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Prototypes of Carbon Nanotube-Based Textile Sensors Manufactured by the Screen Printing Method

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Abstract
In the present work the authors made textile sensors by the screen printing method with the use of carbon nanotubes. The sensors obtained are intended for monitoring dangers in direct contact with the body. For this reason the modification of carbon nanotube dispersion, with the commercial name AquaCyl from the Nanocyl company, was performed in order to give the textiles, apart from increased electric conductivity, bacteriostatic properties, which are extremely important in the case of biomaterials.Assessment of the efficiency of the sensors both for mechanical stimuli and the action of Gram-positive and Gram-negative bacteria was performed.

Key words: *textile sensors, screen printing, carbon nanotubes, breathing rate sensor.*

Introduction

During recent years, an increase in interest in technologies heading towards giving textiles specific properties, i.e. towards manufacturing of so-called intelligent textile materials is visible.

The demand for new applications in the field of intelligent textiles, which can be used for monitoring health, leads to the development of new techniques of their manufacture, miniaturisation and the embedding of electronics and sensors in ready-made products [1 - 6]. The development of new textile sensing devices creates possibilities in the range of manufacturing different kinds of sensors, for example printed sensors are becoming more and more popular.

The printing technique has been successfully implemented in the textile industry, which has made it possible to manufacture multifunctional clothing products.Many advantages arise from the utilisation of intelligent textiles, which includes monitoring of the reaction of the human organism to many stimuli and factors [1, 6].

The main advantages of this type of product are:
- increased convenience of use;
- high flexibility;
- easiness of movement for the user, thanks to eliminating the rigid elements (e.g. wires) connecting the sensors with the textiles;
- dimensions of the sensors.

Textiles with integrated modern sensors are used for assessing different changing parameters, such as pressure, stress and deformation [7 - 10].

Biomedical products manufactured with the previously mentioned properties are utilised for monitoring the heart beating, making an electrocardiogram, and controlling the frequency of breathing or the pulse [11 - 15].

Most modern sensors are based on microelectronics or conductive polymers, which are integrated with the structure of materials or fibrous structures.

In the future, utilising electronic systems to make intelligent clothing will be an integral part of everyday wear [16].

Printing is considered attractive technology in the range of the possible construction of electroconductive paths, leading to the creation of intelligent products. The printing technology of electroconductive paths has wide application in microelectronics, but is mainly used on plates, films, glass and on polymers. Most of the conductive inks used contain nanoparticles of silver, gold, copper, their compositions, and silver nitrate [17 - 21]. The limitation of this process for application in textiles is the necessity of using high temperature annealing in most cases over 200^{o}C. Recently research has been carried out on obtaining Ink compositions, giving conductive properties at temperatures of about 70 °C [22 - 27].

The authors in their work concentrated on a new field of research - giving electroconductive properties to textiles with the use of printing techniques, serving, for example, as a monitor of breathing. This direction of research was caused by the need for elaborating reliable, convenient systems for health monitoring [14, 28].

Physiologically non-invasive or minimally invasive monitoring devices are also of high importance for defense purposes and in applications for sportsmen. The direct integration of detectors and sensors with clothes should be beneficial for the development of health care and soldiers' monitoring systems, as well as in the case of other civil services. The integration of electronics with clothes opens many possibilities in many fields.

The authors used, as a functional carrier, a water dispersion of carbon nanotubes adapted at the Department of Material and Commodity Sciences and Textile Metrology to form an electroconductive transmission line with the screen printing method. It was assumed that the electroconductive paths obtained will be susceptible to deformation. Modification of the carbon nanotube water dispersion was aimed at getting a bi-functional – electroconductive and bacteriostatic – printing composition, which is highly important in the case of using sensors in medical materials contacting with the human body.

Taking into account the lack of data concerning the toxicological effects which

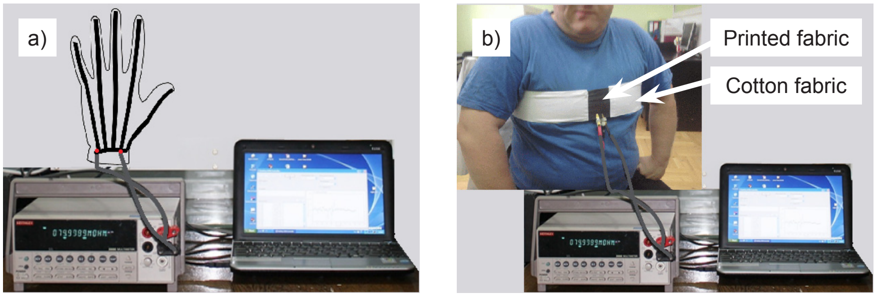

***Figure 1.** Prototype a) glove reacting to the movement of a finger b) band reacting to the breath of a human connected to the Keithley digital multimeter attached to a computer.*

