Chapter 7

Development Trends in Electronics Printed: Intelligent Textiles Produced with the Use of Printing Techniques on Textile Substrates

Wiesława Urbaniak-Domagała, Ewa Skrzetuska,
Małgorzata Komorowska and Izabella Krucińska

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Abstract

The authors concentrated their attention on the new area of research, concerning properties of electrically conductive textiles, produced by printing techniques. Such materials can be used for monitoring, for example, the rhythm of breathing. The aim of this study was to develop a sensor of strains for the needs of wearable electronics. A resistance-type sensor was made on a knitted fabric with shape memory, dedicated to monitor motor activity of human. The Weftloc knitted fabric shows elastic memory—thanks to the presence of elastomeric fibers. The dependence of sensoric properties of the Weftloc knitted fabric on the values of load, its increment rate, and its direction of action was tested. Mechanical parameters including total and elastic strain, elasticity degree, and strength were also assessed. The results indicate an anisotropic character of mechanical and sensoric behaviors of the sensor showing a particularly optimal behavior during diagonal loading. Electro-conductive properties have been imparted to the Weftloc fabric by chemical deposition of polypyrrole dopped with Cl ions. In addition, authors used as a carrier functional water dispersion of carbon nanotubes AquaCyl that was adapted in the Department of Material and Commodity Sciences and Textile Metrology for forming electrically conductive pathways by film printing method. It was assumed that the electrically conductive paths are sensitive to chemical stimuli. Studies of the effectiveness of the sensors for chemical stimuli were conducted for selected pairs of liquids. The best sensory properties were obtained for the methanol vapor—the relative resistance ($R_{rel.}$) at the level above 40%. In the case of nonpolar liquid vapor, the sensoric sensitivity of the printed fabric was much lower, with $R_{rel.}$ level below 29%. Properties of the electrically conductive materials, such as thermal conductivity, electrical conductivity, and resistance to chemicals, allow for widely using them nanotechnology.

Keywords: printed electronics, carbon nanotubes, polypyrrole, graphene, intelligent textiles

1. Introduction

Intelligent textiles, also called active, interactive, and adaptive, become more and more popular, both in scientific area as well as in the companies producing highly specialized clothing and also consumers. Market analysis has shown that there is a strong interest in new textronic materials (smart textiles, e-textiles). The usage of smart textiles brings many possibilities of monitoring the reactions of the human body onto many incentives and factors, as well as their usage as decorations in the public space [1–5].

Intelligent materials have enabled the design and elaboration of a new generation of clothing with integrated sensors and built-in electrodes. The use of biopotential fiber sensors (BFS) allowed miniaturization of ECG sensors. It also granted elimination of the conductive gels, and therefore, the use of new receiving elements was possible. Typical fiber sensor, the registrant biopotential, also acts as a receiver, with electrodes and wire that are connected to the patient. Smart vests have been already used in a limited extent in health monitoring, which enables screening all daily activities. Moreover, they are simple to use and are not causing discomfort while wearing [6]. Fabrics with interleaved weft and knitwear with conductive yarn are widely used. Thus, prepared sensory detectors are sensitive to formability and are used in such areas of life as public safety, police, fire service, medical services and automotive industry [7–9].

Currently, intensive studies are carried out on widening the functions of clothing. Additional functions would consist of warning man about possible danger, monitoring the man's body motoric activity (position, kinematics of body parts) and physiological activities (skin temperature, respiration rate, pulse oximetry, electrocardiogram, electromyogram) [10–12]. In order to provide above functions, it is proposed to use fibrous structures, such as mono- and multi-filaments, or knitted and woven fabrics as elements integrated with clothing, the so-called electronic textiles (e-Textiles). Such type of fibrous structures, under the influence of stimuli, for example mechanical load, electric field, magnetic field, temperature, irradiation, chemical vapors, shows reversing changes in their properties: shape memory [13–16], piezoresistive [17–21], chemo-resistive [22–24], piezo-electrical [25–27], electro-chromic [28, 29], electro-luminescent [30–32] properties, etc. The last decade witnessed the development of e-Textiles prototypes based on functional textile materials: Modular Autonomous Recorder System for measurement of autonomic nervous system activity [33], Clothes for Tele-Assistance in Medicine [34], wearable health care system [35], life shirt (smart shirt for continuous ambulatory monitoring) [36]. A wide review of knowledge and developments in the field of e-Textiles, constructions, materials used and developmental trends has been presented in papers published by Rossi's team [19, 37, 38] and monographs [10, 11].

The monitoring of man's body movement activity is often performed with the use of fibrous materials as sensors of strains. The best results are obtained in the case of fibrous structures which have both elastic memory (e.g. elastomeric fibers) and piezoresistive properties. The elastic memory of elastomeric fibers is determined by their exceptionally high reversing deformability. However, elastomeric fibers being electro-insulating from their nature show the piezoresistive effect that is obtained only after a preliminary modification consisting in imparting electro-conductive properties. This modification is made by applying electro-conductive coatings (doped polypyrrole, polyaniline, polyacetylene), inorganic compounds (silver salts), or mass-doping with electro-conductive particles, for example carbon.

The fibrous structures based on elastomers are often modified with polypyrrole due to its stable physical properties (high resistances to thermal, atmospheric and chemical media) and relatively simple deposition process on the substrate surface [39–41]. Elastomer-polypyrrole systems are used as strain sensors 1D (bandages placed directly on knee or elbow joints) or 2D (shirts worn near body that monitor body movements, local changes in torso, arm etc.). In the second case, the stimuli of sensor integrated with clothing have a multi-directional character; hence, the sensoric properties of the sensor material will be strongly dependent on the direction of load and material structure. There are few studies that consider the effect of both factors on the properties of piezoresistive sensors. Increasingly popular are thick electrochemical sensors, ampherometric, and biosensors made by film printing and ink-jet printing using ink from carbon-derived content, ferrocyanide, by which one can assess the impact of deformation of clothing and monitor physiological functions. The future activities of such sensors will focus on the human body, as well as other health care systems; they will monitor not only soldiers but also other services that require this form of monitoring [15, 19]. In order to print on the textiles, various specific substances are used, for example dyes, various types of polymers, silver, carbon nanotubes, graphite or graphene. These components can also provide other established functions, for example anti-static or antibacterial [9, 42, 43]. Printed electronics produced so far primarily for use as the components of devices (computers, tablets, phones, etc.) currently take an advantage in the textile industry because of the prints on fibrous materials that can act as sensors or electrodes for electrical stimulation of muscles in the components of new functionalized garments [9, 42–46]. In published works, electrical conductivity was successfully given to materials by textile printing method [47, 48], but existing solutions are still being developed. The authors in their works concentrated their attention on new areas of research, conferring properties of electrically conductive textiles using printing techniques for monitoring, for example the rhythm of breathing. The major reason to start this kind of investigation was the need for developing reliable, handy health monitoring systems [5, 7, 9]. Non-invasive or minimally invasive physiological monitoring devices are also of great importance for defense purposes and applications for athletes. The integration of sensors and biosensors directly with clothing should be beneficial in the development of health care and monitoring systems of soldiers, as well as other civil servants. The integration of electronics with clothing opens up many possibilities in various fields [9, 42, 43]. The authors used the functional water dispersion of carbon nanotubes AquaCyl as a carrier that was adapted in the Department of Material and Commodity Sciences and Textile Metrology Lodz University of Technology for forming electrically conductive pathways by film printing method. It was assumed that the resulting electrically conductive paths are susceptible to deformation. Modification of the water dispersion of nanotubes was supposed to result in a composition being bi-functional print—electrically and bacteriostatic, which is extremely important in applications of sensors in medical materials, in contact with the human body. In the present study, attention was focused on assigning specific functionality textiles printing techniques using carbon nanotubes, graphene and polypyrrole. Characteristic properties of the electrically conductive materials, such as thermal conductivity, electrical conductivity and resistance to chemicals, cause that they are widely used in nanotechnology.

