Aspects concerning the mathematical distribution of metal microparticles on the textile surfaces with electroconductive properties obtained by printing method

DOI: 10.35530/IT.070.06.1605

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ABSTRACT – REZUMAT

Aspects concerning the mathematical distribution of metal microparticles on the textile surfaces with electroconductive properties obtained by printing method

This paper presents the aspects concerning the mathematical distribution of metal microparticles on the textile surfaces to model the electroconductive properties of the textiles obtained by a printing method using electroconductive paste based on polyethylene glycol (PEG)/polyurethane (PU) and micro/nanoparticle (nickel, silver, and copper). A direct relationship between surface conductivity and surface pH and an inverse relation surface resistance and pH was observed. Besides this, in this paper, we analyzed the dependences between conductivity, pH and surface resistance by using covariance between two vectors (cov(pH, Rs), cov(C, pH), cov(C, Rs)). The purpose of this research is to define a particles distribution that could be useful in establishing the correct distribution of the microparticles for obtaining the surface with antistatic/dissipative, and conductive properties for sensors or electromagnetic shields.

Keywords: *textiles, electroconductive, plasma technology, microwave, printing, coating, padding*

Astecte privind distribuţia matematică a microparticulelor de metal, cu proprietăţi electroconductive depuse pe suprafaţa textilă prin printare

Această lucrare prezintă aspecte referitoare la distribuția matematică a microparticulelor de metal pe suprafața textilă, în scopul modelării proprietăților electroconductive obținute prin metoda printării pastei conductive pe bază de polietilenglicol (PEG)/poliuretan (PU) şi micro/nanoparticule (nichel, argint şi cupru). S-a observat o dependență directă între conductivitatea suprafeței şi pH şi o relație de dependență inversă între rezistența de suprafață şi pH. În plus, în această lucrare s-au analizat dependențele dintre conductivitate, pH şi rezistența de suprafață, prin intermediul covariației între doi vectori (cov(pH, Rs), cov(C, pH), cov(C, Rs)). Scopul acestei cercetări a fost de a defini distribuția particulelor, care ar putea fi utilă în stabilirea unei distribuții corecte a microparticulelor în scopul obținerii de suprafețe cu proprietăți antistatice/disipative şi conductive, pentru senzori sau ecrane de protecție electromagnetică.

Cuvinte-cheie*: materiale textile, electroconductiv, tehnologia plasmei, microunde, printare, fulardare*

INTRODUCTION

The functionalization of the fabrics is based on pre-treatments by microwave [1–3] or RF plasma [4–6], followed by treatment for the submission of micro/nanoparticles dispersion/paste by padding method (foulard) [7], thin film deposition or direct printing [8–9]. Also, another approach consists of using RF plasma technology to improve the electrical conductivity of the fabric by carbon nanotubes functionalization on poly(ethylene terephthalate) [10–11]. The content of micro/nanoparticule of solution/paste influence finally the electroconductive properties of the surface. Thus, increasing the content of micro/nanoparticles can lead to the effect of the electroconductive surface, when using a low content of micro/nano.

The padding method [7] consists of immersing the textile material in solution or dispersion and squeezing between the drive cylinders and squeezing. By immersion of the textile in dispersion based on metal micro/nanoparticles the distribution of the micro/nanoparticles will be on both sides of the material, by one or more than one pass. These metal micro/nanoparticles can lead to antistatic or dissipative effects. Another method used to improve the electrical conductivity of the composite materials consists of mixing sol-gel method and padding technique using organo-silicon sol with graphene particles [12] or using a “dip and dry” method for textile coating with graphene oxide [13]. Besides, it can be used coating polyester fabric with polypyrrole and doped with graphene oxide [14] in order to obtain conductive polyester fabric.

Fabric coating [15], also named knife coating [16] or doctor blade [17–18], means the application of one or more thin-films using a knife moving over blanket [18]. Based on this method, the thin-film can be applied on one side or both sides of the textile product.

For the submission of micro/nanoparticle by printing [19] using polymeric pasta containing metals (particle

size nano and micro) a metallic or PES screen is used. The method of printing conductive material is the fastest finishing method with low energy consumption and costs. The most used techniques of print are printing on the rotary film, printing on flat film and thermal transfer printing.
To reduce the wastewater and carbon footprint can be used RF plasma oxygen or argon to improve the hydrophily of the fabric and the deposition of the metallic micro/nanoparticles using padding, coating, or screen printing [20].

