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Electrically Conductive Nanocomposite Fibers for Flexible and Structural Electronics

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Abstract: The following paper presents a simple, low-cost, and repeatable manufacturing process for fabricating conductive, elastic carbon-elastomer nanocomposite fibers for applications in the textile industry and beyond. The presented method allows for the manufacturing of fibers with a diameter of 0.2 mm, containing up to 50 vol. % of graphite powder, 10 vol. % of CNT, and a mix of both fillers. As a result, resistivity below 0.2 Ωm for the 0.2 mm-diameter fibers was achieved. Additionally, conductive fibers are highly elastic, which makes them suitable for use in the textile industry as an element of circuits. The effect of strain on the change in resistance was also tested. Researches have shown that highly conductive fibers can withstand strain of up to 40%, with resistivity increasing nearly five times compared to the unstretched fiber. This research shows that the developed composites can also be used as strain sensors in textronic systems. Finally, functional demonstrators were made by directly sewing the developed fibers into a cotton fabric. First, the non-quantitative tests indicate the feasibility of using the composites as conductive fibers to power components in textronic systems and for bending detection.

Keywords: polymer matrix composite; textronic; conductive composite; sensors; carbon nanotubes (CNTs); smart clothing; printed electronics; structural electronics

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1. Introduction

Smart textiles, also called smart clothing, represent an evolving new class of materials with a range of new features, such as flexibility, stretchability, and lightness that allow for many applications and designs previously not possible with the use of traditional electronic technology [1]. As clothes and textiles are in direct contact with about 90% of the skin's surface [2], smart textiles with noninvasive sensors can be used not only for aesthetic purposes, but above all to improve human living standards, health, and safety. For example, wearable electronic devices allow for the continuous monitoring of vital parameters during typical daily activities. This information can reduce the need for the patient to stay in the hospital while providing a great deal of the necessary information to determine the patient's health condition. Similar types of intelligent textiles equipped with sensors can be used in sportswear to monitor heart rate, breathing, body temperature, and other physiological parameters. Smart textiles can also be used in military, fashion, energy harvesting, and wireless data transmission [3–8]. Given the many possible applications of smart textiles, it is highly reasonable to conduct research to develop new electronic components, materials, and manufacturing methods that can serve to broaden the applications of wearable electronics. It is particularly important to develop electrically conductive materials that meet the additional requirements of the textile industry, such as elasticity, stretchability strength, light weight, and low production cost. One of the materials groups that can fulfill the above assumptions are polymer composites with a conductive functional phase in the form of carbon structures, such as carbon nanotubes, graphite, or graphene [9]. Equally important

as the choice of conductive phase is the choice of a suitable polymer matrix, which is mainly responsible for the mechanical properties of the composite.

Here, we introduce a manufacturing process of conductive, elastic, and small-diameter (0.2 mm) composite fibers of an unlimited length in an SBS (poly(styrene-butadiene-styrene)) matrix and CNT (carbon nanotubes), and/or graphite as a functional phase. In this study, the electrical behavior of the fabricated fibers was analyzed and described. The as-produced fibers may be sewn into the fabrics and used as a conductive path in textronics circuits or as a strain sensor, thanks to its piezoresistive properties. Thanks to its efficient processing properties, it is expected that similar composites may be suitable not only for the textile industry, but also, for example, as a filament for 3D printing.

2. Materials and Methods

2.1. Materials

The materials used for the fabrication of the composite fibers consist of Europrene SOL T 166 styrene-butadiene block copolymer (SBS), purchased from Polimeri Europa, Italy, used as a composite matrix; multiwall carbon nanotubes NC7000 purchased from Nanocyl SA., Belgium; and MG1596 graphite powder purchased from Sinograf, Poland. The manufacturing process also involved the use of chloroform with a purity of >98.5%, purchased from Chempur, Poland, as a solvent for the SBS polymer.

2.2. Composite Fibers Preparation

During the research, three types of composites were fabricated, SBS/graphite, SBS/CNT, and SBS/graphite/CNT, with different amounts of functional phases. However, all the materials were prepared using similar procedures. The first stage of preparing the composite was dissolving an SBS polymer in chloroform using a heated magnetic stirrer to achieve a low-viscosity solution. In the meantime, ultrasound mixing of CNT and graphite was performed in chloroform with a small addition of dissolved polymer to break up the agglomerates using a Vibra-Cell VCX130 sonicator with 80% maximum power for 30 min. The maximum power of the used sonicator was equal to 130 W and the repetition rate was 20 kHz. The sonication process was carried out in a cylindrical 45 mm diameter container and using a 6 mm diameter sonication tip placed approximately 10 mm from the bottom of the container. After breaking up the carbon particle agglomerates, the carbon/solvent suspension was added to the remaining part of the dissolved polymer. Our previous studies showed that the breaking of the agglomerates of carbon structures using ultrasound in a polymer solution, allows for the fabrication of a composite with greater homogeneity than the breaking of carbon structures in the solvent alone [10]. Carbon particles were mixed with polymer using an MS7-H550-Pro magnetic stirrer for 2 h in an opened container to slowly evaporate chloroform. When the mixture reached a high viscosity that prevented further mixing with a magnetic stirrer, it was additionally stirred by hand and then poured into a large container to completely evaporate the solvent. Evaporation of the solvent was performed in a dryer at 50 °C for 24 h. After the evaporation of the solvent, the composite was palletized and formed into fiber using a hot mixing extrusion process.

To prepare the composite fibers, a single screw extruder was used. The extruder machine was equipped with two independent heating zones and replaceable nozzles with different diameters. This allowed for the control of the extruded fibers' diameters.