2. Materials and methods

Taking into account the preparation of a textile strain sensor, textiles with high elasticity and reversibility of deformations were used. Such conditions are fulfilled by warp knitted fabrics of the Weftloc type. The elastic structure of Weftloc fabrics is formed by a system of elastomeric yarns (**Figure 1**) introduced in the mutually perpendicular directions by the three-needle bar, thanks to which the fabric is characterized by 2D deformability.

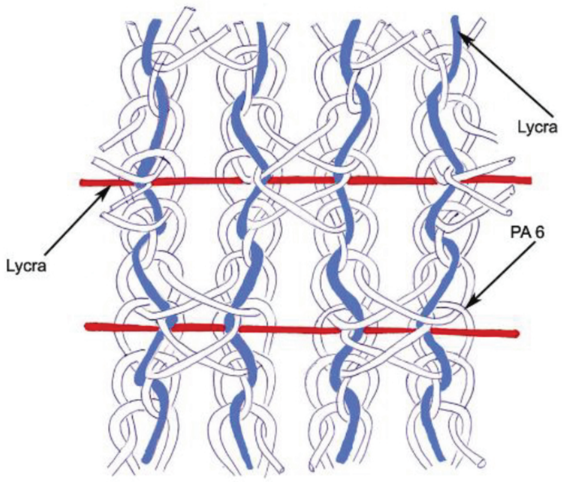

Figure 1. Weftloc PE warp knitted fabric.

Textile substrate	Surface weight,	Thickness	Surface electric resistivity ϱ_S	Raw material composition
	g/m^2	mm	Ωm/m	
knitted fabric Weftloc L (LIBA)	304	0.73 ± 0.01	1.8×10^{13}	PA6 -61% Elastan - 39%
knitted fabric Weftloc PE (PEN ELASTIC)	245	0.52 ± 0.01	6.2×10^{12}	PA6 -64% Lycra - 36%
cotton fabric	206	0.41 ± 0.01	8.7×10^{11}	Cotton-100%

Table 1. Metrological characteristics of textile substrate.

Two Weftloc knitted fabrics with a similar content of elastomeric yarns of different type of elastomer were used, having various surface weights and morphological structures (**Table 1**). Knitted fabrics also contained polyamide yarn that imparts a soft handle and comfort of fabrics in contact with skin. This type of bi-component knitted fabric is exploited in corset-making to make classic lingerie elements fitting to the body, sports and rehabilitation goods.

In addition, cotton fabric twill was also used (**Table 1**) as a reference of the sensitive material for chemical stimulus.

As a base for printing conductive work were used:

- water dispersion of carbon nanotubes trade name AquaCyl (AQ0101) and AquaCyl (AQ0301) from Nanocyl,
- polypyrrole in the form of a water dispersion of nanoparticles prepared in the process of polymerization of pyrrole doped, Sigma-Aldrich,
- flakes of graphene in the form of a dry powder from company Graphene-Supermarket.

Above materials are a well-established in the group of nanomaterials used in consumer printing electronics. The issue of its application is open in order to provide its toxicological safety, in permanent connection with the substrate and ensure the extreme sensitivity of the test stimuli in their minimum content sensory element.

The electrical properties of materials in the study were used by a team of the Department of Materials, Commodity and Textile Metrology Technical University of Lodz [7, 9, 42, 43, 47] to create a conductive printing on transparencies and printing techniques of textile materials.

2.1. Materials

AquaCyl 0101 AQ dispersion comprises from 0.5 to 1.5% MWCNT series Nanocyl®7000 characterized by a purity of approximately 90% with the average diameter of nanotubes 9.5 nm, and the average length of up to approx. 1.5 μm. It is characterized by surface tension approximately 57 N/m, the viscosity of 36 cP and a pH of 7. These parameters were determined in the temperature 25°C. Additionally dispersion comprises a dispersant in an amount of 0.1–3% [7, 9].

Polypyrrole in the form of a water dispersion of nanoparticles produced in the doped polymerization of pyrrole. Pyrrole is a heterocyclic aromatic compound of the empirical formula C_4H_5N, having a 98% degree of purity. Its density is determined in temperature 25°C, was 0.967 g/mL, and the molecular weight of 67.09 g/mol. Pyrrole applied at the beginning was distilled under reduced pressure.

Graphene flakes in dry powder form under the trade name MO-1, a multilayer graphene flakes having a thickness of 5–30 nm in size with a 5–25 μm [43]. As auxiliaries to modify the water dispersions used: DBSA ($C_{12}H_{25}C_6H_4SO_3H$) solution 70 wt% in isopropanol (analytically pure from Sigma Aldrich) and Ebecryl 2002 (Aliphatic urethane acrylate from Cytec, water compatible, UV curable system) and Esacure DP250 (water dispersion of photoinitiators from Lamberti SPA).

2.2. Characteristics of inks

The obtained printing paste having the sensory properties based on graphene and carbon nanotubes was introduced to the dispersion AquaCyl AQ0301, 3% by weight of flakes of graphene MO-1. This kind of compiled printing composition was placed in an ultrasonic bath for 15 min. Then, the so-prepared printing composition as well as the dispersion of AquaCyl AQ0101, auxiliary agents in the form of aliphatic urethane acrylate (Ebecryl 2002), and the photoinitiator (Esacure DP250) were added and stirred for 30 min using a magnetic stirrer.

The polypyrrole layer was formed chemically by the in situ polymerization of pyrrole in an aqueous solution of ferric chloride, in which the sample to be coated was immersed. A molar ratio of pyrrole and ferric chloride was 1:2.5. The polymerization was performed at the temperature of 4°C for 2 h. The acidic character of the process medium was maintained by means of an addition of HCl solution. The samples were taken out after 2 h, rinsed repeatedly with distilled water and dried in a desiccator at room temperature.

Knitted fabrics and elastomeric weft yarns used in knitted fabrics were modified under the above given conditions.

2.3. Investigation methods used

2.3.1. Research on electrical resistivity

2.3.1.1. Testing the current-voltage characteristics of textile substrate

The resistance properties of textile substrate were tested before and after coating with electro-conductive polypyrrole, carbon nanotube and graphene. The surface resistance of fabric samples was measured with the use of a two-electrode system and stabilized voltage sources (type 4218 from RTF and type 55121 from Unitra) and a Keithley's electrometer, type 610C. Samples with a width of 2.5 cm were tested under a constant load of 400 kPa, with the inter-electrode distance being 1 cm. The uncoated samples were tested under a voltage of 500 V in a Faraday cage. In case of the samples coated with polypyrrole, carbon nanotube and graphene their current-voltage characteristics were determined within the voltage range from 1 to 20 V, increasing the voltage from smaller to higher values.