EXPERIMENTAL PART

To obtain the textile models functionalized by submission of nano/microparticles there were used standard technologies such as padding method, coating and printing, and advanced technology (microwave) for textile drying and polymer cross-linking. To obtain the electroconductive properties there were used several polymers, such as polyurethane (PU), polyethylene glycol (PEG), and polyvinyl alcohol (PVA) with the content of silver (Ag) micro/nanoparticles.
In our experiment based on the padding method, we used dispersions based on polyethylene glycol (PEG) with Ag nanoparticles (<150 nm), copper (Cu) microparticles (14–75 μm) and nickel (Ni) (< 50 μm). These samples with different compositions of the metal micro/nanoparticle have been determined the conductivity and pH of the solution (1).
Also, in the laboratory it was tested the surface resistance of the ratio of the direct voltage applied between the two parallel electrodes on the surface of a test-pieces and the current between these electrodes, neglecting any phenomena of polarization of the electrodes, as described in table 1.

$$C = G * k \quad (1)$$

where:
C is the conductivity of the paste [μS];
G – the conductance of the paste [S];
k – the constant of the sensor, k = 0.1 cm^{-1}
For thin-film deposition a laboratory coating device type SV was used. Using the coating method for deposition of the thin-films based on polyurethane (PU) and alcohol polyvinyl (PVA), with Ag_1 microparticles (2–3.5 μm), Ag_2 (<45 μm), Ni (<50 μm), Cu (14–75 μm) and graphite (C) there were obtained the textile surface functionalized according to table 2.
For experimental models obtained by the coating method based on microparticle (figure 1) the resistance of the surface has been measured using the appliance PROSTAT PRS 801 [21] (figure 2) and values in the range of values specific to conductive

Fig. 1. Thin-film based on metal microparticle deposition using laboratory coating device type SV

Table 1

INPUT DATA – PRINTING PROCESS									
Sample	**Ag**	**Ni**	**Cu**	**PEG**	**Ethanol**	**H_2O**	**Conductivity C (μS)**	**pH**	**Surface resistance Rs (Ω)**
1			x	x		x	155	5.9	$1.3x10^{10}$
2	x			x		x	191	7.5	$1.2x10^{9}$
3		x		x		x	268	7.1	$1.1x10^{9}$
4			x	x	x	x	129	5.4	$1.4x10^{11}$
5	x	x	x	x	x	x	164	5.7	$1.2x10^{10}$

Table 2

TEXTILE SURFACE WITH THIN-FILM DEPOSITED									
Sample	**Ag_1**	**Ag_2**	**Cu**	**Ni**	**PU**	**PVA**	**C**	**Synthetic thickening agent**	**Surface resistance Rs (Ω)***
1	x	x			x	x		x	$2.3×10^{1} ÷ 6.6×10^{5}$
2			x			x	x	x	$2.0×10^{10} ÷ 4.0×10^{12}$
3	x					x	x	x	$1.9×10^{10} ÷ 3.1×10^{12}$
4	x	x		x		x		x	$2.9×10^{12} ÷ 5.9×10^{12}$

* Minimum and maximum limits of the resistance values of the surface obtained by individual measurements

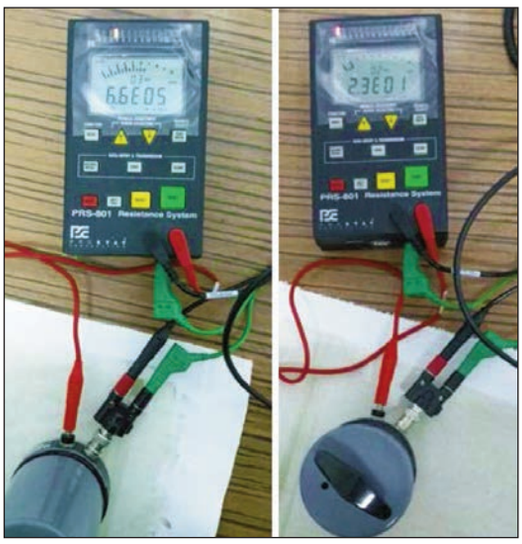


Fig. 2. Surface resistance measurement for sample coated

materials (10^2–10^5) were obtained. In addition, for these samples the main physico-mechanical characteristics that are presented in table 3 have been evaluated.