To fabricate highly homogenous and continuous fibers, the extrusion temperatures were set to 150 °C in both heating zones. Lowering the temperature caused insufficient plasticization of the matrix material, resulting in inhomogeneous fibers and the difficult extrusion of long fibers. On the other hand, a higher extrusion temperature caused the material to flow too quickly, making it impossible to achieve a consistent fiber diameter and also caused the thermal degradation of the matrix.

2.3. Composite Analysis and Testing

The electrical properties of the fibers were measured using the Rohde & Schwarz HM8112 multimeters. The two-point probe method was used for the resistivity measurements. The voltage–current characteristics were measured using a dedicated setup containing multimeters and voltage supply controlled via LabVIEW software, National Instruments Corporation, Austin, TX, U.S.A. Tensile tests were performed using the Cometech QC-506M2 machine, Cometech Testing Machines Co., Ltd., Taichung, Taiwan.

3. Results and Discussion

3.1. Composite Fibres Content

During the research, three types of conductive filler were used to fabricate the composites. Carbon nanotubes, graphite powder, and a mix of carbon nanotubes and graphite were used as a functional phase. Additionally, different amounts of conductive filler were used to fabricate fibers with different electrical and mechanical properties. The compositions of all the tested materials are shown in Table 1, together with the symbols that will be used throughout the rest of the article. In accordance with the datasheets, the densities of the materials used in the calculation of the volumetric content in the composite were 1.08 g/cm^3 for SBS polymer, 2.6 g/cm^3 for CNT, and 2.2 g/cm^3 for graphite.

Table 1. Composition of the composite materials.

		Material Amount [vol. %]		
		SBS	**Graphite**	**CNT**
Composite symbol	G1	95	5	0
	G2	90	10	0
	G3	80	20	0
	G4	60	40	0
	G5	55	45	0
	G6	50	50	0
	C1	98	0	2
	C2	95	0	5
	C3	90	0	10
	M1	96	2	2
	M2	93	2	5
	M3	90	5	5
	M4	85	10	5
	M5	80	15	5

3.2. Acceptance Criteria

In order to obtain a composite fiber that can be used in textronics as a conductive element or sensor, the material must have suitable electrical and mechanical properties and it must be possible to continuously extrude it to obtain fibers of a limitless length.

The first criterion considered in the study was the ability to obtain a continuous fiber with a constant diameter (0.1 mm error allowed) of 0.2 mm, 0.5 mm, and 1 mm, depending on the used nozzle during extrusion, and a minimum length of 0.5 m.

The mechanical criteria considered included the elasticity and extensibility of the developed fibers. The fibers with adequate elasticity were those that, after repeated bending with a bending radius of 0.5 mm, did not crack and no damage visible to the naked eye was observed on their surface. Additionally, the minimum elasticity that the developed fibers should exhibit, should allow the fiber to be stretched by a minimum of 40% without damage.

The last of the considered criteria that the developed fibers should meet was the criterion of low resistivity. It was assumed that fibers with a diameter of 0.2 mm should have a resistivity below 0.2 Ωm. It was also essential that the fibers possessed constant resistivity in the function of voltage in the range of 0 V to 30 V.

3.3. Fabrication of Continous Fiber

Composite fiber extrusion attempts showed a significant effect of the amount and type of functional phase on the ability to produce a continuous fiber with a small diameter. The addition of a functional phase in the form of graphite powder (materials G1–G5), even in large amounts of up to 50 vol. %, did not significantly impair the rheological properties of the composite. Thus, it was possible to continuously extrude the fibers a with high graphite content with a constant diameter. To the best of our knowledge, continuous fibers with such a high graphite content and a diameter of less than 1 mm have not yet been reported in the literature. The polymer/graphite composites reported so far, contained a significantly smaller amount of the functional phase, typically below 35 vol. % [11–15] and/or a higher fiber diameter, especially 1.75 mm to be used in fused deposition modeling 3D printing [16].

During the extrusion attempts of composites containing CNTs as the functional phase (materials C1–C3), significant difficulties were observed in obtaining a continuous fiber. Despite the possibility of extruding long fibers with CNT content up to 10 vol. %, microcracks were visible on the surface. The fibers were characterized by significant roughness. According to the literature, additives of carbon filler in the polymer matrix cause an increase in viscosity [17]. However, this phenomenon is significantly greater for the CNT filler than for the graphite filler. An increase in composite viscosity results in the reduced extrusion efficiency, reduced homogenization in the extruder barrel and a "sharkskin effect" appearing on the fiber surface [18,19]. The microcracks visible on the fiber surface were caused by the presence of high friction at the extruder nozzle exit [20].

Composites containing a mixture of CNT and graphite as a functional phase did not exhibit "sharkskin effect" after extrusion, in spite of the overall higher content of the carbon phase. This was due to the excellent lubricating properties of graphite [21,22]. The addition of graphite to the composite allowed for a significant reduction in the coefficient of friction between the extruder nozzle exit and the extruded composite. It resulted in a reduction in local stresses and the deformation of the composite fiber surface (Figure 1).

