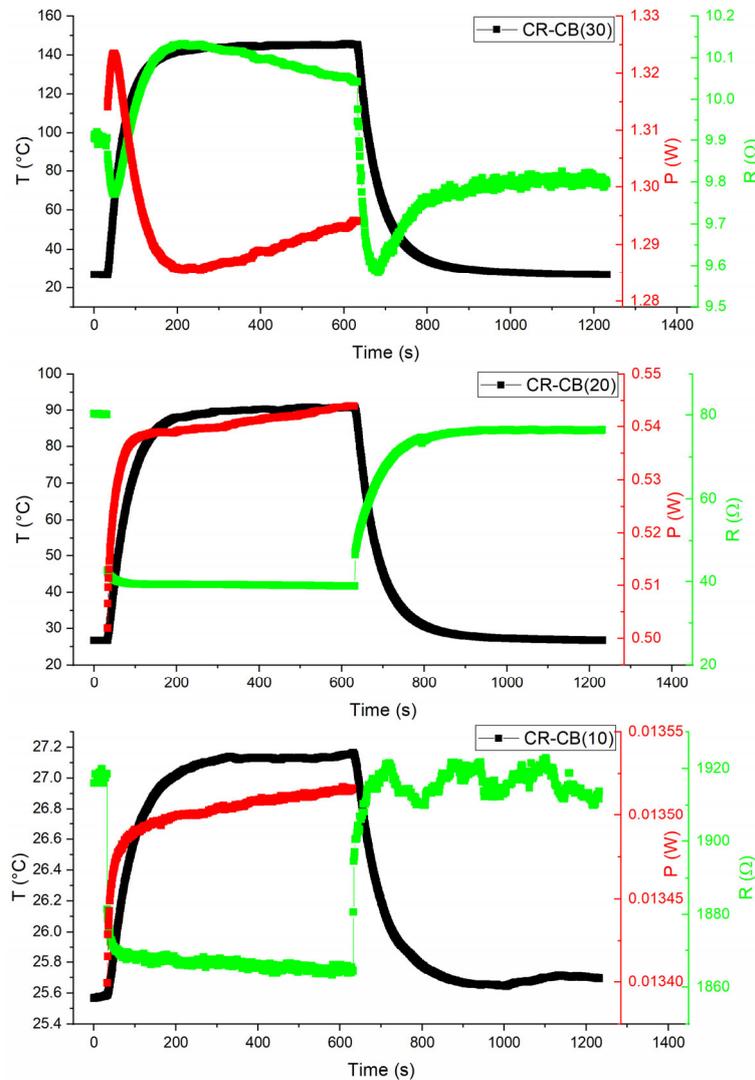


Fig. 1. Dependence of temperature, resistance, and output power on time if the sample is heated in self-heating mode by applying a voltage of 5 V (4 V for a 30 phr of CB sample).

conductivity of the matrix can significantly increase. During cross-linking, various by-products are formed, for example, $ZnCl_2$, which can increase the conductivity of the composite while a voltage is applied. Since conductivity is proportional to the movement speed of charge carriers and their density, the same electrical conductivity value can be obtained by increasing the movement speed or by increasing their density. The applied voltage ensures that more charge carriers are excited to the conduction band, and impurity ions, for example, magnesium, zinc and chloride ions, migrate in the direction of the applied field. In summary, the properties of the matrix can also significantly affect the overall controllability of the composite in the self-heating mode.

When the composite is heated externally from 20 °C to 60 °C, the material shows *NTC* – the resistance decreases when the temperature is increased.

Pristine matrix and filler resistance dependence on temperature

Fig. 2 shows the resistance dependence on temperature for a) pure matrix and b) pure filler. There is a huge difference in conductivity between the matrix and the filler. In terms of resistance dependence on temperature, carbon black has partly metal and partly semiconductor-like properties. Nonetheless, the filler has a very high conductivity, so its temperature-dependent properties are seen to a relatively small extent – only while it stays in close contact with the other particles. The overall resistivity of the CR matrix is relatively low compared to non-polar polymers (polyethylene $> 10^{15} \Omega \cdot \text{cm}$ [16]), suggesting that polar groups, possible locally conjugated double bonds and impurity ions significantly affect the electrical conductivity [17–19].

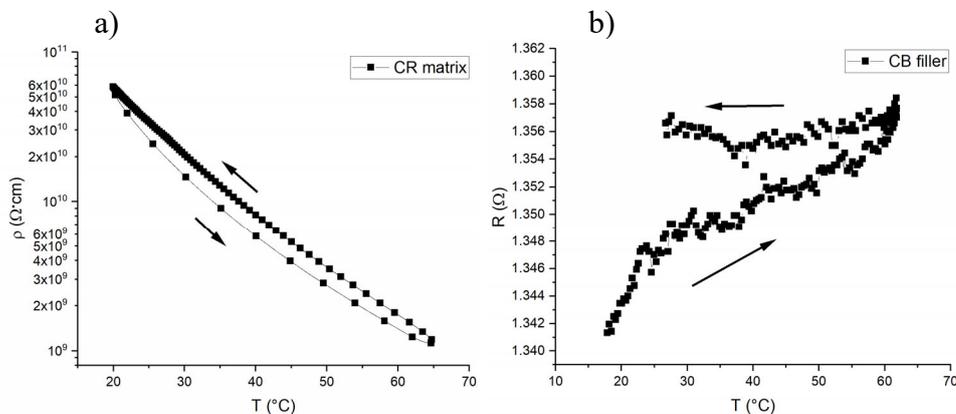


Fig. 2. Temperature dependence of resistivity of pristine polychloroprene matrix (a) and pristine carbon black nanoparticles (b).

Influence of voltage

The change in relative resistance depending on the applied voltage is shown in Fig. 3. From the graph, one can see the initial drop in resistance induced by the applied voltage, which indicates an intense increase in the number or speed of charge carriers in the first second. The aforementioned Maxwell–Wagner interfacial polarisation effect is the key factor for the first sharp drop in resistance. Up to an applied voltage of 5 V, the resistance drops with time, as the increased speed of charge carriers reduces the resistance; however, the higher the increase in temperature, the amount of the resistance drop decreases – effects of the thermal expansion of

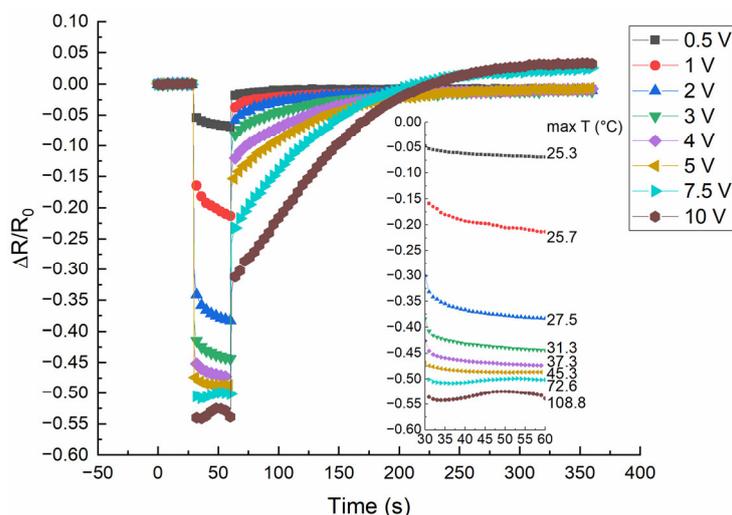


Fig. 3. Dependence of relative resistance change on the applied voltage for CR-CB20 composite samples.