Table 3

PHYSICO-MECHANICAL CHARACTERISTICS FOR SAMPLE NO. 1				
Sample	**Mass [g/m²]**	**Thickness [mm]**	**Air permeability (l/m²/sec)**	**Surface resistance Rs (Ω)***
1	596.5	0.821	16.28	$2.3\times10^1 \div 6.6\times10^5$

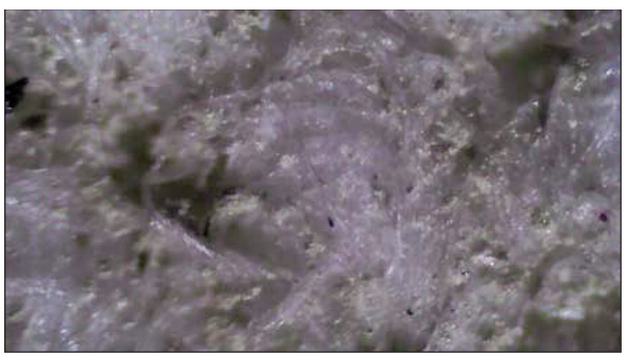
* Minimum and maximum limits of the resistance values of the surface obtained by individual measurements

Also, it was used the morphological analysis by electron microscopy in order to present the surface of the before metal particles deposition (figure 3) and after metal nano/microparticles deposition (figure 3, *b*).
Using printing technology, with paste containing Cu microparticles (14–75 μm), Ni (< 50 μm), Ag (2–45 μm graphite), graphite (C), PVA (polyvinyl alcohol) and synthetic thickener, samples have been carried out following table 4.
Controlled drying of the samples (30 seconds – 1 minute) has been carried out in the field of the microwave power generated by a high voltage generator (magnetron) which converts the current continuously into radiofrequency energy (frequency 2.4 GHz, power 700 W).

Table 4

FUNCTIONALISED SAMPLES BY MICROPARTICLE SUBMISSION USING PRINTING METHOD						
Sample	**Cu**	**Ni**	**Ag**	**PVA**	**C**	**Thickening agent**
M1				x	x	x
M2	x		x	x	x	x
M3	x			x	x	x
M4		x		x	x	x
M5			x	x	x	x

a



b

Fig. 3. Textile sample analysis based on electron microscopy: *a* – initial textile sample; *b* – textile surface coated with a thin film

RESULTS AND DISCUSSIONS

In figure 4 is presented the representation of the 3D surface resistance of the samples obtained by padding method in the function of the pH and dispersion conductivity using Matlab software and multivariate analysis of the surface resistance (Rs) in the function of the dispersion conductivity (C) and pH.

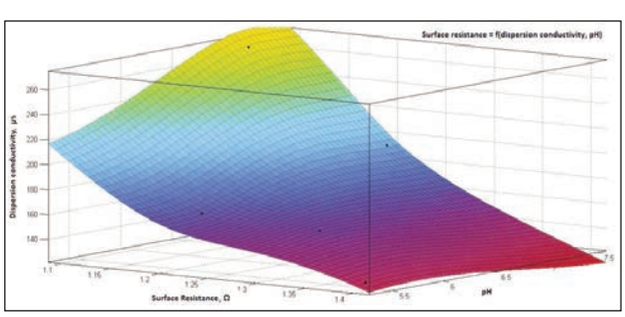


Fig. 4. 3D representation of the surface resistance according to the pH and dispersion conductivity ($Rs = f(C, pH)$)

Based on analysis of the covariation between *pH*, the surface resistance (R_S) and the dispersion electroconductivity (C) (2, 3, 4) it was demonstrated that between the surface resistance and *pH* it is an inverse proportionality, and between the *pH* and dispersion conductivity it is a direct proportionality.

$$\text{cov}(pH, Rs) = \begin{vmatrix} 0.8520 & -0.0760 \\ -0.0760 & 0.0130 \end{vmatrix} \quad (2)$$

$$\text{cov}(C, pH) = 1.0e + 03 * \begin{vmatrix} 0.8343 & 0.0372 \\ 0.0372 & 0.0009 \end{vmatrix} \quad (3)$$

$$\text{cov}(C, Rs) = 1.0e + 03 * \begin{vmatrix} 2.8343 & -0.0054 \\ -0.0054 & 0.0000 \end{vmatrix} \quad (4)$$

For the assessment of the electromagnetic shielding effectiveness (SE_{dB}) the fabrics have been cut in the shape with an outer diameter of 100 mm and an inner diameter of 30 mm to be able to be fitted inside the measuring cell used. After they have been cut, on the edges of the samples has been coated with conductive paint based on the silver to ensure a suitable electrical contact with the measuring cell. The tests have to be performed at a temperature of 22°C and humidity 40%. For the investigation of the electromagnetic shielding attenuation [22–23], we have used the following specific equipment (of the equipping INCD-ICPE-CA): coaxial cell model TEM 2000 (figure 5); oscilloscope Tektronix MDO model 3102; power amplifier Model SMX5; signal generator type E8257D. To evaluate the electromagnetic shielding efficiency the Schelkunoff equation (5) it was used:

$$SB_{dB} = 10 \log_{10} \frac{P_1}{P_2} \quad (5)$$

where:

P_1 [dB] is the power of the signal detected in the absence of the electromagnetic screen;

P_2 [dB] – the power of the signal detected in the presence of the electromagnetic screen.