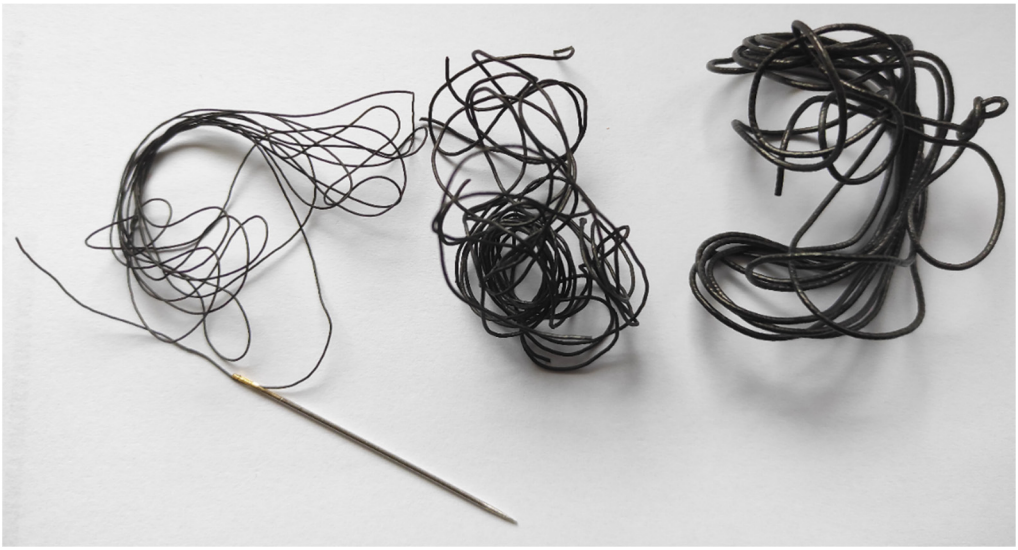

Figure 1. M5 composite fibers extruded using different diameter nozzles—0.2 mm (**left**), 0.5 mm (**middle**), and 1 mm (**right**).

3.4. Electrical Properties

DC resistivity measurements of the fabricated composite fibers were carried out using a four-probe method. For each fiber, the electrical resistivity of multiple 5 cm long sections was measured. Additionally, the average diameter of each fiber was calculated as the mean value of the diameters of the measured fragments. Due to the high elasticity of the

tested materials, the diameter measurement was performed using an optical method. It should be noted that the sections with resistivity values above 200 MΩ were considered as non-conductive. To calculate the resistivity of the samples, the relation

$$\rho = \frac{\pi d^2 R}{4l} \quad (1)$$

was used, where ρ is a composite resistivity, d is the average diameter of the fibre, R is the average resistance of fiber, and l is the length of the measured fiber section.

The calculated values of each composite fiber resistivity, depending on the diameter of the nozzle used during extrusion, were summarized in Table 2. It should be noted that the measurements were performed at a constant voltage value of 12 V.

Table 2. Average resistivity of the tested composite fibers with different diameters. Symbol "-" was used for non-conductive fibers (* composite C3 could not be extruded using a 0.2 mm diameter nozzle).

		Resistivity [Ωm]		
		Nozzle Diameter [mm]		
		0.2	**0.5**	**1**
Composite symbol	G1	-	-	-
	G2	-	-	-
	G3	-	42.9 ± 8.5	11.8 ± 5.2
	G4	-	0.384 ± 0.025	0.155 ± 0.008
	G5	0.817 ± 0.007	0.252 ± 0.002	0.453 ± 0.008
	G6	0.510 ± 0.006	0.0412 ± 0.0116	0.175 ± 0.011
	C1	-	-	-
	C2	1.45 ± 0.04	0.790 ± 0.019	0.367 ± 0.030
	C3	- *	0.00212 ± 0.00056	0.0426 ± 0.0089
	M1	-	-	-
	M2	1.57 ± 0.06	0.479 ± 0.026	2.96 ± 0.02
	M3	0.337 ± 0.015	0.271 ± 0.007	0.581 ± 0.029
	M4	0.233 ± 0.004	0.0738 ± 0.0040	0.0263 ± 0.0031
	M5	0.190 ± 0.006	0.0275 ± 0.0020	0.0153 ± 0.0015

It can be observed that at a low concentration of filler, conductive carbon particles are isolated by the polymer matrix material and a conductive network cannot be formed. It was observed that the percolation threshold of the CNT filler is much lower than that of the graphite powder filler, which is in agreement with literature reports [13,23–26].

The main disadvantage of using CNTs in conductive polymer composites is the typical nature of conductivity in semiconducting materials, mainly based on the phenomenon of electron tunneling between individual conductive particles. This is evident in the non-linear current–voltage characteristics of such composites. Composites containing graphite powder do not show such properties and their conductivity character is more similar to metallic conductivity, according to Ohm's law. In order to determine the dominant type of conductivity in the composites developed, especially those containing a dual functional phase, the current–voltage characteristics were determined. Composites G6, C2, C3, M3, M4, and M5, with a diameter of 0.5 mm, were tested for voltages ranging from 1–30 V. Other composites were excluded from the study due to too high resistivity, not meeting the initial criteria.

Table 3 shows the average resistivity values of the respective composites, together with their minimum and maximum values and the coefficient of variation (V) determined according to Equation (2), in which s is the standard deviation and $\underline{x}$ is the mean of measured resistivity values.

$$V = \frac{s}{\underline{x}} \quad (2)$$

Table 3. Resistivity values of the selected composites fibers with a 0.5 mm diameter.