can be caused by carbon nanotubes deposited on textile surfaces, as well as the necessity of ensuring the durability of their connection with the textile base, the authors carried out research on manufacturing bi-functional dispersion with a share of auxiliary agents such as aliphatic urethane acrylate and photoinitiator, and established optimal conditions for the cross-linking process of the printing compositions.

Materials and methods

In this work, the water dispersion of carbon nanotubes with the commercial name AquaCyl (AQ0101), from the Nanocyl company, was performed. This dispersion contained from 0.5 to 1.5% MWCNT from the Nanocyl®7000 series, characterised by a purity of about 90%, average diameter of the nanotubes – 9.5 nm and average length of up to about 1.5 μm. The Aquacyl showed a surface tension of about 57 mN/m, viscosity 36 cP and pH 7. The parameters were determined at a temperature of 25 °C. The dispersion was modified with sodium lauryl sulfate. In order to obtain a printing paste, the dispersion was mixed with a selected cross-linking composition of a photoinitiator and aliphatic urethane acrylate.

The electroconductive layer was printed on 'Weflock' knitted fabric from the Penn Elastic company. The knitted fabric contains 64% of polyamide continuous filaments and 36% of lycra. The surface mass of the knitted fabric used amounted to 245 g/m^2.

The printouts were made with the technique of screen printing on a warp-knitted fabric, manufactured with a three-needle bar weft weave with additional threads implemented on the weft level. In order to increase the flexibility of the knitted fabric, two perpendicular systems of weft threads were implemented into the structure. Vertical threads were implemented by a needle bar comb in the knitting section, while horizontal threads were implemented by a special weft device. Selection of the knitted fabric was based on the need for material that does not permanently deform and possesses reversible properties.

Depending on the requirement, the whole surface of the knitted fabric was reduced or there were electroconductive paths formed with different widths.

The printouts obtained were next fixed and bound with the base by cross-linking. The cross-linking was done with the use of a UV radiator (Philips UV lamp with a power of 2100 W and working length of 195 mm). UV-C 335 W radiation was used [29], dosage of which was selected to match the conditions required for the cross-linking mixture prepared and to maintain the durability of the knitted fabric at a constant level, equal to 3.5 J/cm^2.

Research methods used for the assessment of the functionality of the textiles obtained

The main goal of the research performed was to obtain sensors sensitive to mechanical deformation. The sensitivity of the printed knitted fabrics functionalised to elastic deformation was assessed on the basis of the change in resistance caused by the mechanical action of stress. The kinetics of the change in resistance under the influence of the stress action used was recorded with the use of a Keithley 2000 digital multimeter.

The electrical resistance of the printed fabrics was characterised with the use of the surface resistance, performed by the direct electrometer method with the use of a Keithley 610C electrometer. The source of voltage was a direct current power supply - RFT 4218 with the range of voltages 0 - 3000 V. The circuit of the electrodes with a sample was secured by a Faraday screen.

Constant conditions of conditioning and researching the sample were maintained: a temperature of 23 °C, RH = 25%.

The measurement of electrical conductance was in accordance with the PN-EN 1149-1:2008 standard.

Assessment of the antibacterial activity of the printed fabrics was made on plates with agar culture. The behaviour of bacteria was assessed in the zone of contact between the agar and the working sample, and the suppression zones around the sample were determined.

Next the width of the suppression zone was calculated, i.e. the zone without bacteria near the edge of the working sample, with the use of the equation

$$H = \frac{D - d}{2}$$

where:
- H – width of the suppression zone in mm,
- D – total diameter of the working sample and width of the suppression zone in mm,
- d – diameter of the working sample in mm.

Another step was to place the working samples under a microscope at 20-times magnification with bottom lighting. The growth of bacteria was assessed in the zone of contact on the underside of the sample.

The assessment of the antibacterial effect of the sample was in accordance with the EN ISO 20645:2006 standard.

Prototypes of the functional textile products

The positive effect of the research performed was the designing of a prototype of a glove reacting to the movement of a finger (***Figure 1.a***). On the glove electroconductive paths with a width of 0.8 mm were printed using the method of screen printing. The thickness of the electroconductive paths was 22.0 μm ÷ 24.0 μm.