The small graph shows the trend of the relative resistance changes in the period when the corresponding experimental voltage is applied and the maximum temperature reached after 30 s of heating with the applied experimental voltage. For the first 30 s constant current mode 1 mA (measuring voltage), next 30 s the experimental voltage is applied, afterwards the relaxation is measured in constant current mode 1 mA for 9 min.

the matrix begin to show with the subsequent increase in resistance (the temperature at 5 V is 45.3 °C). In the applied voltage region of up to 5 V, the voltage-induced properties are still dominant. By increasing the voltage further, above 7.5 V, we can see that the initial resistance drop is followed by an increase in resistance, which can be explained by the already significant reduction of tunnelling currents in the sample caused by matrix expansion. At 7.5 V and 10 V, a further decrease in resistance can be observed after 50 s of an applied experimental voltage, which can be explained by the further change of the dominant mechanism to the formation of new electroconductive channels through kinetic agglomeration, which happens because the matrix temperature is above the softening point and the CB particles can rearrange (the reached temperature is above 70 °C). According to the literature, the melting point of non-crosslinked polychloroprene is in the range of 45–75 °C [20, 21].

The highest relative change in current strength (see Fig. 4) is observed at a voltage of 2 V when the sample has not yet reached 30 °C. When the temperature increases by 3 °C above the ambient temperature, voltage-induced electrical resistance reducing effects are dominant – increasing the voltage increases the movement speed of charge carriers. Starting from 3 V, temperature effects begin to play a noticeable role as the relative current change decreases, which should not be the case if only voltage-induced effects were dominant. In this region of the applied voltage, the matrix expands under the influence of temperature, which results in an increase in the distance for the tunnelling currents and a subsequent increase in the electrical resistance. The decrease in tunnelling currents caused by the expansion of the matrix becomes the dominant mechanism in the temperature range from 50–70 °C, which corresponds to the applied voltage region of 5–7.5 V. In the region above 7.5 V, a drop in the relative current strength is observed with a further increase in temperature when the kinetic agglomeration effect of the filler particles takes over as the dominant mechanism, resulting in the particles regrouping into new electroconductive channels.

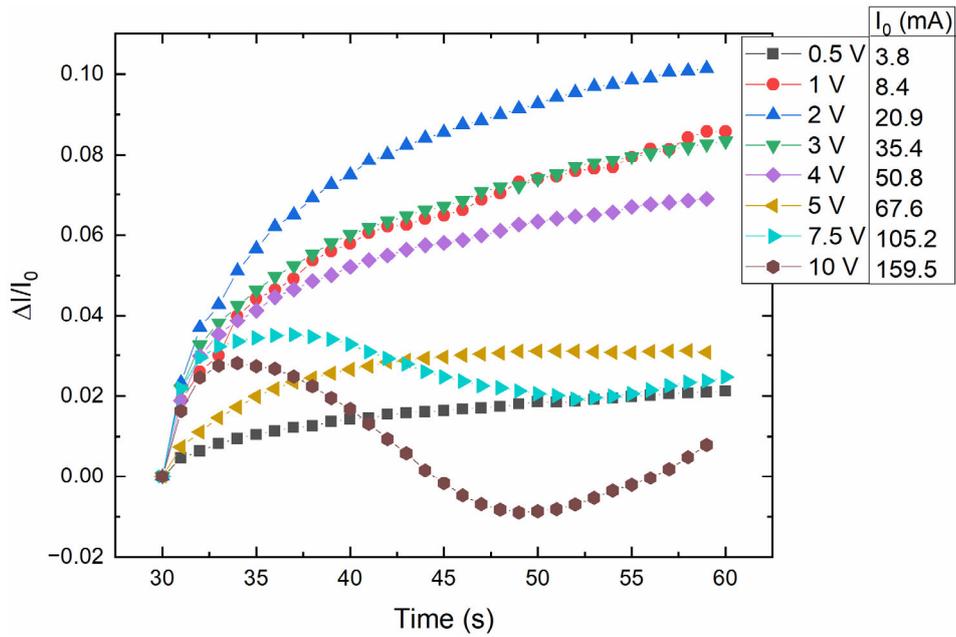


Fig. 4. Dependence of relative current strength on applied voltage for CR-CB20 composite. Initial current values 1 s after the applied voltage are added to the legend.

Current-voltage characteristic curve

By determining the current-voltage characteristic curves for pure matrix and CR-CB composite, it was concluded that the current-voltage characteristic curve of the matrix has a linear shape – the process obeys Ohm's law, but for the CR-CB composite, the current-voltage characteristic curve is not linear, which indicates non-Ohmic effects. The conductance mechanism is neither variable range hopping since plotting $\ln(I)$ as a function of $T^{-1/3}$ or $T^{-1/4}$ for 2D and 3D systems, respectively, does not show a linear curve, nor Fowler–Nordheim tunnelling, for which the characteristic plot $\ln(I/U^2) \propto U^{-1}$ would give linear curve, which it is

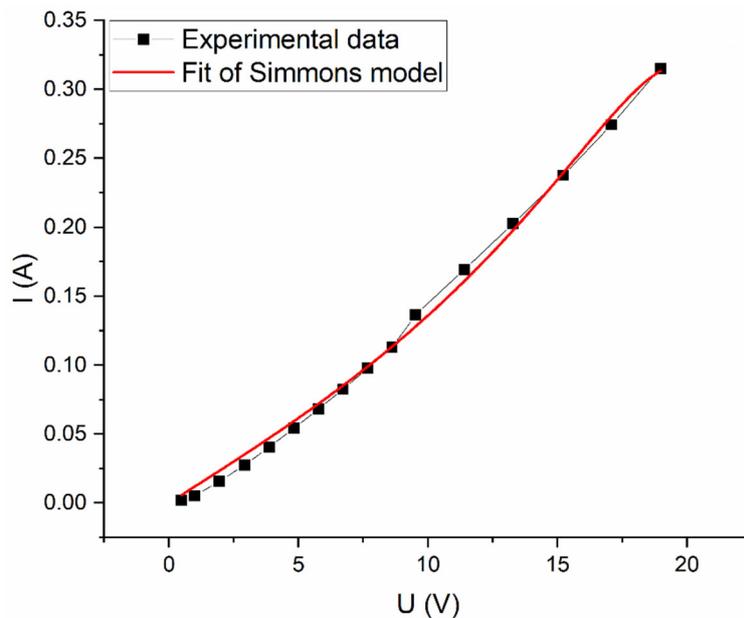


Fig. 5. Current-voltage characteristic curve and fitting of Simmons model for the general theory of tunnelling at intermediate voltages of CR-CB20 composite.