		Average Resistivity [Ωm]	Maximum Resistivity [Ωm]	Minimum Resistivity [Ωm]	Coefficient of Variation (V)
Composite symbol	G6	0.0412	0.0422	0.0407	0.0101
	C2	0.790	0.837	0.771	0.0186
	C3	0.00213	0.00264	0.000975	0.265
	M3	0.271	0.284	0.267	0.0157
	M4	0.0738	0.0743	0.0735	0.00303
	M5	0.0275	0.0280	0.0272	0.00509

The obtained resistivity measurement results clearly indicate that the composites containing CNTs as a functional phase show a significant voltage dependence of the electrical conductivity. The C3 composite, despite its low resistivity, had a coefficient of variation equal to over 26%. In the case of the G6 composite, which had graphite powder as the functional phase, the coefficient was only 1.01%, which means that it had an almost constant value of resistivity regardless of the applied voltage. Composites containing a conductive phase in the form of a mixture of graphite and CNTs also showed a relatively constant resistivity value as a function of voltage. The M3, M4, and M5 composites studied had a constant CNT content of 5 vol. %. It was observed, however, that the M3 composite containing 5 vol. % of graphite in its composition was characterized by a slightly lower resistivity constant, similar to the C2 composite in which there was no graphite, compared to the M4 and M5 composites, in which the graphite addition was 10 vol. % and 15 vol. %, respectively. This means that the addition of graphite to the conductive composite containing CNTs allowed for an improvement in the linearity of the current–voltage characteristics. The graphite in the composite reduced the semiconducting character of the conductivity and allowed us to obtain a material with conductivity close to that of the metal. This was a significant advantage enabling a more comprehensive application of this type of conductive material in a wide voltage range.

Figure 2 shows the ratio of the resistivity at voltages different to the resistivity at 12 V for each tested material. Composites C2 and C3 were observed to exhibit higher resistivity at lower voltages. The sudden decrease in resistivity is particularly evident for composite C3, which was due to the higher CNT content. A similar phenomenon of an increase in the dynamics of conductivity changes of composites with an applied voltage, depending on the CNT content, was presented in the literature in the examples of the polyaniline and epoxy matrix composites [27,28]. The resistivity of the C3 composite decreased by almost 60% at 30 V compared to the resistivity at 12 V. Above a certain voltage, an exponential decrease in resistivity occurred. This phenomenon is due to two properties characteristic of CNTs: a negative temperature coefficient of resistivity (NTC effect) [29,30] and electron tunneling [31,32]. Firstly, an increase in voltage causes heat to be released in the material being tested, which reduces its resistivity. Secondly, in order to start electron tunneling between carbon nanotubes, it is necessary to apply a sufficiently high electrical potential. Once this is exceeded, a rapid flow of electrons occurs, which results in a significant increase in electrical conductivity.

The G6 composite containing 50 vol. % of graphite showed a slight increase in resistivity with the increase in the applied voltage. Graphite, in contrast to the CNTs, had a positive temperature coefficient of resistivity. As the applied voltage increased, the power dissipated on the tested composite increased, which caused the temperature of the sample to rise, at the same time increasing its resistivity.

Composites M3, M4, and M5, containing both of the above functional phases, showed a high resistivity constancy independent of the applied voltage. This was due to the superposition of the properties characteristic of graphite and CNTs.