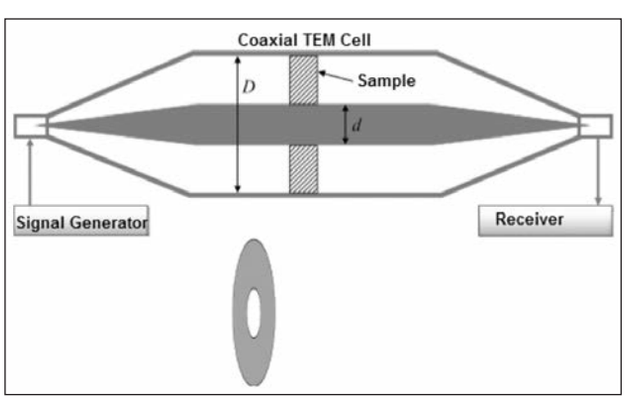


Fig. 5. Schematic representation of the sample and coaxial measuring cell TEM 2000

SE_{dB} represents the difference between the measured signal without the sample and the signal level measured with the sample mounted inside the cell, and both measured in dB (according to the standard IEEE Std 299-2006). The tests were based on the following standards: ASTM D4935-89, ASTHMA ES7-83, IEEE Std 299-2006. The electromagnetic shielding effectiveness depending on the frequency in the field 0.3 MHz – 1GHz is presented in figure 6. During the investigation for electromagnetic shielding, only the samples M4 and M5 have proved useful.

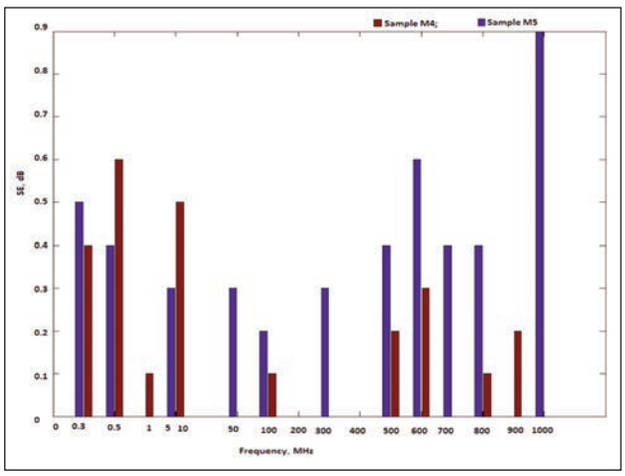


Fig. 6. 2D representation of the electromagnetic efficiency attenuation vs. frequency

CONCLUSIONS

As a result of the evaluation of the results (experimental models) the textiles with electroconductive properties can be classified as a conductive, antistatic, or EM shields.

The experimental models obtained by padding method with dispersions based on Ni microparticles in polyethylene glycol, have the best antistatic properties because the resistances of the surface for the samples are within the range of 10^9 to 10^{10}. It can be concluded that the experimental models obtained by the padding method have the surface resistance within the range specific to the materials with antistatic properties ($1.0 \times 10^5 – 1.0 \times 10^{12}$).

The experimental models obtained by printing based on polimeric solutions (alcohol polyvinyl and polyurethane) with graphite and Ni microparticles content present the best value for the electromagnetic shielding effectiveness (SE_{dB}).

The experimental models made by thin film deposition based on silver microparticles dispersed in the polymer such as polyurethane (PU) and alcohol polyvinyl (PVA), show the lowest values for resistance ($2.3 \times 10^1 – 6.6 \times 10^5$) and the most significant default values for the electrical conductivity having the potential for use for the constituents of the sensors.

In conclusion, the increase in the pH value or the amount of conductive microparticles particle causes an increase in conductivity of the solution, which leads by default to obtain conductive surfaces with low surface resistivity. The surface resistance variation for the same sample can be explained by the fact that the distribution of the nano/microparticle in pastes used for printing/coating or in the dispersions used for padding method is not uniform.

ACKNOWLEDGMENTS

The research presented in this paper was prepared in the INCDTP laboratories. Funds support this work from MCI, National Project "Optimizing the performance of the functional textile by advanced technologies", Contract PN 18 23 01 05. The evaluation of the electromagnetic shielding effectiveness has been performed by using the equipment available in INCD-ICPE-CA, Contract 2048/11.2018.

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