The second prototype proposed is a band reacting to the movement of the chest, enabling the monitoring of breath (***Figure 1.b***). The band was made from Weflock knitted fabric covered with a print over its whole surface and sewn between two stripes of cotton fabric. The dimensions of the sample were 5 cm × 8 cm. The thickness of the printed surface layer was 22.5 µm ÷ 23.5 µm.

Results and discusion

On the graphs given in ***Figure 2*** and in ***Table 1*** the results of the initial research are presented, which characterise the sensory sensitivity of the printed knitted fabrics to mechanical deformation. The research were performed on an Instron tensile tester at a distance between the clamps of l = 20 mm, width of the sample 20 mm, and constant speed of pulling 2 mm/min. The sensitivity of the sample to mechanical deformation was determined by relative changes in electrical resistance, calculated according to the following formula.

$$S_r = (R_p - R_k)/R_p$$

where:
S_r – sensor rate,
R_p – initial resistance,
R_k – final resistance.

Data from ***Table 1*** are illustrated in ***Figure 2.***

For better comparison, the results showed in ***Figures 2*** and ***3*** are presented as relative changes in resistance calculated in accordance with the formula:

$$R_{rel} = (R_O - R_N)/R_O$$

where:
R_{rel} – relative resistance,
R_O – initial resistance,
R_N – final resistance.

On ***Figure 3*** are presented the resistance changes of the sample forced by cyclic elongation.

The fact that the results of research of the resistance in the range of reversible deformation are repeatable is worth emphasising. The printed knitted fabrics loaded with directional force at constant speed show simultaneously an increase in deformation and electrical resistance. The character of the rate sensory increase in the function of elongation is linear.

On the basis of the research performed, it can be stated that together with the change in deformation of the material, the resistance changes proportionally, which allows to use such printed knitted fabrics as resistive sensors.

Table 1. *Results of the sensory indicators of the printouts.*

Parameters	Knitted base printed		
Force, N	0.46	0.99	1.74
Elongation, mm	2	4	6
Sensory rate	2.08	6.90	9.36

The characteristics of the resistance changes caused by the loading and relieving of the printed knitted fabric are repeatable, allowing the designing of the previously mentioned band reacting to the movement of the chest and glove.

In ***Figures 4*** (see page 82), results of the research are presented, characterising the sensory sensitivity of the printed knitted fabrics to mechanical deformation. The research was performed on a 35-year old male. Recording of the signal presenting the bending and stretching of an index finger is shown in ***Figure 4.e*** (see page 82).

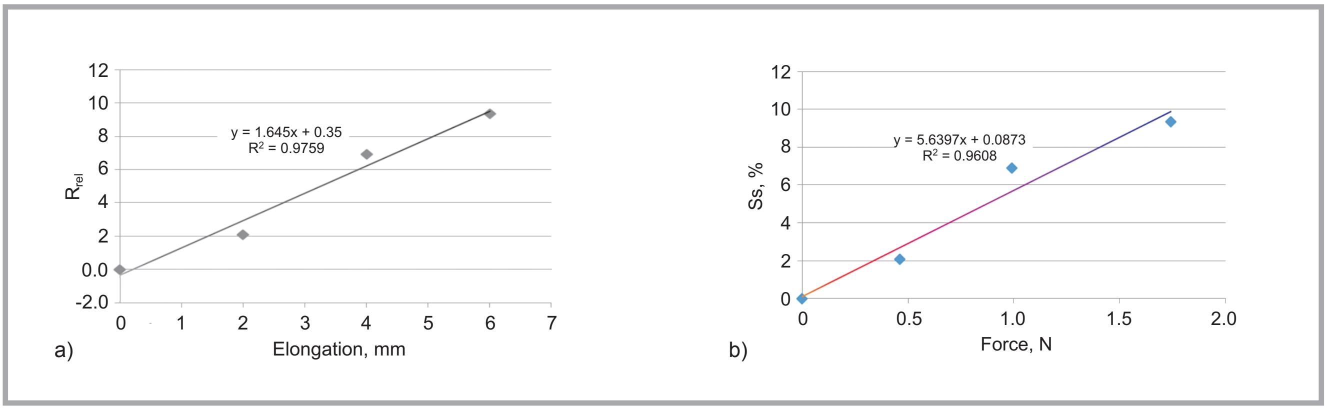

Figure 2. *Research results of the rate sensory response of printed knitwear in the ranges of elongation of 2, 4 & 6 mm a) rate sensor as a function of the elongation, b) rate sensor as a function of the force.*

