

# Electroconductive properties of nylon 6,6 and cotton fabrics by “In Situ” polymerization of aniline in one step reaction without re-doping

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Polyaniline coated conducting fabrics (woven textile material) have been obtained by “in situ” polymerization of aniline in one step reaction without redoping. Different aniline: oxidant: HCl molar ratio were used and the best results of surface electrical resistivity were obtained when molar ratios were 2.2:1:3 and 1:1:3. The powders obtained after removing the material from reactor and filtering the reaction product were characterized by FT-IR spectroscopy, UV-Vis spectroscopy and scanning electron microscopy (SEM). Coated Nylon 6,6 and cotton fabrics were characterized by infrared spectroscopy with ATR device, scanning electron microscopy (SEM), electrical resistivity measurements and diameter measurements.

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## 1. Introduction

Conducting polymers found new applications in industry as batteries, sensors, or conductive textiles [1-4]. Polyaniline (PANI) is one of most used electroconductive polymers due to low cost of monomer, good thermal and mechanical properties.

PANI presents three forms: leucoemeraldine, emeraldine and pernigraniline of which emeraldine is the conductive form. They are differentiated by oxidated respective reduced form. The emeraldine form of PANI contains equal numbers of imine and amine nitrogen atoms, the former being more basic and more prone to protonation compared with the amine sites, which become protonated only at high acid concentration [5]. The conversion of PANI in non conductive form after treatment with alkali is the most known reaction named undoping. The transformation of non conductive form in a more conductive form by protonation with an acid was named re-doping.

The disadvantage of polyaniline for textile industry is the partial dissolution in most of the solvents. Thus the immersion of textile in polyaniline solution did not give results.

Previous studies about the coating of materials with polyaniline were made on polyester [6-19], wool [9,15], cotton [9,15,20], Nylon 6 [5,9,15,21] and acrylics [9,15].

Polyamide type of textile materials include Nylon 6 and Nylon 6,6 [22].

In literature data it is known that Nylon 6,6 consists of chains of 12 carbon atoms in each repetitive unit, which gives a density greater than the structure of Nylon 6 which contains only 6 carbon atoms in a repetitive unit [22]. This

type of structure (Nylon 6,6) is harder paints and uniform covered but shows a high resistance of colour [22].

Cotton is a natural material with celluloid structure, sensitive at acid media [22].

Previous studies were followed by Nouri [15] on yarn of cotton or Nylon 6 but the coated yarns weaving could create problems. Nouri [15] in his study used hydrochloric acid solution as solvent for both aniline and ammonium persulphate and a molar ratio aniline: oxidant of 1:1. After reaction, the coated-yarns were doped and undoped in desiccator for 1 h. Hydrochloric acid vapour was used for doping and ammonia vapour for undoping.

Hirase [9] has coated cotton fabrics with polyaniline using 4 and 8 hours for polymerization and the obtained surface resistance was  $2.6 \times 10^6$ - $2.8 \times 10^6$  ohm/cm. As oxidants potassium iodate ( $KIO_3$ ), ammonium persulphate ( $(NH_4)_2S_2O_8$ ) and potassium bichromate ( $K_2Cr_2O_7$ ) were used, but good results for surface resistance of cotton fabrics were obtained only with ammonium persulphate. The re-doping of textiles after the polymerization was realized by immersion in 0.5N HCl for 15 min.

Hong et al [20] redoped the PANI-nylon 6 with 0.1M  $NH_3OH$  aqueous solution. The samples were then redoped with HCl by immersing in a 0.3M acid aqueous solution for 24 h.

The aim of this paper was the coating of Nylon 6,6 and cotton fabrics by in-situ polymerization of aniline.

The textile materials can be obtained by weaving or knitting of yarns. The woven textile materials are named fabrics.

The highlights of present paper were obtaining of coated fabrics in one step and elimination of re-doping by

control of reaction parameters and improving of electrical properties.