2.3.1.2. Testing sample resistance under mechanical load

Changes in the electric resistance of samples were examined simultaneously with sample load using Instron machine, recording the elongation of samples as a function of load $F(\lambda)$. The changes in load as a result of changing resistance had a dynamic character, which required an automated measuring system.

A sample in the form of a strap, cut out in the assumed direction, was fixed in Instron clamps set up within a distance of 50 mm. The sample in clamps were equipped with elastic electro-conductive electrodes from 3M ($R < 1\Omega$), which provided two-sided contact with the sample.

The electrodes were isolated from the clamp surfaces with a polyester film. Similarly, the samples of elastomeric yarns were fixed.

The electrodes were connected to a multimeter, type Metex KN DMM M-3890DT, coupled with a computer (**Figure 2**). Results in the form of R = f(t) files were sent to computer through USB by means of Metex software.

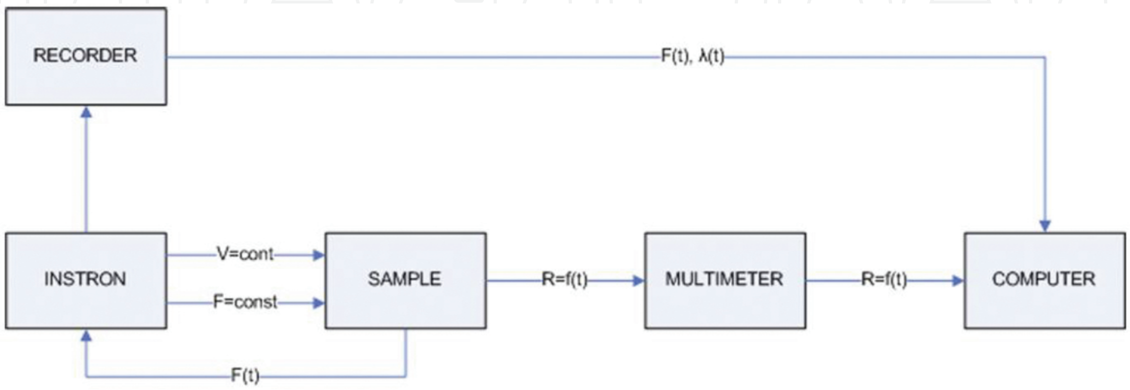

Figure 2. Schematic diagram of the measurement stand for testing the electric resistance of knitted fabrics and elastomeric yarn.

The examination of the resistance behavior of samples consisted of recording the changes in resistance in the process of sample loading and relaxing and examining the repeatability of resistance under the given load and a constant frequency of loading.

The resistance sensitivity of the system was calculated according to the formula:

$$\mathrm{Ss} = \frac{\Delta R}{R_0 * \varepsilon_{\mathrm{elast}}} \tag{1}$$

where Ss—strain sensitivity, $\Delta R = R_{max} - R_0$, R_{max}—the value of resistance at the point where the sample is loaded with the maximal force F, R_0—initial value of resistance, ε_{elast}—relative elastic strain, %.

2.3.1.3. Research on electrical resistivity of samples exposed to chemical stimulus

Sensory tests for the presence of solvent vapor were performed in a laboratory measuring system [49]. The equipment allows measurements of the humidity and temperature of the atmosphere prevailing in the system as well as creation and introduction of a system measuring liquid vapor at a given concentration (**Figure 3**). The measurement technique is described in [43].

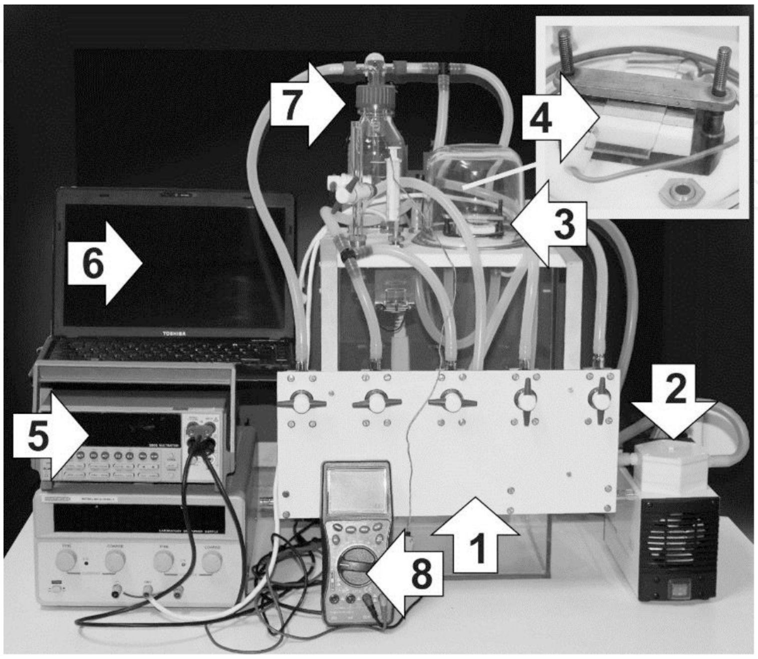

Figure 3. Measuring system for investigating the vapor textile sensors: (1) gaseous chamber with the volume of 0.024 m^3, (2) pump, (3) measurement chamber, (4) measuring electrodes, (5) Keithley multimeter, (6) computer, (7) system ensuring proper humidity of the environment, (8) thermometer [49].

2.3.1.4. Microscopic observations of knitted fabrics

The structure and surface of the tested samples were observed using two microscopic techniques. The morphological structure of yarn and fabrics was examined by the optical microscopy, observing the deformation of fabric structure under the influence of loads. The reflected light microscope coupled with the camera and image analysis system "Lucia" was used for morphological evaluation of tested fabrics.

The surfaces of fibers and knitted fabrics were observed by scanning electron microscopy (SEM), using a JSM-520 LV microscope from Jeol (Japan). The technique of specimen preparation is described in paper [50].

3. Results and discussion

3.1. Morphological properties of deposits conductive layers

Figure 4A–F shows the results of the PPy deposition on the multifilaments forming knitted fabrics, and on knitted fabrics, **Figure 4G–I** shows the results of the deposition of carbon