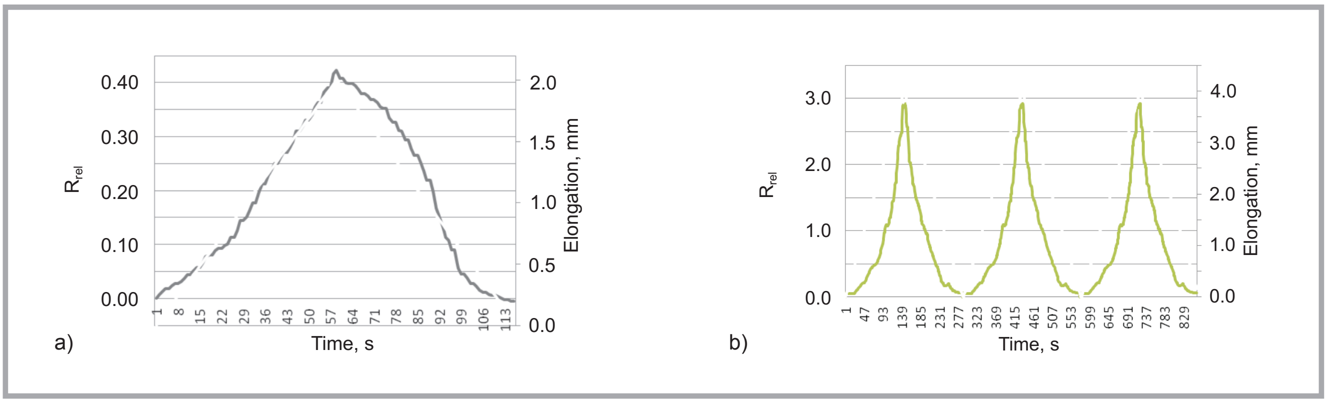

Figure 3. *Electrical resistive responses of printed knitted fabrics a) having undergone the process of elongation by a value of 2 mm, b) having undergone the process of cyclic elongation by a value of 4 mm.*