## 2. Experimental

### 2.1. Reagents and chemicals

For the preparation of conductive fabrics the following reagents were used: aniline 99% (Sigma-Aldrich), HCl 37% (Sigma-Aldrich), ammonium persulphate (Sigma-Aldrich), cotton etalon and Nylon 6,6 fabrics (cotton and Nylon 6,6 from Romanian market).

### 2.2. Synthesis

The polymerization of aniline was carried out according to the procedure used by Cao [23]. In a 1L reactor with stirrer a piece of 10x10 cm size fabrics (previously washed with distilled water) was inserted and to cover it 400 ml distilled water were added. The ratio of material amount to water was 1:15. Exact quantities of aniline and 37% hydrochloric acid were poured into the reactor and were stirred at a temperature of 0-5°C to obtain aniline hydrochloride. In another beaker the ammonium persulphate  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  was dissolved in 100 ml distilled water. Oxidant solution cooled to a temperature between 0-5 °C was dropped for 50 minutes into reactor, with continuously stirring. Reaction temperature was maintained at 5°C by external cooling with an ice bath. After oxidant dripping, reaction mass was stirred 90 minutes at 5°C, for reaction completion. The fabrics was removed from the reactor and washed with distilled water and methanol and allowed to dry at room temperature. In Table 1 the molar ratio of the reagents used in experiments were presented. The procedure was repeated for each composition for Nylon 6,6 fabrics and for cotton fabrics.

After removing the material, the mass of reaction was filtered and the precipitate was washed with distilled water, methanol and dried in oven at 100 °C. The obtained powders were also characterized.

The obtained polyaniline powders were noted PANI 1, PANI 2 and PANI 3. The covered cotton samples were noted C-PANI 1, C-PANI 2 and C-PANI 3. The covered Nylon 6,6 fabrics were noted N-PANI 1, N-PANI 2, and N-PANI 3.

Table 1. Polyaniline synthesis parameters

No. exp.	Aniline (mol)	HCl (mol)	$(\text{NH}_4)_2\text{S}_2\text{O}_8$ (mol)
1	1	3	1
2	2,2	3	1
3	2,2	5	1

### 2.3. Analysis and measurements

The polyaniline powders were characterized by UV-Vis, FT-IR spectroscopy and SEM, while the fabrics was characterized by ATR, SEM, surface electrical resistivity and yarn diameter measurements.

UV-VIS spectra were recorded with a Perkin Elmer spectrometer in 200-900 nm range.

Infrared spectra were carried on a Cary 630 spectrometer at room temperature, with 32 scans and sensitivity of  $4 \text{ cm}^{-1}$ . The powder samples were prepared in pellet form using 1 mg powder to 200 mg spectroscopic grade KBr. The mixture was pressed to form a pellet, and the spectra were recorded in  $400\text{-}4000 \text{ cm}^{-1}$  range.

ATR spectra on the fabrics were recorded with diamond crystal device between  $650\text{-}4000 \text{ cm}^{-1}$  with an interruption in  $1800\text{-}2300 \text{ cm}^{-1}$  range, where the absorption of diamond are present.

Surface morphology of coated fabrics and bulk structures of the powders were observed using scanning electron microscope (Quanta 200 -FEI).

The surface resistivity of the fabrics was measured according to standard SR EN 1149-1:2006 employing the 2 electrodes method, using a PROSTAT 800 meter.

The diameter measurements were made according to the standard SR 13152: 1993 on yarns removed from fabrics coated with polyaniline. The method consists in projection on the screen of optical microscope with 50x magnification of yarn profile and measuring the diameter. The Projectina optical microscope was used.

## 3. Results and discussion

### 3.1. Characterization of polyaniline powders

In figure 1 the SEM images of polyaniline powders obtained in the experimental conditions described above, after removing the fabrics were presented.

SEM images have revealed that the characterized polyaniline are formed of globular granules aggregates. In all powders the particle size was of hundreds nm. Particles formed in experiment 1 were smaller than those formed in experiments 2 and 3. It is found that the particle size increases with increasing of molar ratio aniline: oxidant.