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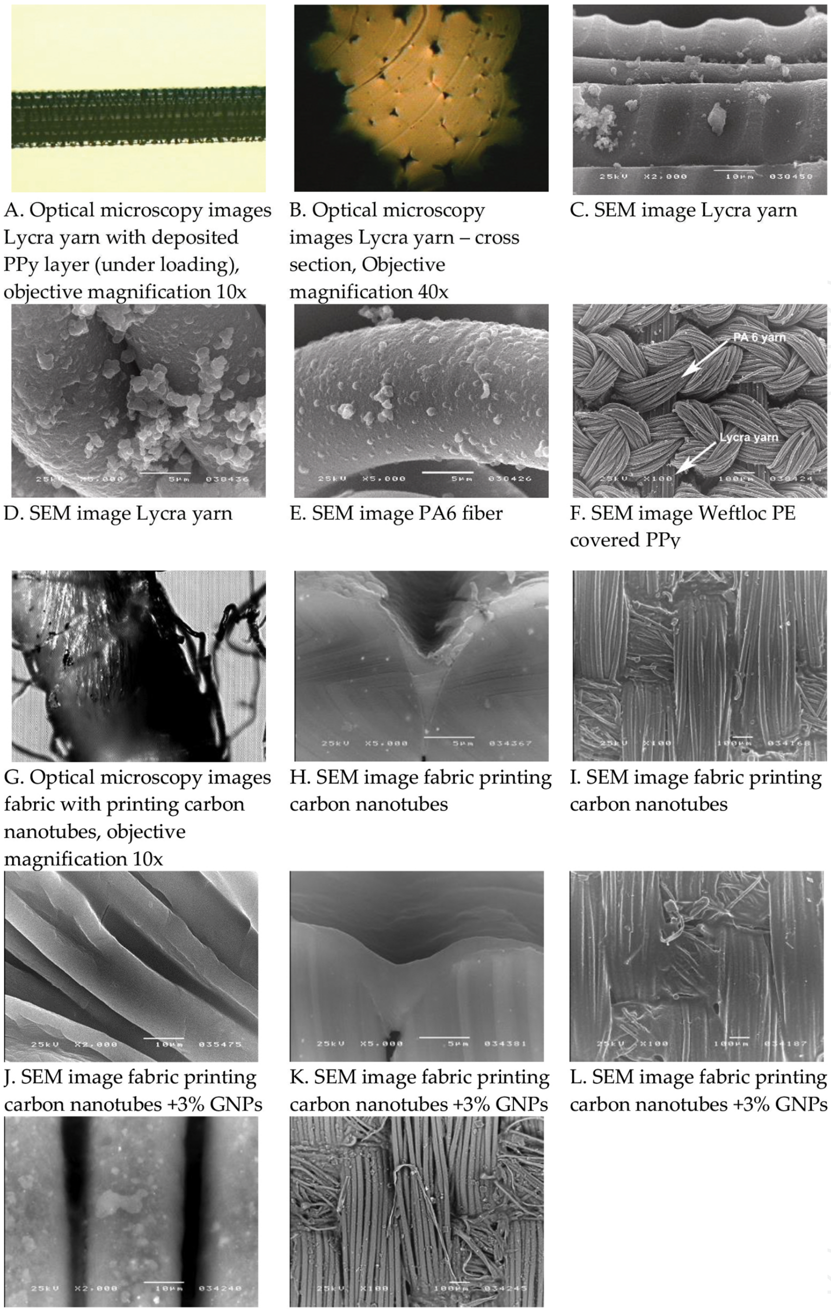

A. Optical microscopy images Lycra yarn with deposited PPy layer (under loading), objective magnification 10x

B. Optical microscopy images Lycra yarn – cross section, Objective magnification 40x

C. SEM image Lycra yarn

D. SEM image Lycra yarn

E. SEM image PA6 fiber

F. SEM image Weftloc PE covered PPy

G. Optical microscopy images fabric with printing carbon nanotubes, objective magnification 10x

H. SEM image fabric printing carbon nanotubes

I. SEM image fabric printing carbon nanotubes

J. SEM image fabric printing carbon nanotubes +3% GNPs

K. SEM image fabric printing carbon nanotubes +3% GNPs

L. SEM image fabric printing carbon nanotubes +3% GNPs

M. SEM image fabric printing PPy

N. SEM image fabric printing PPy

Figure 4. SEM and optical microscopy images of: (A–F) PPy coating on Lycra and PA6 yarns and Weftloc PE knitted fabric, (G–I) AquaCyl AQ3001 + cross-linking compound printed on fabric, (J–L) AquaCyl AQ3001 + 3% GNPs + cross-linking compound printed on fabric, (M–N) Polypyrrole + cross-linking compound printed on fabric.

nanotubes, and **Figure 4J–L** shows the results of the deposition of graphene with carbon nanotubes. The cross-section and longitudinal view of Lycra multifilament (**Figure 4B**, **C**) indicate a strong integration of elastomeric filaments in yarn, which are locally stuck together and deformed at interlacements. In the *in situ* polymerization of pyrrole, PPy layers on both surfaces of the knitted fabrics were formed with the average thickness of 68 nm on Weftloc PE fabric and 192 nm on Weftloc L fabric. The combination of PPy with the fiber surface in Weftloc knitted fabrics is durable and resistant to washing what was confirmed by appropriate tests. The formed PPy layer consists of PPy micro-spheres with a grain diameter of approximately 1 μm (**Figure 4D**, **E**). **Figure 4B**, **C** indicates a limited penetration across the micro-spheres in the elastomeric multifilament.

Analysis of microscopic images also allowed for determination of the average thickness of the applied layers of ink compositions on fabric, using an image analyzer Luccia. Microscopic examination showed that the thickness of the layer applied to the textile printing technique film contained within 18.5–20.0 μ (**Figure 4H**, **K**). Moreover, analysis of microscopic images shows that the ink compositions are applied in a uniform manner on the textile substrate. Not observed, the resulting thickening of a significant size.

3.2. Electric properties of PPy layers on Weftloc knitted fabrics

The samples of Weftloc knitted fabrics coated with PPy show conductive properties in the electrostatic field. The PPy layer has created conditions for the percolation flow of charge carriers reducing the fabric resistance by about eight orders of magnitude from TrΩ (**Table 1**) to kΩ. The current intensity of the surface conductivity increases proportionally to voltage (**Figure 5**). The above linear behavior with high correlation coefficients ($R^2 \sim 1$) has been found for all knitted fabric samples under conditions of directed action of electric field (in the direction of wales $\varrho_S = 158 \pm 20\ \Omega m/m$, courses $\varrho_S = 170 \pm 15\ \Omega m/m$ and diagonally $\varrho_S = 160 \pm 30 \Omega m/m$). One can state that in the mechanically unloaded condition, PPy layers show isotropic electric conductivity.

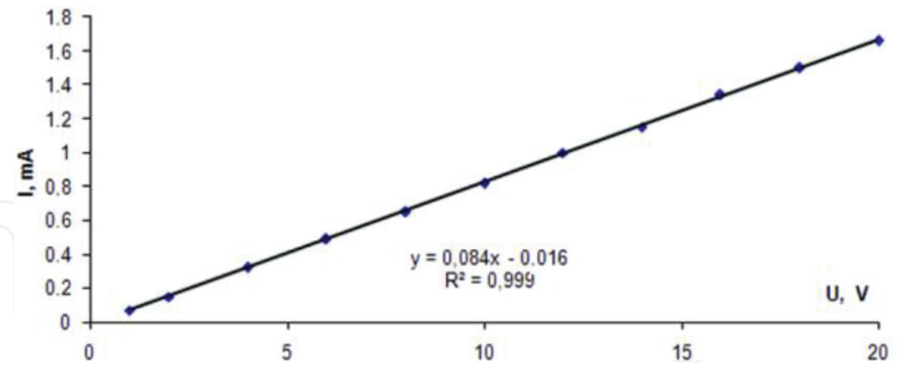

Figure 5. Characteristics of $I_{surface} = f(U)$ of Weftloc PE fabric (diagonal field direction to wales).

3.3. Mechanical properties of elastomeric yarns used in Weftloc fabrics

Weftloc knitted fabrics are characterized by a high content of elastomeric yarn that imparts elastic memory to the material. In order to present the full picture of electro-mechanical properties, both fabrics and elastomeric yarns of these fabrics were tested (100% Lycra and 100% Elastan).