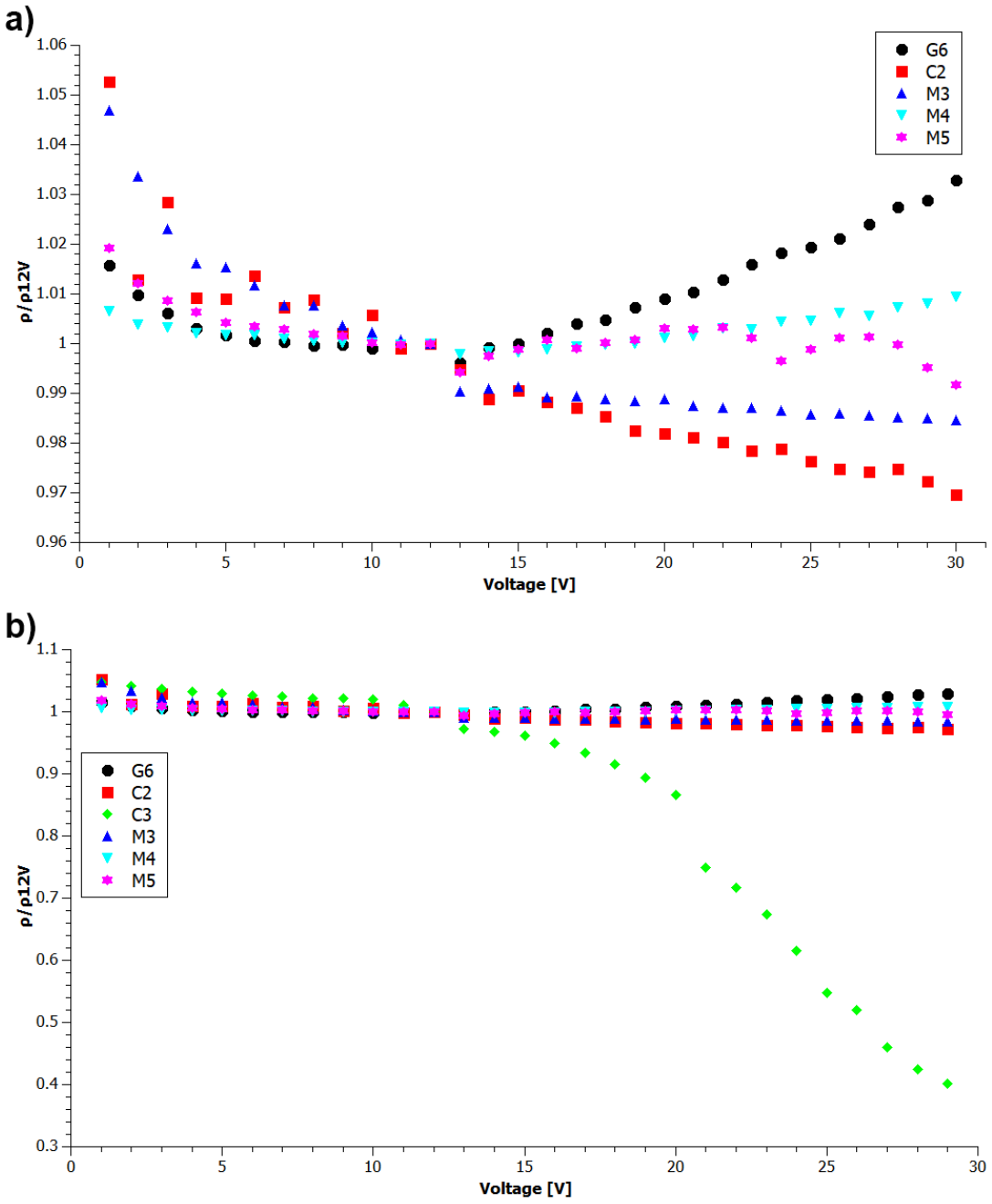

Figure 2. Changes in resistivity under different voltages compared to resistivity at 12 V for different composites; (**a**) excluding the C3 composite and (**b**) including the C3 composite.

As the developed composite fibers may be used in the textile industry, they should have mechanical properties that are no worse than the fabrics in which they will be placed. The fabric material must be resistant to the influence of external forces causing the change of its shape. The individual fibers in the fabric were mainly exposed to tensile and compressive forces. According to this, one of the most important mechanical requirements composite fibers must meet is sufficient maximum elongation. Typical textile fabrics, such as cotton, silk, and wool, and polymer fabrics, such as polyester, have an extension ratio from 7% to 40% [33–35]. According to these values, during the research, it was decided that the fibers must have a minimum of 40% elongation without breaking to be considered as meeting the basic mechanical requirements. In addition, it was desirable that the composite fibers in this range of stretches did not increase their resistance significantly. A change in resistivity in the range of several hundred percent may allow the developed materials to be used as

strain sensors located directly in textile materials. However, more significant changes in resistivity could cause difficulties in using composite fibers to transmit and receive electrical signals, or to power electronic components in textronic systems.

The present paper analyzed the effect of strain on the change in resistance of the composite fibers. The relative resistance change versus the extension ratio is shown in Figure 3. It was observed that the resistance of each fiber increased in a different way, depending on the filler type. The resistance of the G6 composite rapidly increased, even for a low extension ratio. On the other hand, the C3 composite containing CNT as the functional phase, had a much smaller increase in resistance during the entire tensile test until rupture. Composites containing a mixture of CNTs and graphite as the functional phase, presented a change in the resistance similar to the C3 composite, especially for the extension ratio below 40% (Figure 3b).