Literature data have shown that UV-VIS spectra of polyaniline can present the following transitions [24, 25]:

- The band at 340 nm is ascribed to the electronic transitions  $\pi - \pi^*$  between conduction and valence bands;
- A band at 430 nm is associated with  $\pi$  transitions of a polaron;
- A strong band at 600 nm is attributed to intramolecular charge transfer associated to chinoide rings;
- A band at 740 nm assigned to  $\pi^*$  transition of a polaron .

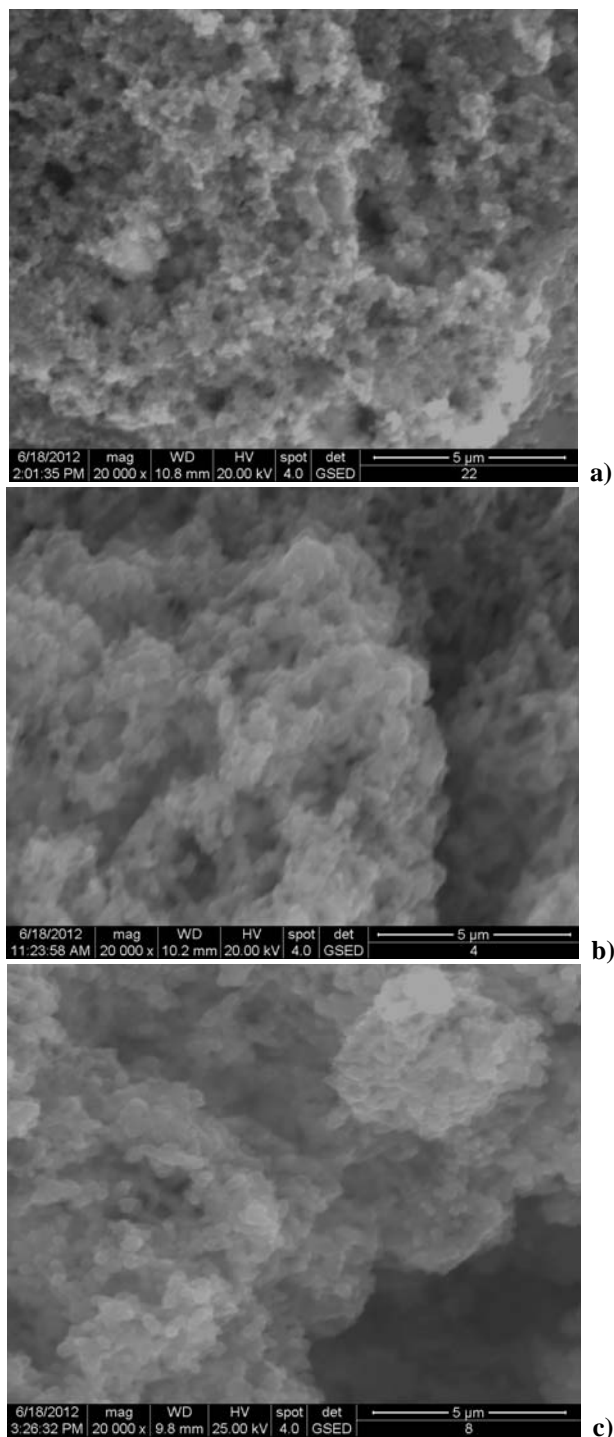


Fig.1 SEM images of polyaniline powders: a) PANI 1; b) PANI 2; c) PANI 3

It should be mentioned that UV-VIS bands are dependent on the conformation of the polyaniline polymer, because there is a close relation to conjugated polymers which have a high degree of coupling between electronic and geometric properties.

The UV-VIS spectra of the synthesized polyaniline powders are presented in Fig. 2.