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The yarns are characterized by a high degree of elasticity that does not significantly depend on the load value within the range of loads used (up to 0.4 N). However, the relative elastic and total strains strongly increase during load increase (**Figure 6** shows the results for Lycra yarn).

The PPy coating deposited on the fiber surface insignificantly decreases the tensile strength and breaking strain of yarn (**Table 2**). No significant effect of PPy on the degree of yarn elasticity was found (**Table 2**; **Figure 6**).

Type of indicator	**Lycra yarn**	
	without PPy	**with PPy**
Degree of elasticity S_{elast}, %	93.6 ± 1.0	94.32 ± 0.9
Elastic strain ł$_{elast}$, %	160.6 ± 4.7	159.1 ± 7.1
Total strain ł$_{total}$, %	171.3 ± 4.6	166.0 ± 8.9
Breaking strain ł$_{break}$, %	574.2	469.3
Tensile force at break F, N	0.85	0.58

Table 2. Effect of PPy on mechanical behavior of Lycra yarn in Weftloc PE (P = 0.4 N).

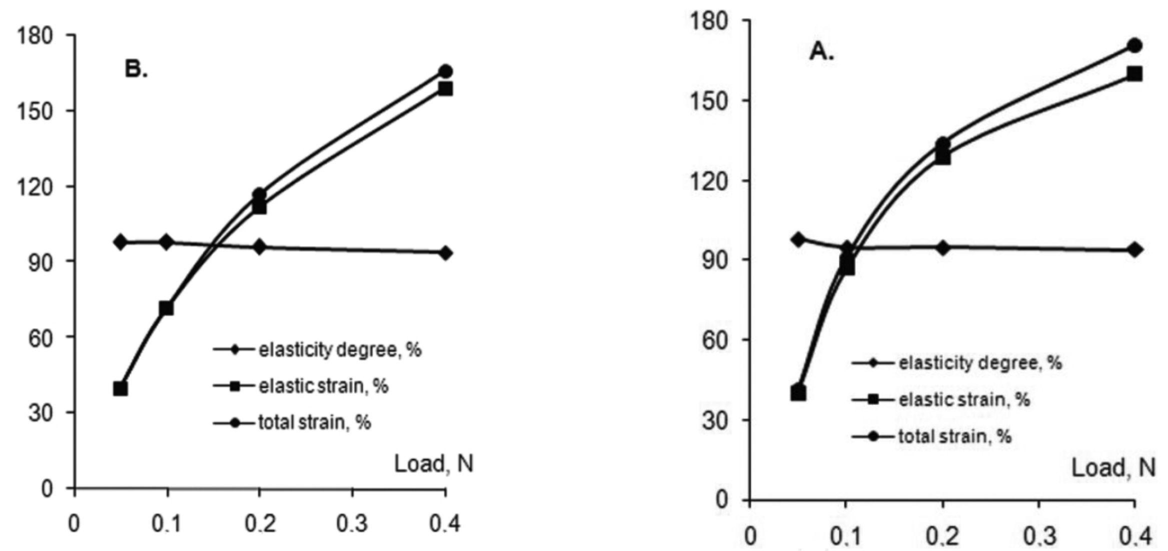


Figure 6. Effect of load on mechanical parameters of Lycra yarn (A) before and (B) after coating with PPy.

3.4. Mechanical properties of Weftloc knitted fabrics

3.4.1. Strength of knitted fabrics

The tensile strength of Weftloc knitted fabrics was tested using forces directed along wales, courses and diagonally. The strength of knitted fabrics without the elastomeric yarn worked-in along courses was also tested to find out how it affects the directional strength at break

(**Table 3**). The removal of the course yarn decreases the directional strength and strain at break. One can assume that the mechanical stability is determined to a large extent by the stitch structure of knitted fabrics.

Type of knitted fabrics	Direction of force	Breaking force, N	Breaking strain, %
Weftloc L	Wales	240.0 ± 2.0	450.0 ± 3.0
	Diagonal	135.0 ± 1.2	482.0 ± 2.5
	Courses	122.5 ± 1.0	607.6 ± 2.6
	Courses, without weft	113.1 ± 1.0	535.7 ± 9.0
Weftloc PE	Wales	161.8 ± 4.0	400.0 ± 1.0
	Diagonal	114.0 ± 1.0	434.5 ± 1.0
	Courses	160.1 ± 4.0	558.1 ± 20.0
	Courses, without weft	116.6 ± 3.0	500.1 ± 8.0

Table 3. Strength parameters of Weftloc knitted fabrics before coating with PPy.

Under the conditions of directional loading, knitted fabrics show the anisotropy of strength and strain (**Table 3**; **Figure 7**). The maximal mechanical parameters are obtained during the course-wise loading. The directional strain of Weftloc PE fabric is, in each case, higher than that of Weftloc L fabric.

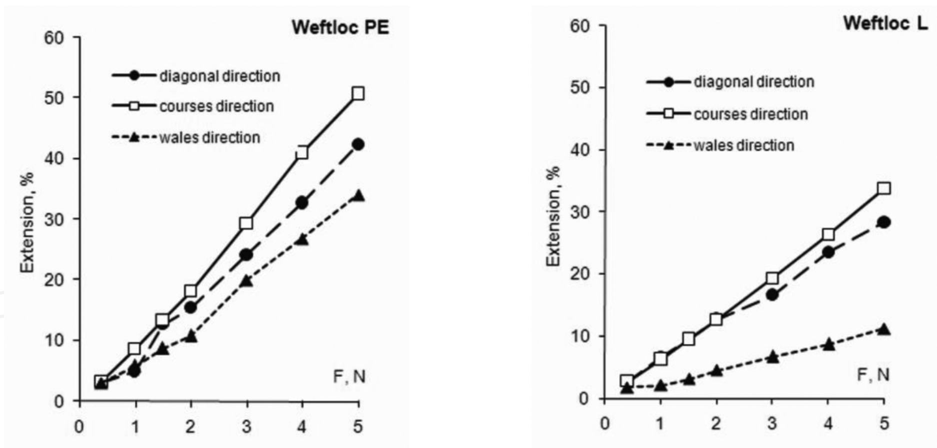


Figure 7. Directional strain of Weftloc fabrics coated with PPy (loading rate: 50 mm/min).

3.4.2. Elasticity of Weftloc fabrics

Weftloc knitted fabrics containing Lycra elastomeric fibers in PEN ELASTIC fabrics are characterized by a higher contribution of elastic strains in comparison with LIBA knitted fabric. The values of elastic strains created during diagonal loading are shown in **Figure 8**. The deposited PPy layer has decreased the elastic strain within the whole load range (0.4–5.0 N).