not in our case. The best fit to our experimental data is obtained by Simmons generalised formula (3) for the electric tunnel effect ($I \propto Ue^U$), shown in a solid red line in Fig. 5, with the adjustment parameters given in Table 1. The parameters obtained from this fit show that the average distance between neighbouring filler particles is around 1.6 Å, which is reasonable at high degrees of filling. The cross-sectional area for the current flow is 6861.55 nm². The potential barrier height (~ 11 eV) is higher than usually considered for polymer composites (1–5 eV) [22,23]. This can be explained by the unusually close tunnelling distance because the height of the barrier and the tunnelling distance both influence the probability of tunnelling. The closer the distance, the higher the barrier height can be for the tunnelling probability to remain constant. The obtained parameters are reasonable, which proves the presence of the tunnelling effect in CR-CB composites.

$$I = C \cdot \frac{e}{2\pi\hbar s^2} \left(\left(\varphi_0 - \frac{eV}{2} \right) e^{-4\pi s \sqrt{\frac{2m(\varphi_0 - \frac{eV}{2})}{\hbar}}} - \left(\varphi_0 + \frac{eV}{2} \right) e^{-4\pi s \sqrt{\frac{2m(\varphi_0 + \frac{eV}{2})}{\hbar}}} \right), \quad (3)$$

where

e – the charge of an electron;

\hbar – Planck's constant;

s – thickness of the insulating film;

φ_0 – the height of rectangular barrier;

V – the voltage across film;

m – mass of an electron;

C – constant that is comparable to the cross-sectional area of the current flow.

Table 1

Fitting parameters for Simmons generalised formula for the electric tunnel effect for intermediate voltages

Model	Simmons generalised formula for the electric tunnel effect for intermediate voltage
s	$1.60 \cdot 10^{-10} \pm 0.06 \cdot 10^{-10}$
φ_0	$1.81 \cdot 10^{-18} \pm 0.08 \cdot 10^{-18}$
C	$6861.55 \cdot 10^{-18} \pm 847.11 \cdot 10^{-18}$
Reduced χ^2	$3.72 \cdot 10^{-5}$
R^2 (COD)	0.9967
Adjusted R^2	0.9962

The linear thermal expansion coefficient for CR-CB30 obtained in the temperature range 20–60 °C is $\alpha = 1.95 \pm 0.10 \cdot 10^{-4}$ 1/K.

EOK-CB composites

Non-crosslinked nEOK-CB composites

nEOK-CB composites exhibit an intense *PTC*, especially samples with 10 phr of CB. The measurements show a significant change in relative resistance, but the change is unstable and irreversible – such a material cannot be used for practical application.

In the self-heating mode, the temperature of 15 phr of CB samples increased for less than 1 °C and they exhibited *NTC* which can be explained by the applied voltage-induced increase in carrier velocity.

For the samples with 20 phr and 25 phr, the released power decreased with the increase in temperature. In order to stabilise the large matrix effects, nEOK needs to be cross-linked.

Crosslinked EOK-CB composites

Self-heating and external-heating mode

Looking at EOK-CB composites of different filling levels in the self-heating mode (see Fig. 6), it can be seen that voltage-induced effects occur at small loads of CB and very low heating temperatures. Starting from the 20 phr of CB samples (see Fig. 6 d), the influence of temperature is dominant – the reduction of tunnelling currents caused by the expansion of the matrix is the main conductivity influencing mechanism, as the attained temperatures are already sufficient enough for the material to thermally expand.

Differential scanning calorimetry thermograms of EOK-CB indicate that at 60 °C the material goes through a minimum, which is the melting region of the crystalline part of EOK.

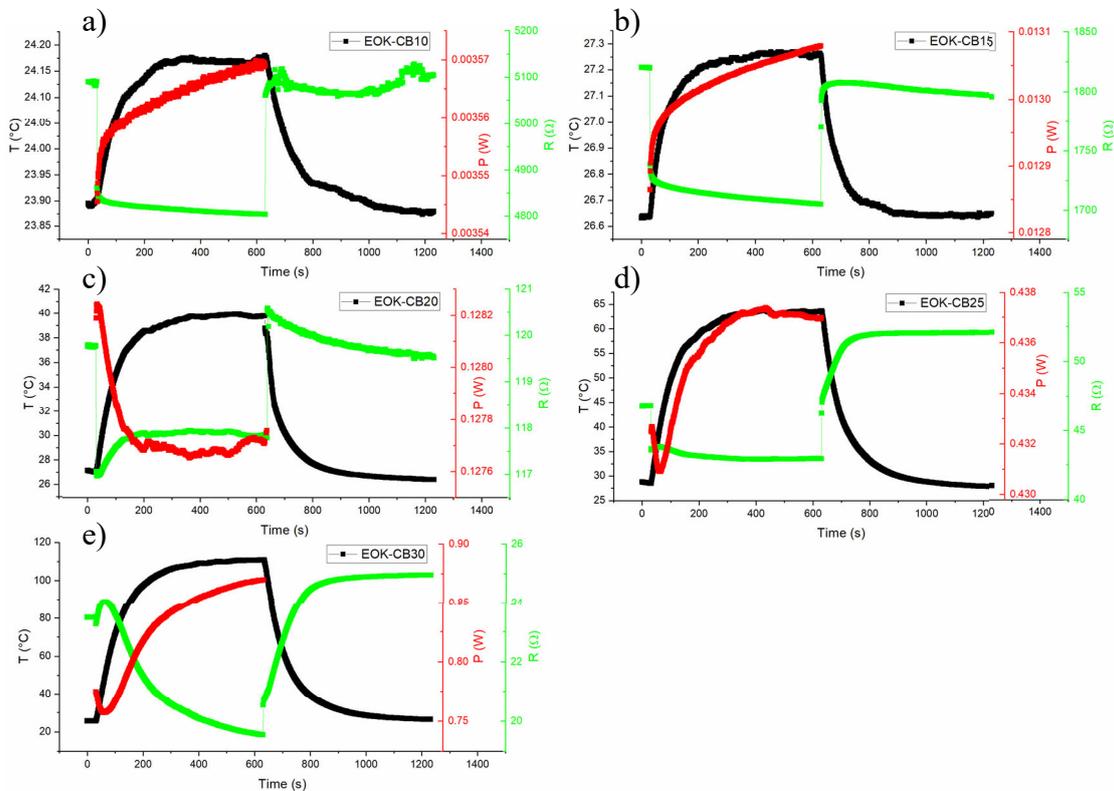


Fig. 6. Dependence of temperature, resistance and output power on time if the sample is heated in self-heating mode by applying a voltage of 5 V for cross-linked EOK-CB composites with different degrees of CB filling.