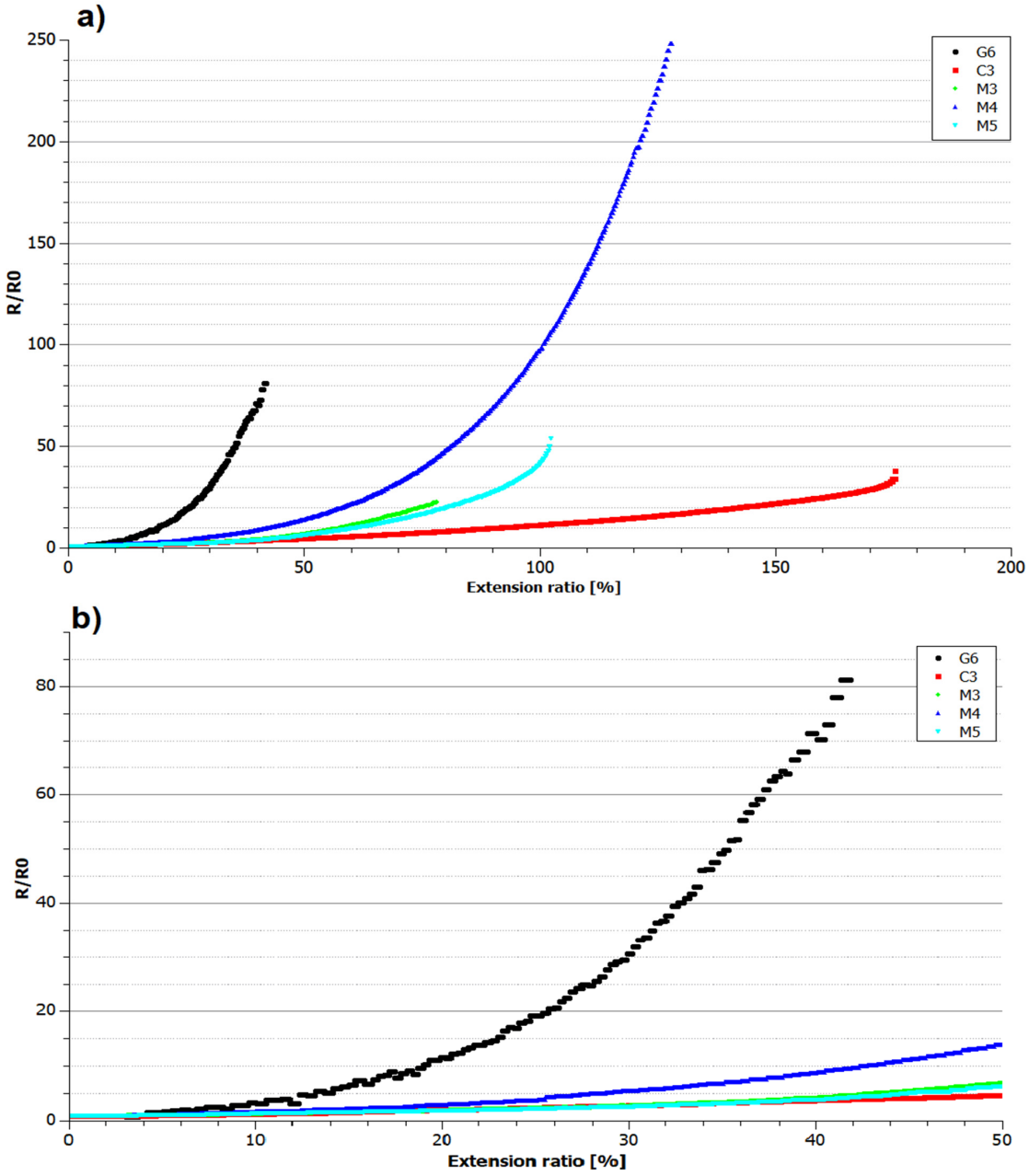

Figure 3. Dependence of relative resistance on elongation, for 0.5 mm diameter composite fibers, (**a**) for the maximum extension ratio, and (**b**) for and extension ratio of up to 50%.

4. Applications

The developed composite fibers can be used both as electrically conductive paths in textronics and as tensile sensors due to the piezoresistive phenomenon. According to the literature, there are many methods to integrate conductive fibers into the fabric, but two main ways can be determined: sewing [36–38] or deposition directly into the fabric [39–43]. Both methods of producing conductive paths on the fabrics were tested during our research.

The 5 mm-diameter fibers were hand-sewn into the cotton fabric. This example demonstrates the possibility of efficiently fabricating a conductive path by directly sewing a single composite fiber into the fabric without necessarily manufacturing the entire fabric with composite material. The LED was glued to the sewn-in fibers with conductive glue. Applying a voltage caused the LED to light up, which meant that the process of sewing-in the fibers did not negatively affect their electrical conductivity (Figure 4).

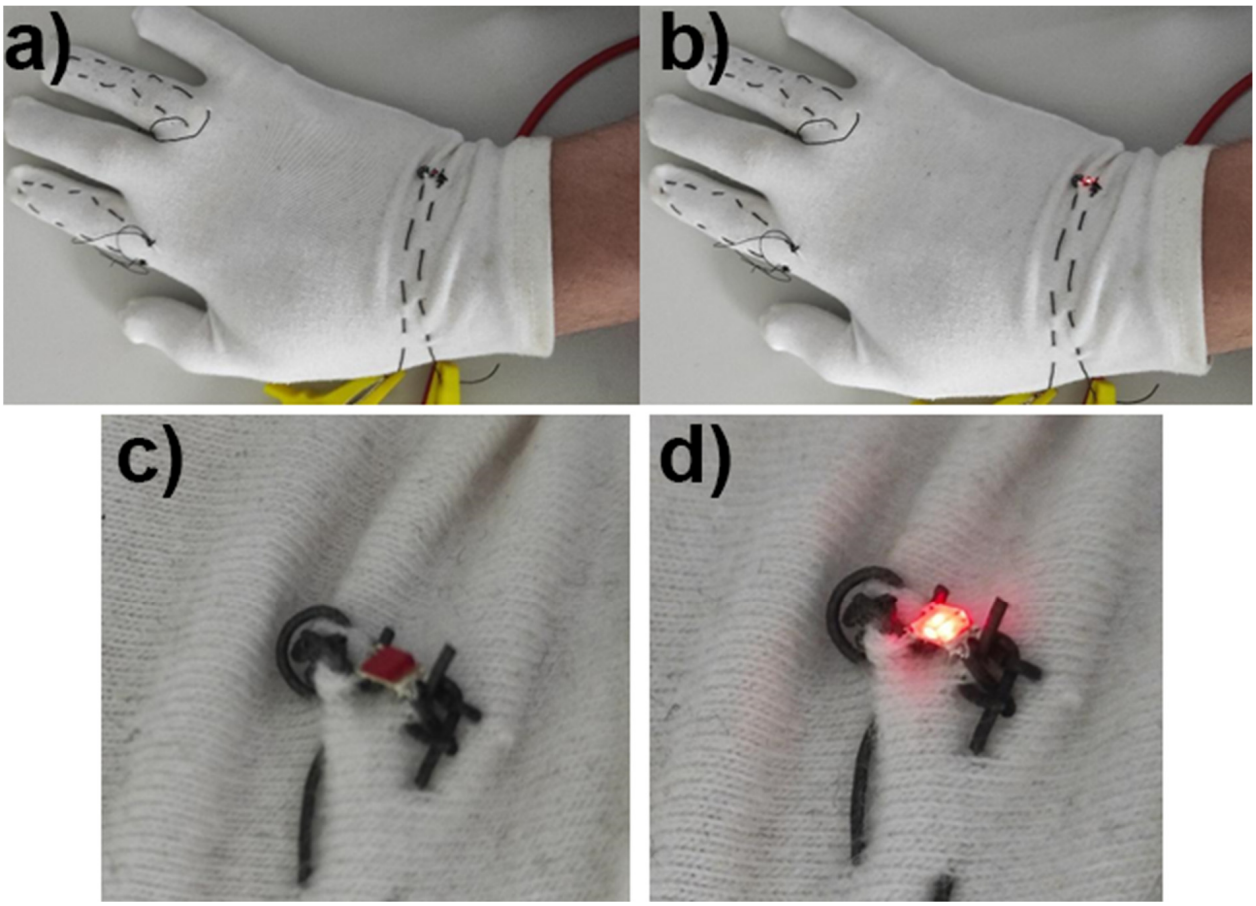

Figure 4. The sewing-in of the composite M5 fiber into a cotton glove; (**a**,**c**) unpowered and (**b**,**d**) powered.