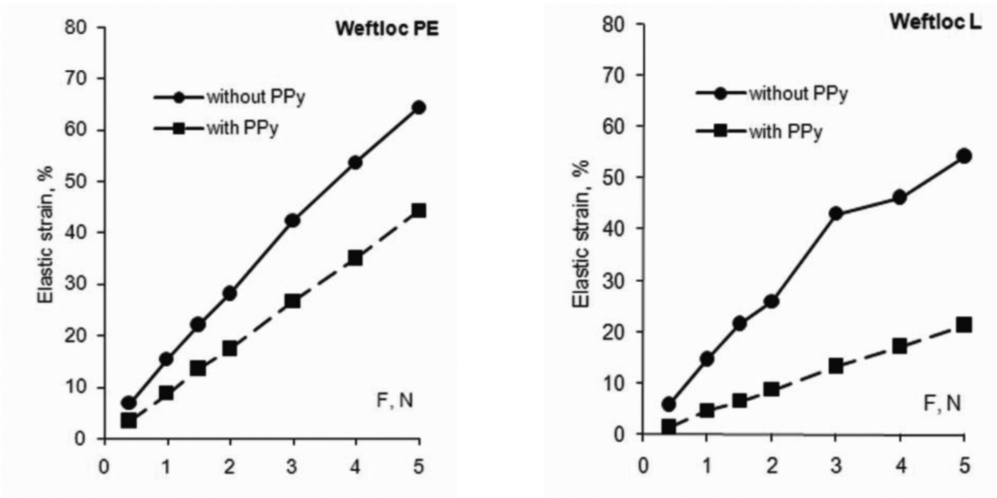


Figure 8. Effect of PPy on the elastic strain of Weftloc knitted fabrics in the diagonal direction (loading rate: 200 mm/min).

3.5. Resistance responses of elastomeric yarns during straining

In order to assess the repeatability of electromechanical behavior of elastomeric yarns, their temporal changes in electric resistance during axial mono- and multi-cyclic tension at a constant rate of load increase in each cycle were examined. **Figure 9A** shows resistance response, R/R_0, (instantaneous values of resistance R of the yarn being loaded in relation to the initial resistance R_0) during the single cycle of tensioning. The resistance increases linearly during the linear load build-up (and the strain proportional to it); after yarn relaxation the resistance returns nonlinearly to the initial condition. The delay in resistance return of the yarn under relaxation indicates processes of stress relaxation in the elastomer. The strain sensitivity Ss of Lycra yarn is at a level of 200. The yarn resistance changes during load build-up are characterized by good repeatability and a high degree of correlation between resistance and strain, which was confirmed also in the multi-cyclic yarn loading (**Figure 9B**).

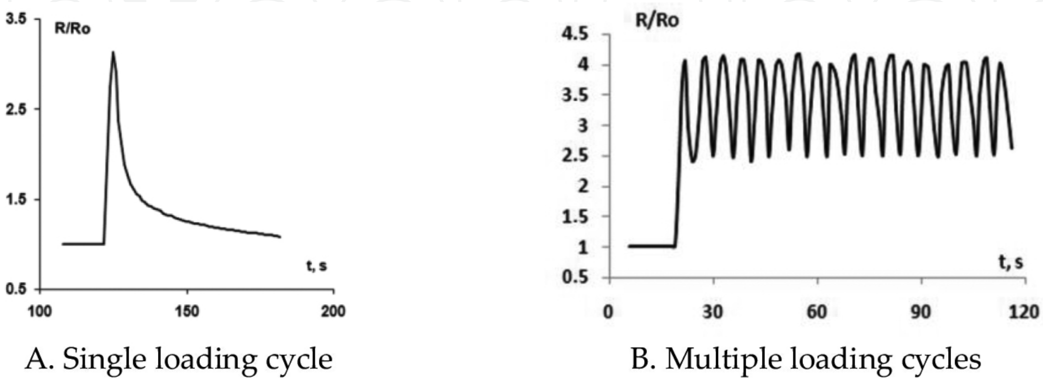


Figure 9. Resistance responses of Lycra weft yarn tensioned axially, tensioning rate 50 mm/min, load 8cN. (A) Single loading cycle, (B) multiple loading cycles.

3.6. Resistance responses of Weftloc knitted fabrics during straining

The knitted fabrics coated with PPy and directionally strained (**Figures 7** and **8**) show an increase in electric resistance with increasing strain. The value and character of resistance changes depend on the value of load and its build-up rate and direction (resistance anisotropy). In **Table 4**, exemplary resistance responses of PEN ELASTIC knitted fabric loaded in the direction of weft at a loading rate of 50 mm/min are listed. In **Table 4**, **A–D** show relative changes in the electric resistance of a knitted fabric loaded in four single cycles followed by a

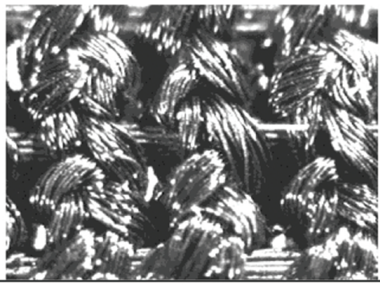
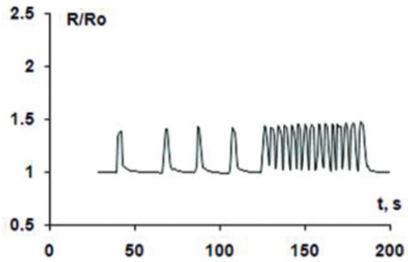
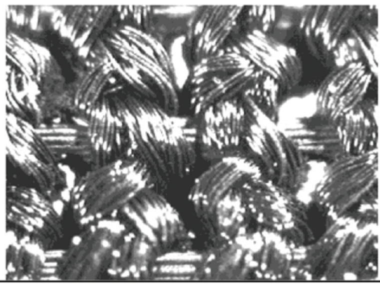
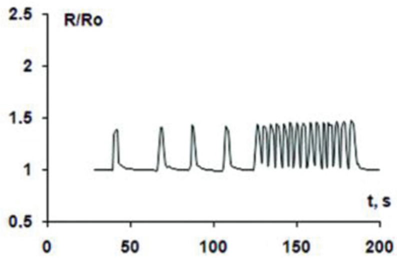
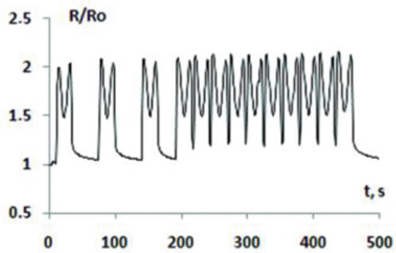
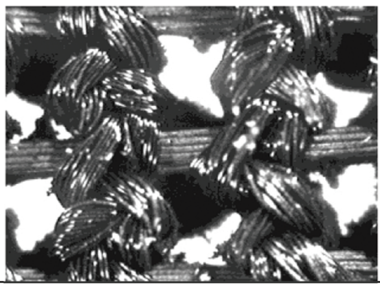
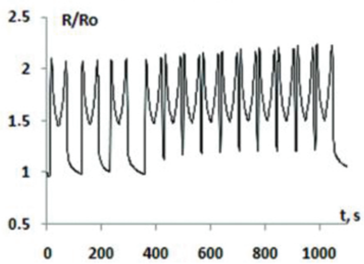
A 	
B 	
C 	
D 	

Table 4. Weftloc PE fabric—images during straining and the accompanying changes of fabric surface resistance in loading time (loads: 0.4; 1; 2 and 5 N; loading rate 50 mm/min).

dozen or so cycles succeeding with a higher frequency. In cases A–D, maximal loads were use: 0.4, 1, 2 and 5 N, respectively. The diagrams confirm the repeatability of resistance changes during sample loading in both single and multiple cycles. The resistance increases with increasing sample load. For low loads, the process is of a linear character, while for higher loads, after exceeding about 0.8 N the resistance is decreased (“saddle point”), which may indicate disturbances of charge carrier flow on percolation paths formed by polypyrrole. This effect was found for three loading directions in both knitted fabrics (in the direction of knitting, perpendicular and diagonal directions). This effect is reversible. To illustrate this phenomenon, microscopic simulations of tensioning Weftloc PE loaded in the weft direction at a load rate of 50 mm/min were performed. (**Table 4A–D**). The images show that with the increase in load the distances between wales increase and multifilaments relocate in the knitted fabric loops, which results in the resistance change of mutual contact and consequently in reduced resistance of the knitted fabric. Xue et al. [51] previously indicated the importance of the resistance of fiber contact in knitted fabric loops for the electromechanical properties of knitted fabrics. As far as woven fabrics are concerned, these authors believe that a higher influence on the electromechanical behavior is exerted by the crimp of the weave and density of the fabric. The appearance of the “saddle” phenomenon in the electromechanical response of Weftloc fabrics limits the range of linear behavior of the sensor based on these fabrics.