This melting region is rather wide because it consists of two parts. At lower temperatures the less ordered regions formed by the branches of the hexyl groups are melted. At 60 °C the more ordered crystallites formed by the ethylene chains are melted. The fastest expansion in the matrix occurs in the phase transition region.

If the EOK-CB composite is heated passively (external-heating mode), it shows *PTC* up to 55–60 °C. The most significant change in the relative electrical resistance is observed for the 10 phr of CB samples because the CB concentration is the closest to the percolation threshold concentration. The samples with 20 phr of CB show the second highest change in relative electrical resistance.

Pristine matrix resistance dependence on temperature

Pristine matrix resistance dependence on temperature is shown in Fig. 7. Since the EOK matrix is completely non-polar, the dependence of its resistance on temperature forms a straight line on the logarithmic scale (cooling part) and indicates that the conductivity is thermally activated. In the heating part of the graph, the sample was most likely heated unevenly, which explains the non-linear nature.

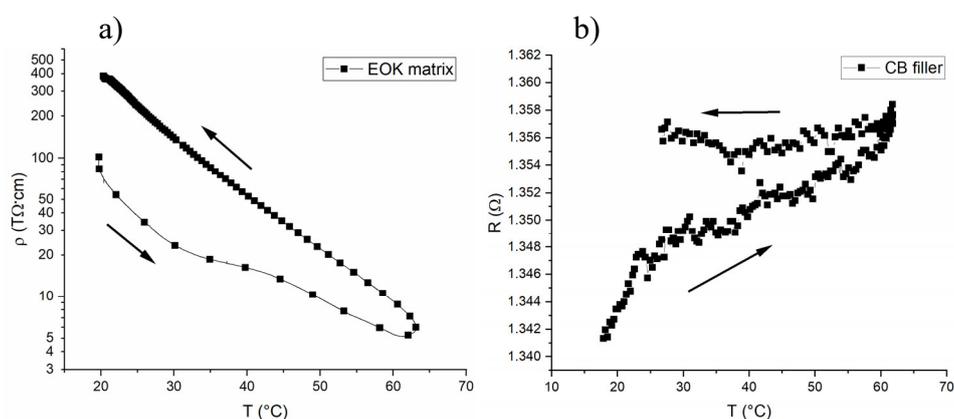


Fig. 7. Temperature dependence of resistivity of pristine ethylene-octene copolymer matrix (a) and pristine carbon black nanoparticles (b).

Influence of voltage

Looking at the dependence of the relative current strength on the filler loading for an applied voltage of 5 V (see Fig. 8), one can see that starting from 20 phr of CB, the relative current strength drops rapidly and only for the 25 phr and 30 phr of CB samples it starts to later increase. At this degree of filling, the reached heating temperature is high enough for the matrix to expand and decrease the tunnelling currents. The further increase in current strength occurs because the matrix becomes soft, the mobility of the polymer chains increases rapidly, and the CB particles can easily rearrange themselves and form new electroconductive channels. The temperature-induced effects – thermal expansion and softening of the matrix are the dominant conductivity influencing factors.

Taking one specific concentration (EOK-CB25) and looking at the effect of voltage on the composite (see Fig. 9), we notice that for all applied voltages, the relative current strength change is decreasing, which is explained by the decrease in tunnelling currents due to the matrix expansion. When the temperature of the sample greatly exceeds the melting temperature (at

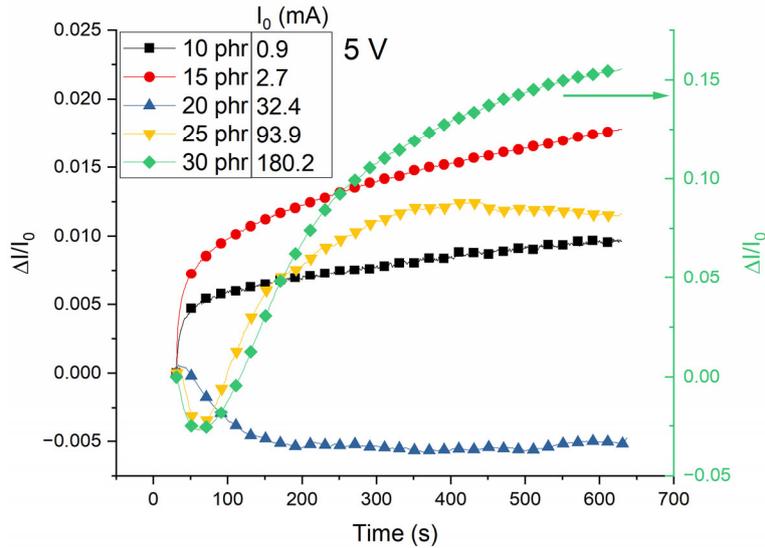


Fig. 8. Relative current strength depending on the degree of CB filling in the EOK-CB composite material at an applied voltage of 5 V. The legend additionally indicates the absolute values of the initial current strength.

applied 7.5 V), irreversible changes take place in the sample, resulting in the rapid decrease of the resistance and the according increase in the current strength. This occurs mainly because of the rapid rearrangement of the particles under an applied voltage and the formation of new electroconductive channels, as the temperature greatly exceeds the softening temperature. Partial destruction of the matrix is also possible, resulting in some polymer chain scission and an increase in the number of impurity charge carriers.

In Fig. 10, for all applied voltages, a *PTC* is observed. As the applied voltage increases, so does the relative change in resistance. The dominant mechanism for the conductivity is the reduction of tunnelling currents caused by matrix expansion. Above an applied voltage of 7.5 V, the generated heat is so immense that the sample temperature is higher than 76 °C exceeding the softening temperature, and irreversibly thermally deforming the sample.