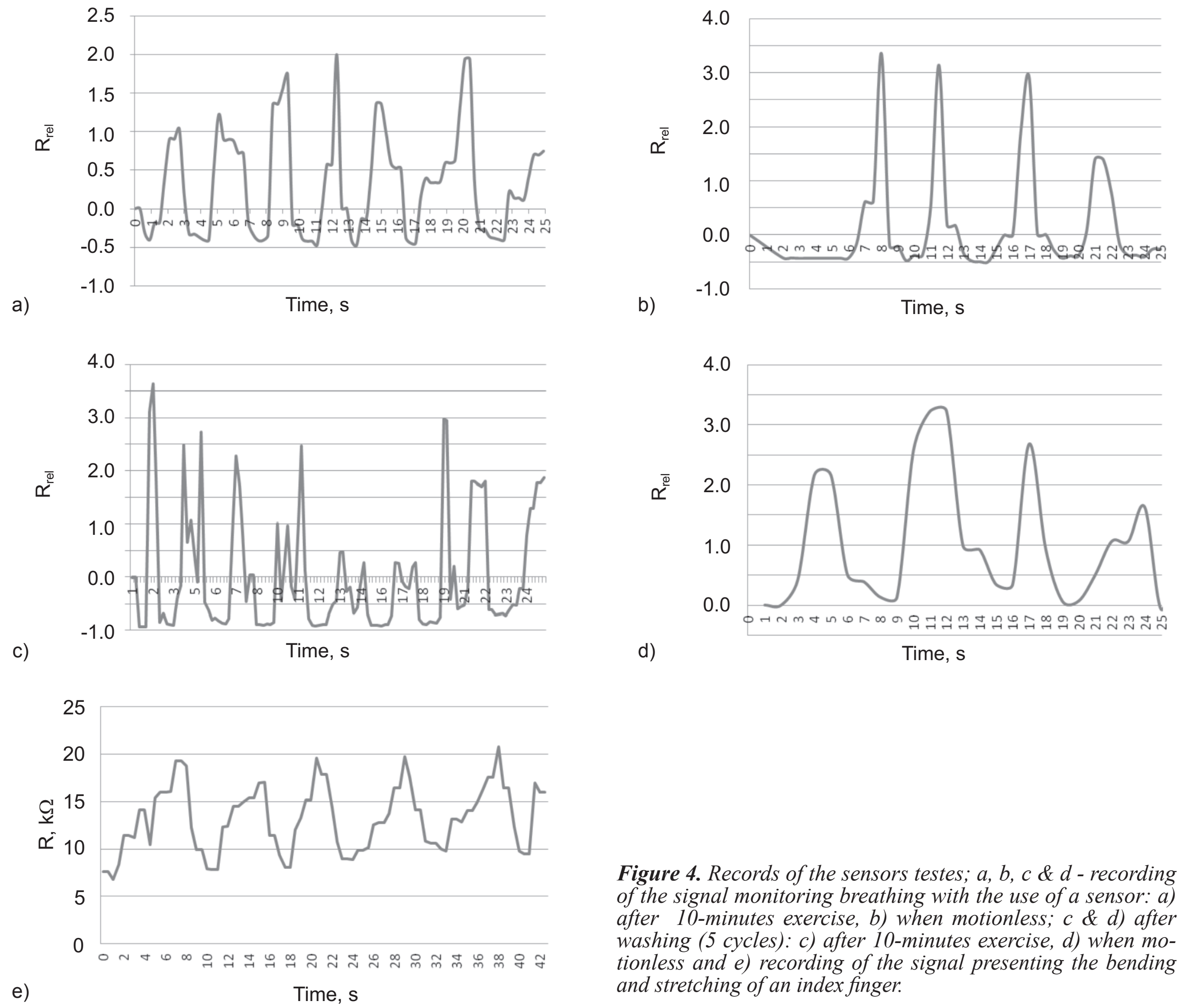

Figure 4. *Records of the sensors testes; a, b, c & d - recording of the signal monitoring breathing with the use of a sensor: a) after 10-minutes exercise, b) when motionless; c & d) after washing (5 cycles): c) after 10-minutes exercise, d) when motionless and e) recording of the signal presenting the bending and stretching of an index finger.*

The ink compositions obtained can be successfully used for manufacturing of the textile sensors used in medical applications, for monitoring the state of sick people, in elements of protective clothing for the military and civil services.

Conclusion

Thanks to using the screen printing method for manufacturing the textile resistive sensors, one can manufacture intelligent textile useful in many fields of life, in a cheap and fast way.

Based on the survey, it can be concluded that the measurements results are fully reproducible. Analysing the results, a reduction in antibacterial activity and conductance can be seen after the washing process, which is the greatest during the first cycles of washing, but desirable properties are still preserved.

The prototype of an elastic band obtained can successfully replace the rigid plastic bands used so far by runners. Moreover it can monitor the regularity of breathing of seriously ill people.

The glove proposed can aid blind people in reading Braille writing by converting an electric signal into digital data. The sensor detects irregularity in the surface and sends the information to a computer which digitises it and converts it into speech.

The characteristics and comfort of the elastic textile sensors and their close contact with the user's body should be, in the future, especially attractive for the direct monitoring of the state of the human body.

Clothing equipped with integrated sensors creates significant hope for the future of health care as well as for military

Recording the monitoring of breathing signal was simulated for a male watching TV and for a male after a 10-minute run.

The frequency of breathing after a 10-minute run increased, equal to about 20 breaths per minute, which is caused by the fact that the heart gets tired faster and that systoles occur more often. The recording of a signal monitoring breathing with the use of a sensor when the subject was motionless proceeded satisfactorily - equal to about 12 breaths per minute. In the experiment, a person was used, instead of an artificial instrument.

The results of research of the antibacterial activity of the textile sensors obtained are compared in ***Table 2***.
The results of research of the electrical resistance of the textile sensors obtained before and after washing are compared in ***Table 3***.

Table 2. *Results of microbiological research of the printouts obtained.*

Contents of ink	Bacteria suppression zone, mm			
	E. coli (Gram-)		*B. subtilis* (Gram+)	
	Before washing	After washing (5 cycles)	Before washing	After washing (5 cycles)
Aquacyl+cross-linking composition+SLS	0.5	0.0	5.5	4.0

Table 3. *Results of the surface electrical resistivity of the printed knitted fabric before and after washing.*

Contents of the ink	Surface electrical resistivity (Ω)	
	RH = 25%, t = 23 °C	
	Before washing	After washing (5 cycles)
Aquacyl+cross-linking composition+SLS	21.2	280.0

and sports applications. The proposed non-invasive monitoring based on textile products requires much greater study connected with the calibration of the sensors and mutual interconnections between the power supply and textile base. The work presented in the article will be continued in the direction of protecting the print received against mechanical damage and the effects of sweat.

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