3.7. Strain sensitivity of Weftloc knitted fabrics

Based on the resistance responses and corresponding strains of Weftloc fabrics loaded successively in three directions: along wales, courses and diagonally, the strain sensitivity (Ss) of these fabrics were calculated. The results of Ss of electro-conductive knitted fabrics are shown in **Figure 10A–C**. The comparison of the behavior of Weftloc fabrics indicates beneficial parameters of the sensor based on Weftloc PE. This fabric, with a similar content of elastomeric yarn and wale density, is characterized by a slightly higher course density (**Table 2**). As far as the metrological parameters are concerned, Weftloc PE is characterized by lower surface weight and thickness, but higher elastic strain in comparison with Weftloc L. The differences in fabric physical parameters have brought different conditions of the PPy micro-sphere diffusion on the fiber surface and in the fabric structure. On Weftloc PE fabric, a thinner PPy layer is formed. During the loading of this fabric, with its higher strain, one could observe considerably greater changes in resistance in comparison with Weftloc L fabric, which resulted in a higher strain sensitivity.

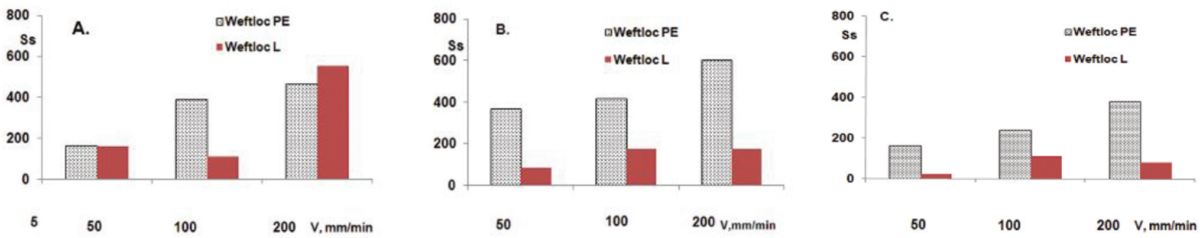


Figure 10. Effect of tensioning rate on the strain sensitivity (Ss) of Weftloc knitted fabrics during loading in the direction of: (A) courses, (B) diagonal, (C) wales.

The sensitivity of both Weftloc fabrics has an anisotropic character. One can assume that it results from the anisotropy of fabric strainability as well as from the anisotropy of the contact resistance of fibers deformed in fabric loops.

The strain sensitivity of Weftloc knitted fabrics increases with the increasing tensioning rate. This behavior results from the fabric strainability and the changes in PPy layer resistance with shortening the loading time, that is increasing the tensioning rate. For both knitted fabrics, it was observed that the increase in load build-up rate was accompanied by twofold reactions: increase in the fabric strainability or unchanged values. The clear increase in the fabric sensitivity with increasing loading rate (**Figure 10**) allows one to state that changes in resistance have a predominant influence of the phenomenon. It has been previously found that the fiber electric resistance considerably increases with increasing rate of loading in the process of drawing PA6 fibers coated with PPy [27].

Based on the results obtained, one can conclude that beneficial operating conditions of the sensor based on Weftloc knitted fabrics can be obtained at higher load build-up rates and short relaxation times. From among the knitted fabrics tested, Weftloc PE shows optimal piezoresistive properties and the best strain sensitivity in the diagonal direction.

3.8. Electrical properties of conducting layers on cotton fabric

The samples of fabrics coated with conductive ink compositions exhibit the electrostatic conductive properties. The conductive layers have created conditions for the percolation flow of charge carriers reducing the fabric resistance by about 10 orders of magnitude from TrΩ (**Table 1**) to Ω for ink compositions based on carbon nanotubes **and graphene,** and approximately six orders of magnitude for the ink compositions based on polypyrrole.

The **Table 5** summarizes the results of the electrical conductivity of the printed textile substrates [7, 9, 43].

Composition of ink	Type substrate	Surface electrical resistivity [Ωm/m] (RH = 25%, t = 23°C)	
		Before the washing	After the washing (25 cycles)
AquaCyl AQ3001 + cross-linking compound	cotton fabric	12.0	129.0
AquaCyl AQ3001 + 3% GNPs + cross-linking compound	cotton fabric	4.7	79.0
Polypyrrole + cross-linking compound	cotton fabric	6.6×10^5	8.8×10^6

Table 5. The test results of electric conductivity of the printed textile substrates [7, 9, 43].

Commercial AquaCyl character shows worse electrical conductivity than the prints obtained with addition of graphene. The composition of the print based on polypyrrole results in the weakest conductivity.

In the course of the experiment, there was no significant effect observed on grapheme-based ink properties taking in account the amount of added graphene, uniformity of obtained paste before and after printing.

It has been found that the presence of auxiliary agents in the form of aliphatic urethane acrylate and the photoinitiator has no effect on the properties of the conductive ink compositions tested, but significantly improves the durability of prints.

3.9. Responses resistive printed fabrics treated with chemical stimulus

Table 6 and **Figure 11A–C** summarize the results of testing the functionality of the textile resulting in a film printing technology.

As an indicator of quantitative sensory properties assumed as the relative resistance changes, R_{rel} expressing the relative changes in electrical resistance in the surface of the printed fabrics induced chemical stimulus of a given type, calculated in accordance with the formula (2).

$$R_{\mathrm{rel}} = \frac{R - R_o}{R_o} 100\% \qquad (2)$$

where R_{rel}—relative resistance

R_0—initial value of resistance

R—final value of resistance.

Composition of ink	Concentration, ppm	Relative resistance, %		
		Acetone	Methanol	Toluene
AquaCyl AQ3001 + cross-linking compound	200	15	50	13
	300	19	57	18
	400	27	68	25
AquaCyl AQ3001 + 3% GNPs + cross-linking compound	200	27	78	23
	300	31	86	29
	400	36	123	34
Polypyrrole + cross-linking compound	200	15	38	6
	300	19	41	9
	400	21	47	11

Table 6. Results of R_{rel} of liquid vapor to prints obtained from compositions based on graphene and carbon nanotubes on a textile substrate [43].