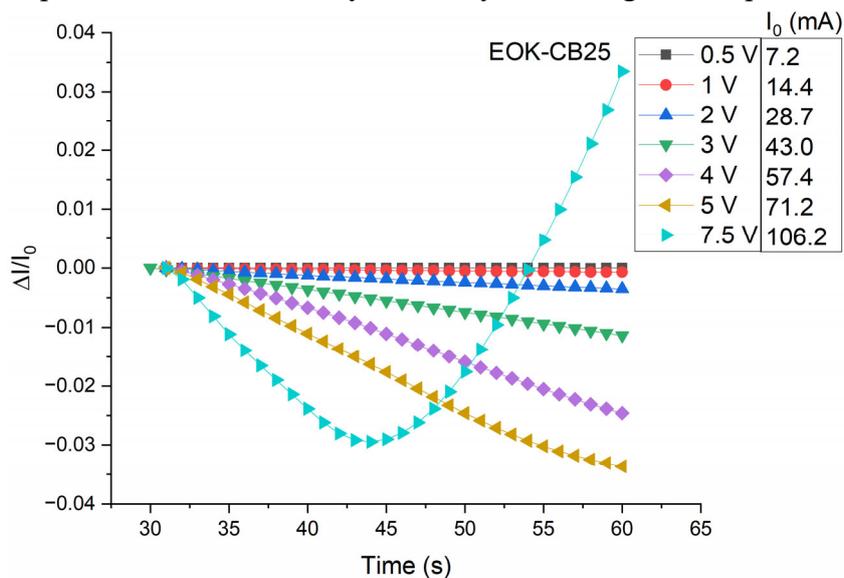


Fig. 9. Dependence of relative current strength on the applied voltage for the EOK-CB25 composite. The legend additionally indicates the absolute values of the initial current strength.

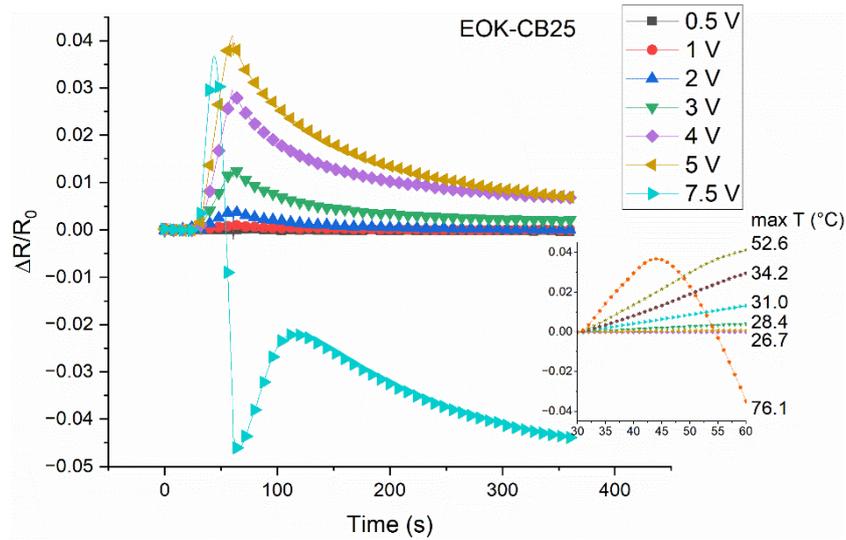


Fig. 10. Dependence of relative resistance of the EOK-CB25 composite on the applied voltage. The attached small graph shows more closely the change in relative resistance during the time of applied experimental voltage and the maximum temperature reached.

Current-voltage characteristic curve

Looking at the current-voltage characteristic curves for EOK-CB composites with different degrees of CB filling (see Fig. 11), the current strength increases with the increase in the filler load, as a higher concentration provides a greater electrical conductivity. All the curves show a small nonlinearity, which confirms the occurrence of electron tunnelling. Evaluating possible conductivity mechanisms, it was found that the mechanism is neither VRH for 2D or 3D systems nor FNT, as the corresponding characteristic graphs do not show a linear dependence. By fitting each current-voltage characteristic curve (straight lines in Fig. 11) to the Simmons model (3), the obtained accuracy is very good – $R^2 > 0.997$, so we conclude that the electrical conductivity of EOK-CB composites follows this mechanism.

The main trends for the constants obtained from fitting the model are s – the thickness of the insulating barrier layer increases as the degree of filling increases (from 15 Å 10 phr CB to 18 Å 30 phr CB). For composites with a higher degree of CB filling, the resistance of the samples is lower and for the same applied voltage, the generated heat is bigger. Since the heat output is higher, the sample expands more significantly compared to samples with a lower concentration of CB. This can lead to the false impression that for a higher degree of filling, the particles are further apart, which is not logical, so this tendency is most likely due to thermal expansion.

The size of the rectangular tunnel barrier ϕ_0 decreases as the concentration of CB increases (from $1.2 \cdot 10^{-18}$ J 10 phr of CB to $0.9 \cdot 10^{-18}$ J 30 phr of CB). This can be explained by an easier transition from particle to particle when a larger number of particles are available in the composite. Additionally, a higher degree of filling introduces more impurities, which can also reduce the barrier height.

The last parameter C is considered to be the cross-sectional area of the current flow. The parameter increases with the increase in CB filling. This tendency can be logically explained with the fact that when the quantity of particles within the material is increased, both the current

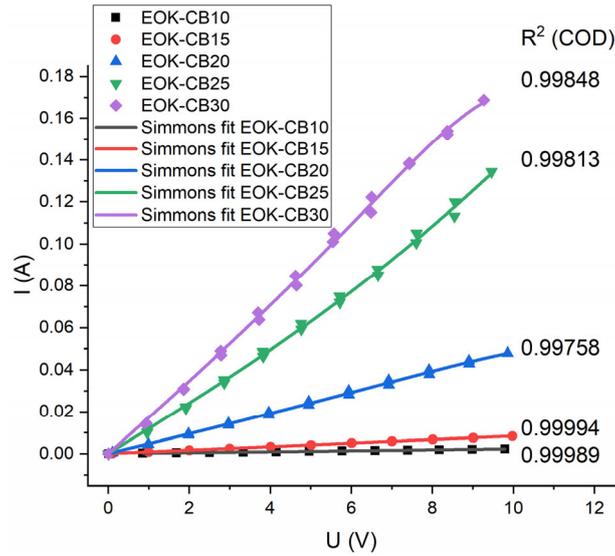


Fig. 11. Current-voltage characteristic curves of EOK-CB composites (experimental points) and fitting lines (solid lines) to Simmons generalised formula for the electric tunnel effect.

flow and the overall cross-sectional area through which the current passes are likewise increased.

The α values obtained for the EOK-CB composites are summarized in Table 2. It can be concluded that as the degree of filling increases, α decreases, because the filler prevents the matrix from expanding.