Another way to create a conductive path directly on the fabric is to transfer the composite fiber by a thermal process, in which the composite fiber is plasticized and bonds to the fabric. Such a "print" on the cotton fabric was made using an ordinary iron by plasticizing the composite fiber and exerting pressure causing a good mechanical bonding. The manufactured path presented high adhesion to the fabric and could not be removed by hand. In addition, the composite did not lose its elastic properties. It was possible to bend and fold the fabric with the "printed" path without significant deterioration of the electrical conductivity (Figure 5).

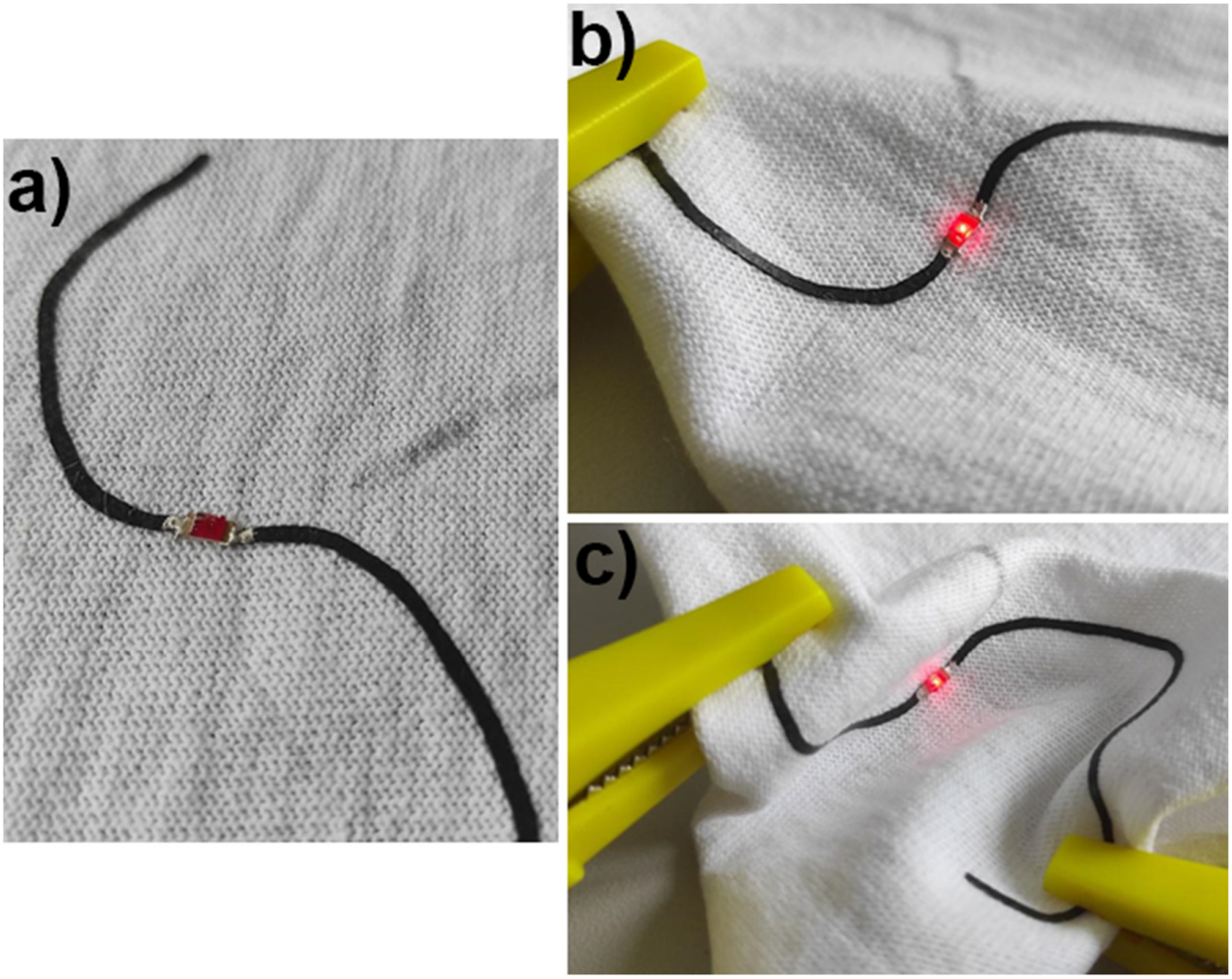

Figure 5. Conductive path fabricated by the thermal process on the cotton fabric; (**a**) unpowered, (**b**) powered, and (**c**) powered and bent.

The developed composite fibers also show piezoresistive properties, which allows them to produce stress, displacement, and bend sensors. Similar piezoresistive composites have been successfully used to monitor human movements [44]. In order to examine if developed conductive fibers could be used for a similar purpose, a single 0.5 mm diameter fiber was sewed into the cotton glove. The ends of the fiber were connected to a multimeter to detect any resistance change upon movement of the finger. After the authors put on the glove and flexed the finger, a change in the path resistance was observed (Figure 6). This effect could be repeated for each finger of the glove. Each finger was bent multiple times and the resistance increased with bending. The magnitude of the response is significant at around 10%. The sensitivity of such a fabricated sensor can be modified by using a composite fiber with a smaller diameter, which results in a smaller sensor response when bent, or by making several parallel stitches, which will increase the sensor response when bent. It is worth noting that the fabricated sensor does not require additional circuitry to amplify the received signal. Such printed devices could be used in the field of biomechanics to print customized sensors for patients to assist in their rehabilitation after accidents and injuries.