Analyzing the test results summarized in **Table 6** and **Figure 11**, it can be seen that the addition of 3% graphene improves the sensitivity of the reaction liquid to vapor tested. It was also observed that the superior sensory stimuli properties are characterized by the chemical compositions of the sample printed based on carbon nanotubes. The increased concentration of tested liquid vapors has a significant impact on the response sensitivity of printed textile substrates. Research on sensory sensitivity to the chemical stimuli indicates that printed textiles retain sensitivity to cyclical impact, which is presented at **Figure 12**. Essential, however, is the relaxation time of the sample on exposure to vapors of organic liquids.

The test results of sensory sensitivity of the printed textile substrates, compositions based on polypyrrole on the chemical stimuli in the form of liquid indicates that the sensory response to polar liquids is stronger than non-polar liquids. This is probably related to the presence in the structure of polypyrrole-conjugated bonds that markedly enhanced its polarity.

The examinations show that the change of vapor concentrations varies proportionally to the sensory properties. This phenomenon allows the use of so-printed textiles as sensors measuring the changes in concentrations of the relevant vapors in the surrounding they are located in.

The obtained results indicate the potential possibility of using printing methods designed to production of the textile sensors that will be used as components of protective technical clothing, that is fire services and mining industry.

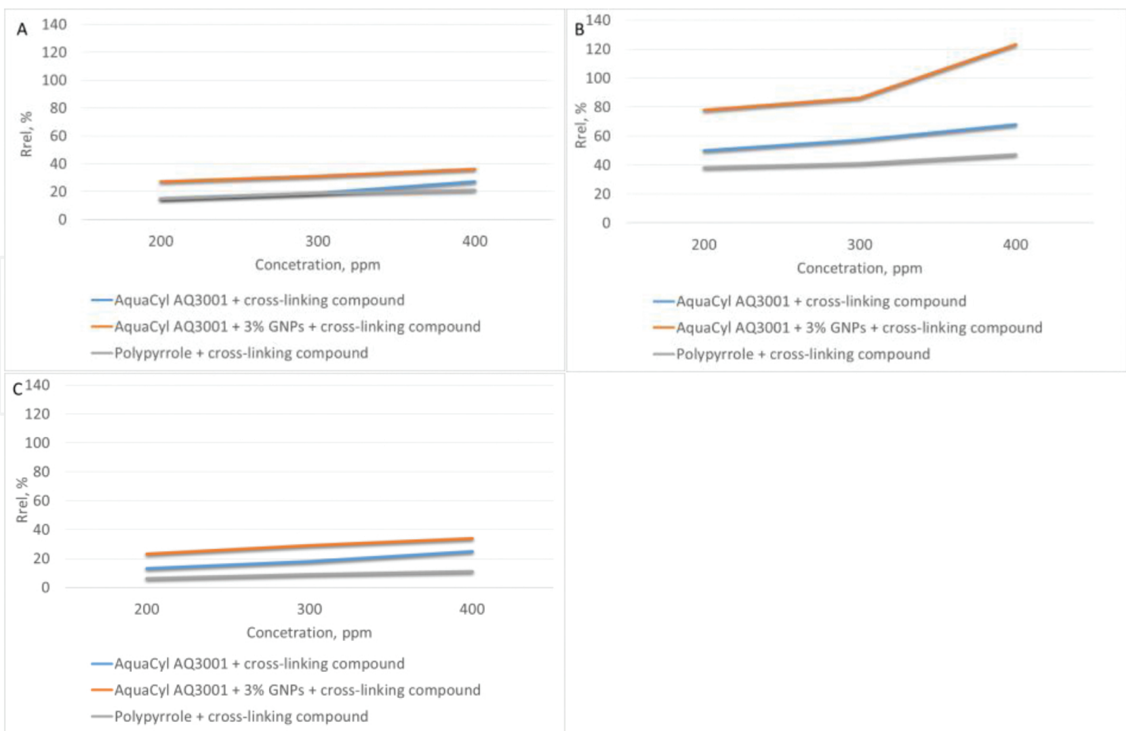


Figure 11. Summary of the sensory properties of the presence of vapor (a) acetone, (b) methanol, (c) toluene.

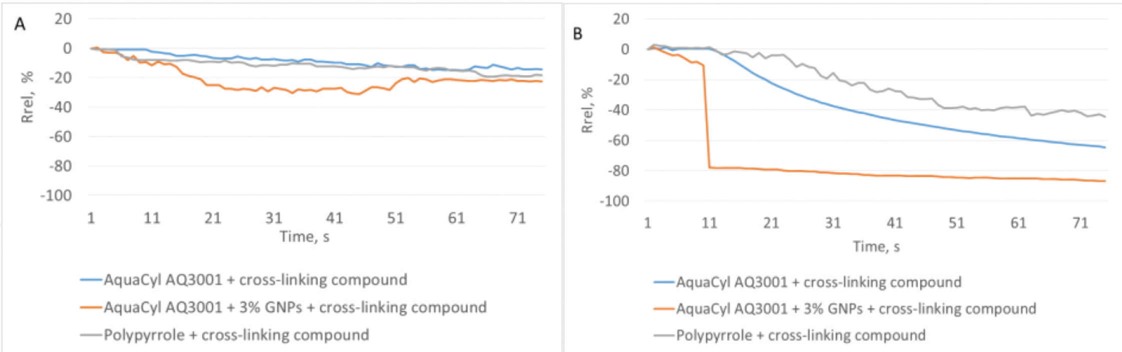


Figure 12. Features of the sensory properties the presence of: (a) the vapor of acetone with a concentration of 200 ppm, (b) methanol vapor at a concentration of 300 ppm.

4. Conclusions

Two Weftloc knitted fabrics from LIBA and PEN ELASTIC companies have been selected as potential strain transducers. These fabrics are characterized by similar raw material composition and content: elastomeric fibers and PA6 fibers, while the existing differences concern the type of elastomeric fibers, surface weight of fabrics, their thickness and structure filling degree. The properties of both fabrics are atypical due to the elastomeric yarn introduced additionally in the course direction, which imparts a high strainability 2D to the fabrics. The surface of fabrics has been chemically coated with a layer of electro-conductive polypyrrole. Thus, Weftloc knitted fabrics as highly strainable and electro-conductive materials can be used as piezoresistive sensors. The electro-mechanical tests of Weftloc fabrics prove their high strain sensitivity. The reaction of the fabrics as piezoresistive sensors is of an anisotropic character. For the sake of the construction of strain sensor, it is particularly beneficial to load the piezoresistive element in the diagonal direction in relation to knitting direction. The piezoresistive effects recorded are repeatable during loading Weftloc fabrics in both single and multiple cycles. They have a linear character to a specified limit for the given fabric. Weftloc PE which characterizes specific structure and content of elastomeric yarns has shown a better performance as a piezoresistive sensor.

The studies support the use of ink compositions for modification of textile substrates, as sensors for mechanical and chemical stimulus. By using printing methods for modifying the surface of textiles can be inexpensive and fast way to create RTDs.

Textile sensors presented in the paper have potential application in health care, in the area endangered of chemical explosions, military and sporting applications.

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Author details

Wiesława Urbaniak-Domagała, Ewa Skrzetuska*, Małgorzata Komorowska and Izabella Krucińska

*Address all correspondence to: ewa.skrzetuska@p.lodz.pl

Department of Material and Commodity Sciences and Textile Metrology, Lodz University of Technology, Lodz, Poland

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