Table 2

Linear thermal coefficient of expansion values for EOK-CB composites with different loading of CB filler

CB, phr	$\alpha \cdot 10^{-4}, 1/K$
30	3.50 +/- 0.25
20	3.71 +/- 0.25
10	4.49 +/- 0.31

Comparing the obtained values with the coefficient of thermal expansion of pure filler $\alpha_{CB} \approx 0.06 \cdot 10^{-4} 1/K$ or CR composites of the same CB concentration $\alpha_{CR-CB30} = 1.95 \cdot 10^{-4} 1/K$, one can understand why, for EOK-CB composites, the matrix expansion effects are already noticeable at small temperature changes. The value of $\alpha_{EOK-CB30}$ is one third higher than that of the CR composite. For a more extensive thermal expansion of the matrix, a lower temperature difference is required to achieve the same distance of expansion. This is why for EOK-CB composites even for small temperature changes the influence of tunnelling current decreasing effects is more pronounced.

EC-AFM characterisation

EC-AFM images of EOK-CB composites with different concentrations of CB are shown in Fig. 12. The blue regions depict the dielectric matrix and the red are the electroconductive channels. With an increase in filler content, the number of electroconductive channels and the strength of the current flowing through them (peak height) increases.

Basics about the indexes

To effectively analyse the obtained index values at different current planes, it is essential to identify and understand the fundamental factors that influence the indexes and how they impact the results. The value of the indexes can be in the range from 0.5 to 1.

d-Index (1) will be smaller if:

- there is a larger distribution of the values of fill percentage for each of the 9 segments;
- there is a greater difference between the average and the largest fill percentage of the segments.

s-Index (2) will be smaller if:

- more channels are larger than the limit (5 px) in terms of size;
- there is a greater difference between the largest formed channel and the total area taken up by all the channels.

The higher the values of the indices, the more homogeneous the distribution is, either of channel size or spatial filling; however, the lower the values, the worse these distributions are.

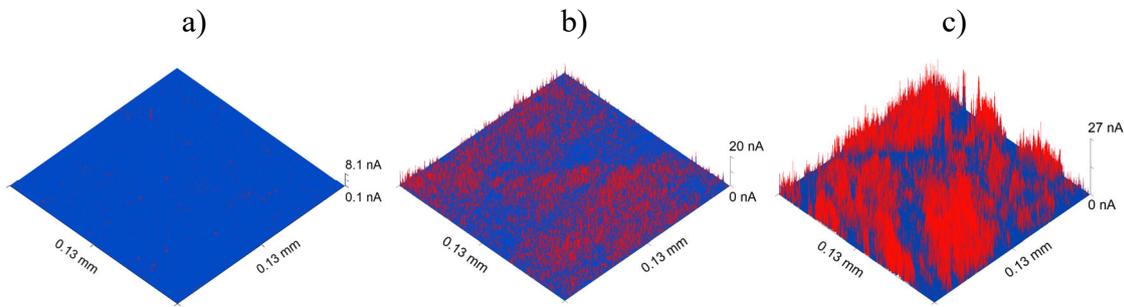


Fig. 12. EC-AFM images of EOK-CB composites with a) 10 phr, b) 20 phr, and c) 30 phr of CB. The blue regions are the dielectric matrix regions, while the red peaks are the current strength regions where there is a CB particle channel going through to the opposite electrode. The higher the peak, the more intense current flows through that channel. The area dimensions of one region are $130 \mu\text{m} \times 130 \mu\text{m}$.

The average values of the calculated indices of a sample, depending on the filler load, are shown in Fig. 13. These data were obtained from EC-AFM images using a 0.17 nA current

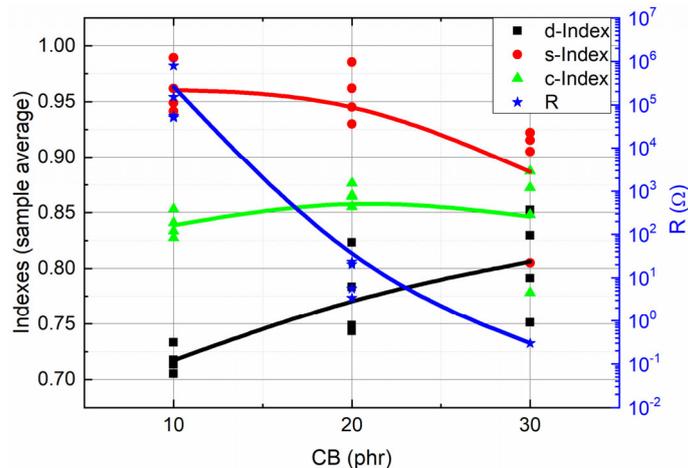


Fig. 13. Values of dispersion degree characterisation indexes (average for sample) depending on the filler loading (left axis) for EOK-CB composites and the average resistance of the sample (right axis).

strength base plane (“current plane” for short) for calculations. The index values obtained for the 20 phr and 30 phr of CB samples are strongly scattered compared to the samples with 10 phr of CB. This can be explained by the very high degree of filler resulting in merged channels due to the large number of low current strength channels, which at the 170 pA base plane show up as a single monolithic channel, distorting the calculated indexes. This dispersion is the largest for the samples with 30 phr of CB whose resistance is 0.5–1 Ω . On the other hand, the scattering of the index values observed for samples with 10 phr of CB is relatively small because the lower concentration of the filler results in a smaller number of channels that can be measured. Since the channel distribution by current strength is not considered when calculating these indexes, the merged channels strongly influence the index values.

To improve this method’s composite characterisation capability, we could look at the indices calculated in different current base planes of the EC-AFM image. In this way, composites with significantly different levels of filling can be mutually characterised.

EC-AFM image analysis by current base planes

For a better understanding, Table 3 summarises images of individual current planes within one measurement for EOK-CB composites with 10 phr, 20 phr, and 30 phr of CB. In each of the current planes, only those channels whose strength is greater than the value of the specific current plane are displayed; therefore, at a plane of a lower current strength, significantly more channels are observed than at a plane of a higher current strength. From the images it can be seen that the distribution of the channels of the sample with 10 phr of CB is uneven, as one large collection of channels can be observed, while the images for samples with 20 phr and 30 phr of CB are already much more evenly filled. For samples with 30 phr of CB in the 0.17 nA current plane, it is possible to see the merging of the channels into one large channel, which shows that the method for describing the uniformity of the dispersion, is not optimal.