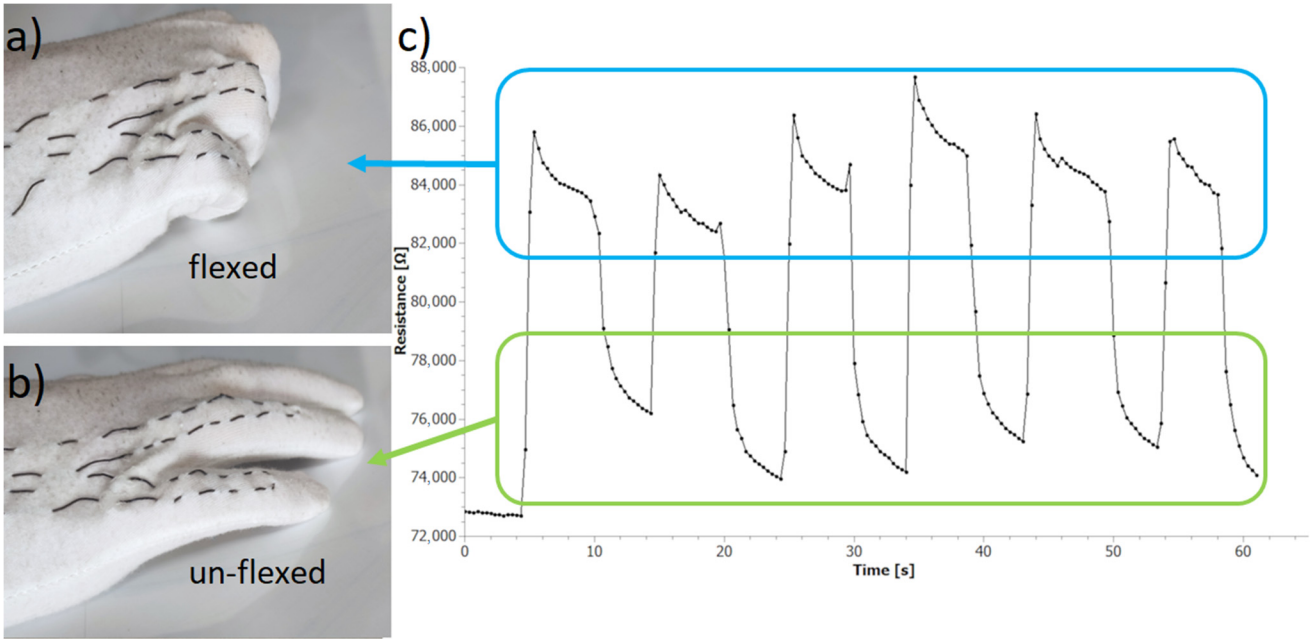

Figure 6. Cotton glove with sewed flex sensor; (**a**) during flexing, (**b**) un-flexed, and (**c**) the resistance response.

The conductive fibers in the example applications were in direct contact with human skin. Therefore, it is essential to be aware of the potential dangers of using carbon nanoparticles, especially CNTs, which are recognized as potentially hazardous to human health [45,46]. However, it must be taken into account that such a risk to human health is posed only by nanoparticles in their free, unbanded state and not in the form of the polymer nanocomposites from which the fibers are made. The literature that CNTs cannot be released from the polymer composites, despite the visible mechanical damage and wear of the composite. Especially safe are the composites with a flexible polymeric matrix, which is the SBS polymer used in this study [47–49]. Considering this, the studies presented were found to have both the intended functional properties and to be harmless to human health.

5. Conclusions

The research study has investigated the possibility of manufacturing composite conductive fibers with a small diameter to be used in textronic systems. During the research, we used a flexible SBS polymer as the composite matrix and investigated three types of functional phases—CNTs, graphite, and a mixture of these carbon structures.

The main objective of the research was to develop composite fibers with diameters below 0.5 mm, electrical conductivity above 0.2 Ωm, together with high elasticity and stretchability.

The lowest resistivity characterized the composites containing CNTs, but the high content of the functional phase made it impossible to extrude fibers with diameters below 0.5 mm in a continuous manner. Additionally, such composites were characterized by a non-linear current–voltage characteristic, which is typical for the semiconducting character of carbon nanotube conductivity.

Composites containing graphite as a functional phase were characterized by worse electrical conductivity and only the content of 50 vol. % allowed us to obtain resistivity below the assumed value of 0.2 Ωm. However, fibers with such a high content of graphite content presented unsatisfactory mechanical properties and broke below 40% of the relative elongation.

Using a functional phase in the form of a mixture of CNTs and graphite made it possible to obtain fibers with optimal electrical and mechanical properties. Composite fiber

containing 5 vol. % of CNT and 10 vol. % of graphite showed an average resistivity below 0.2 Ωm and an elongation on the break above 100%. In addition, the use of a two-component conducting phase allowed for a significant increase in the linearity of the current–voltage characteristics in the measurement range from 0 to 30 V. Thanks to the constant resistivity of the composite, it was possible to use it more widely, independent of the value of the supply voltage. The present research also presented methods for the practical application of the developed composite fibers. Tests have shown that the composite fibers can be integrated into standard fabrics in two ways. Thanks to the small diameter of the composite fibers, it was possible to sew them directly into the fabrics, similar to sewing-in textile fibers. Another way of creating conductive paths on the textile substrates was to press the fiber into the fabric structure, thermally. Both methods made it possible to produce conductive paths on the textile substrates and thus use the developed fibers in textronics.

The piezoresistive properties of the developed fibers were also observed during testing. As the stretching of the fiber increased, its resistance increased. An example of a bending sensor sewed directly into a cotton glove was presented using this phenomenon. This example presented the possibility of using the developed materials not only in engineering solutions, but also in bioengineering, sports, and medicine, including telemedicine, which plays an increasingly important role in health care.

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