As can be seen, the 10 phr of CB EC-AFM image has many low current channels, the 20 phr of CB map shows low to medium (~ 5 nA) current channels, while the sample with 30 phr of CB has mainly medium to high (~ 10 nA) current channels. Since such a significant difference in channel strength and occurrence density is observed and it is difficult to compare images with highly different filling degrees, it would be necessary to evaluate the current plane, which is taken for the index calculation, so that low and high filling degree composites could be rationally compared with each other. One option would be to choose a current plane where the remaining number of channels compared to the 0.17 nA plane is a specific percentage value (for example, a 10 % threshold). This would mutually normalise the base current plane for composites with different filling degrees. For instance, in the EC-AFM cases mentioned previously, the current plane selected for the analysis would be 10 phr – 0.5 nA, 20 phr – 2nA, and 30 phr – 10 nA.

A combined graph for all indices depending on the amount of filler and the current plane chosen for index calculation (starting from 1 nA) is shown in Fig. 14.

For samples with 10 phr of CB, high-current-strength channels are only observed in a few places – *d-Index* decreases for higher current planes and tends to 0.5, which is the value for the greatest non-uniformity. Looking at the *s-Index* value in Fig. 14 for samples with 10 phr of CB, it drops until the current plane of 5 nA but then again increases. From this, it can be concluded

that this is the threshold value, and most of the channels are below this plane. A further increase in the index indicates that the remaining current channels are of similar size to each other and are not merged.

Table 3

EC-AFM image different current base planes for EOK-CB composites of different filler loading.*

	0.17 nA	0.5 nA	2 nA	10 nA	20 nA
EOK-CB10					
EOK-CB20					
EOK-CB30					

*Blue – dielectric matrix, red – conductive channel, the strength of which is greater than the strength of the current plane. The area dimensions of one region are $130 \mu\text{m} \times 130 \mu\text{m}$.

Analysing the indexes obtained at different current planes, samples with 20 phr of CB have gradual trends (see Fig. 14), indicating a uniform spread in terms of both the number and strength of the channels. *d-Index* decreases at higher current planes – the uniformity of channel distribution throughout the area decreases because the channels of low current strength, formed by tunnelling currents through the thicker insulating layers, disappear, but channels of high currents remain, which are unevenly arranged.

On the other hand, the value of *s-Index* at the beginning is close to the maximum, but then a sharper drop is observed, which indicates a decrease in the uniformity of the channel sizes in the current planes above 10 nA.

In general, if a significant change in phenomena based on percolation and tunnelling effects is desired, this distribution of channels is the most effective because this arrangement has the greatest variation in the possibilities of channel breakage and reforming due to particle rearrangements.

Analysing the obtained data for composites with 30 phr of CB, one can observe the opposite trend to 10 phr of CB samples – both *d-Index* and *s-Index* values are mostly increasing.

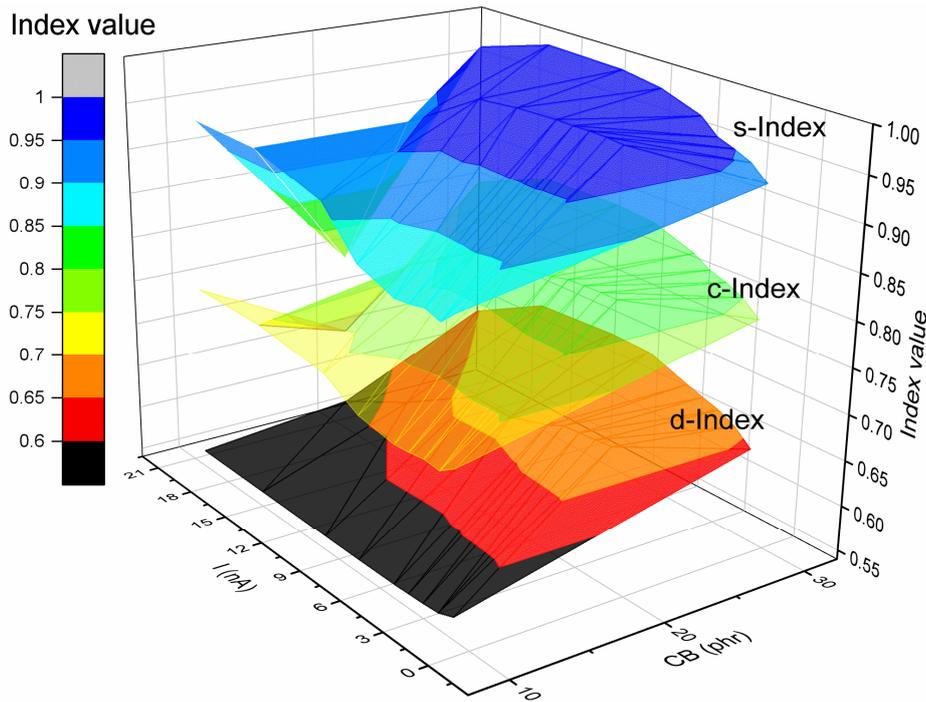


Fig. 14. Values of dispersion degree characterization indexes depending on filler loading and selected current base plane for EOK-CB composites starting from 1 nA current base plane.

Composites of this concentration have a lot of electrically conductive channels passing through the material, which is why most of the channels are above 20 nA in terms of current strength and can be observed in all the current planes – the index values depend little on the chosen plane. For such a composite, the effects of matrix expansion will give a relatively small change to the electrical conductivity because if one channel breaks, there are a lot of other channels of similar strength that will provide an unchanging resistance.

In Fig. 14, it can be clearly seen that for samples with 30 phr of CB, the *c-Index* does not change throughout the different current planes, but for samples with 10 phr of CB it is the smallest. For the samples with 20 phr of CB, it does not change until the 15 nA current plane, where it starts to drop off sharply. The most favourable arrangement to obtain self-regulating composites is *c-Index*, which is close to 1 but gently falling for larger strength current planes because it indicates a system that is not “oversaturated” with channels and can respond more intensely to minor changes.

If we take a current plane whose remaining channel amount compared to the 0.17 nA plane is 10 % as the base plane for the index calculation, the obtained index values are shown in Table 4. According to the calculated indices, it can be seen that for the EOK-CB10 sample, the distribution of particles in the volume is worse than for the samples with a larger phr of CB. Since, for this sample one large cluster of channels is observed (see images in Table 3), the resulting indexes describe the overall particle dispersion appropriately. On the other hand, for samples with 20 phr and 30 phr of CB, the indexes indicate an equivalent dispersion over the sample, as the *c-Index* for both is in the range of 0.84–0.85. By comparing the images in Table 3 it can be concluded that, regardless of the effect of the degree of filling, the general arrangement of the particles throughout the measured area is comparable, and no clusters of channels can be

seen for both samples. Therefore, this type of analysis can be used to mutually characterise composite materials with significantly different filling degrees.

Table 4

Indexes characterising the dispersion degree if the current base plane is chosen as the plane in which the remaining number of channels is 10 % compared to the 0.17 nA current plane.

Sample	Current base plane	<i>d-Index</i>	<i>s-Index</i>	<i>c-Index</i>
EOK-CB10	0.5 nA	0.58	0.90	0.74
EOK-CB20	3 nA	0.68	1.00	0.84
EOK-CB30	10 nA	0.70	0.99	0.85

Practical application

Both investigated polymer composites are flexible and with a 20 phr to 30 phr of CB degree of filling, they are sufficiently electroconductive to provide temperatures from 40–100 °C with an applied voltage of 5–10 V. By adjusting the size, filler content, electrode material and electrode placement, both CR-CB and EOK-CB composites can be used for different applications.

The advantage of CR-CB composites is their high heat power output, as their electrical resistance is almost an order of magnitude lower than EOK-CB composites of a similar filling degree. If the application requires a sufficiently large amount of heat quickly, and the surrounding environment can absorb the excess heat, then a CR-CB composite with an adjusted filler content and shape will be ideal. The main drawback of CR-CB is its *NTC* effect, which means that the conductivity will only continue to grow if the temperature continues to increase – there is a possibility of overheating.

The advantage of EOK-CB composites is their positive temperature coefficient of resistivity starting from the degree of filling of 20 phr of CB. This is the most desirable effect for the use as a self-regulating heating element, as it means that the material cannot overheat. A major drawback of these materials is their relatively high base electrical resistance, as a much larger amount of filler is required to obtain an equivalent starting resistance compared to CR-CB composites. On the other hand, increasing the volume fraction of the filler increases the rigidity of the material (reduces flexibility) and reduces the relative intensity of the PTC effect.

By carefully considering the parameters required for the application – electrode material, design, achievable temperature and flexibility – it is possible to model a heating element of exactly the design and achievable temperature required for a specific case.

Conclusions

1. To create a heating element of a comfortable temperature for the human body, the most optimal concentration for CR-CB composites is 20 phr of CB because at 5 V, the temperature reached in 30 seconds is 45 °C. By adjusting the distance between the electrodes, it is possible to obtain a composite with a working temperature of 50–60 °C, which is the recommended temperature for body heating.

2. CR-CB composites up to 50 °C show *NTC* – negative temperature coefficient of resistivity – the resistance decreases with increasing temperature. Unfortunately, such a composite does not have self-regulating properties.
3. The mechanism of electrical conductivity dependence on voltage for CR-CB composites can be divided into four different regions:
 - The initial region of up to 2 V is dominated by the increased speed of charge carriers as a result of voltage increase.
 - Starting at 3 V, the matrix expansion-induced decrease in tunnelling currents reduces the voltage-induced increase in conductance until it becomes the dominant conduction mechanism at voltages above 5 V.
 - In the temperature region 50–70 °C corresponding to the applied voltages of 5–7.5 V, the dominant conduction mechanism is the reduction of tunnelling currents due to the thermal expansion of the matrix.
 - Above 70 °C, for the applied voltage of 7.5 V and 10 V, the temperatures are so high that kinetic agglomeration occurs because the matrix exceeds the softening temperature and filler particles can reorient themselves and form new electroconductive channels increasing the electrical conductivity.
4. Evaluating various electrical conductivity models, the best for our experimental data is the formula for the electric tunnel effect for medium voltages described in the Simmons model. By fitting the data to the formula, we obtain the average distance of the insulator layer – 1.6 Å, which is a reasonable distance in highly filled composites.
5. The thermal expansion of the composite matrix starts to affect the overall conductivity at relative expansion of 0.4 %, and it becomes the dominant mechanism for CR-CB20 composites at relative expansion larger than 0.9 %.
6. nEOK-CB composites exhibit an intense *PTC*, especially for the sample with 10 phr of CB. The measurements show a significant change in relative resistance, but the change is unstable and irreversible – such a material cannot be used for practical application. In order to stabilise the significant matrix effects, nEOK needs to be cross-linked.
7. In the self-heating mode, the temperature increase of nEOK-CB samples with 15 phr of CB was less than 1 °C, and they exhibited *NTC*, which can be explained by the applied voltage-induced increase in carrier velocity. For the samples with 20 phr and 25 phr of CB, the released power decreased with the increase in temperature.
8. In external-heating mode, all EOK-CB composites exhibit *PTC*, especially the samples with 10 phr of CB. In the self-heating mode, the *PTC* effect starts to be observed for compositions with 20 phr of CB or higher.
9. Since the EOK is a non-polar matrix, the dominant effects are temperature-induced; the voltage-induced effects are observable in a noticeable form only at applied voltages lower than 2 V when the matrix has not had the means to heat up.

10. At temperatures above the melting point of the matrix, the *NTC* effect is observed, which is caused by the rearrangement of the particles because the matrix has become soft.
11. All EOK-CB composite current-voltage characteristic curves show a small nonlinearity, which indicates the occurrence of electron tunnelling. The Simmons model fits our experimental data the best. The obtained fitting parameters have the following tendencies with an increase of filler load in the composites:
- s – the thickness of the insulating layer increases, which can be explained by the fact that at a higher degree of filling but for the same applied voltage, the sample heats up and expands more because the electrical resistance is lower. This can lead to the false impression that for a higher degree of filling, the particles are further apart from each other, which is not logical, so it is most likely due to thermal expansion.
 - φ_0 – the size of the rectangular tunnel barrier decreases, which can be explained by an easier transition from particle to particle if a larger number of these particles are available in the composite, as well as a higher degree of filling introduces more impurities, which can also reduce the barrier height.
 - C – a constant that characterises the cross-sectional area of the current flow. It increases with the increase in phr of CB because increasing the number of particles (phr) in the material increases the current flow and the total cross-sectional area through which it flows.
12. As the degree of filler increases, the linear coefficient of thermal expansion α decreases because the filler particles impede the expansion of the matrix. For the EOK-CB30 composite, α is almost a third higher ($\alpha_{\text{EOK-CB30}} = 3.50 \cdot 10^{-4} \text{ 1/K}$) than for the CR-CB30 composite ($\alpha_{\text{CR-CB30}} = 1.95 \cdot 10^{-4} \text{ 1/K}$), which, together with the non-polar nature of the matrix, explains the significant effect of temperature on the electrical conductivity of the composite material.
13. The greater the thermal expansion of the matrix, the smaller the temperature difference needed to obtain the same amount of expansion. For EOK-CB25 composites, the effects of thermal expansion influence the electrical conductivity even at very small relative expansions of 0.07 %.
14. If the current base plane for the calculation of the dispersion degree characterising indexes is chosen according to the remaining percentage of channels compared to the 0.17 nA current base plane, which is slightly above the noise level, it is possible to characterise the samples and compare the resulting indexes even in the case of a significant difference in the degree of filling.

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