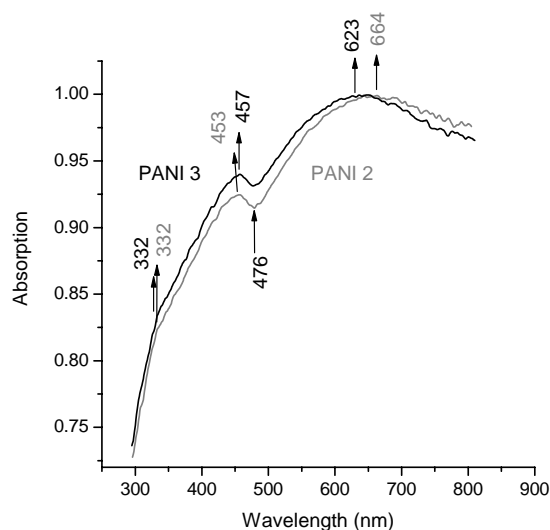


Fig.2 UV-VIS Spectra of PANI-HCl powders.

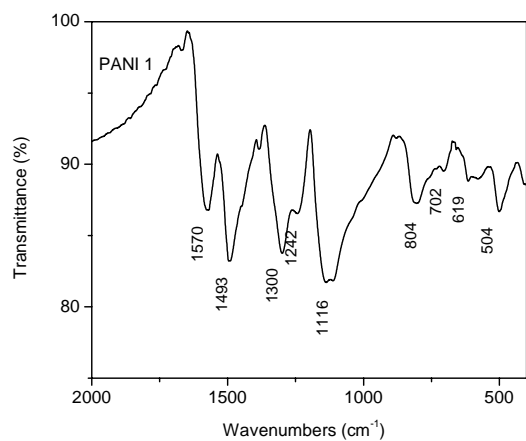
In the spectra observed in figure 2 the bands with maxima at 332 nm, 450 nm and 623-664 nm were evidenced showing the formation of conductive emeraldine form. UV-Vis spectra collected for PANI reveal the characteristic isosbestic point (i.p.) at 476 nm (Fig. 2), similar to that observed by Braga et al. [26] and Vieira et al. [25].

In the Figure 3 the FT-IR spectra of polyaniline powders are presented, while in the Table 2 the characteristic vibrational frequencies and assignments of these bands are shown.

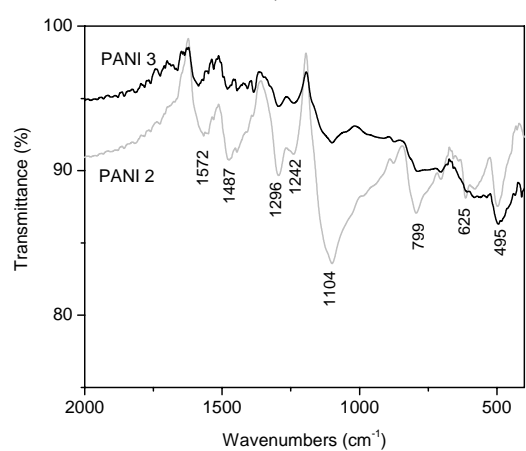
FT-IR spectroscopy brings valuable information on the structure of polymer obtained. Polyaniline bands highlight the following issues:

- Stretching bands of chinoid ring (Note Q) of type  $N = Q = N$  are observed at  $1570 \text{ cm}^{-1}$ ;
- Stretching bands of the benzenoid ring (note B)  $N-B-N$  type are observed at  $1490 \text{ cm}^{-1}$ ;
- Stretching bands such as  $CN^+$  of the polaron structure are observed in  $1242 \text{ cm}^{-1}$ ;

When bands at  $1570 \text{ cm}^{-1}$  and  $1490 \text{ cm}^{-1}$  have similar intensities means that oxidation of polyaniline is 50% [25]. Similar intensity bands at  $1570 \text{ cm}^{-1}$  and  $1490 \text{ cm}^{-1}$  demonstrated the obtaining of emeraldine, 50% oxidized form. If the difference in intensity is lower than 10% indicates that 50% of the aromatic rings are oxidized to chinoid form. From FT-IR spectra it can be conclude that the conductive polyaniline was formed. PANI 3 had the lower intensities of bands.



a)



b)

Fig.3 FT-IR Spectra of PANI-HCl powders in KBr pellet:  
a) PANI 1; b) PANI 2 (grey) and PANI 3 (black).

High values of transmittance in infrared spectra (100%-80%), characteristic to materials with good optical properties were shown by all powders.

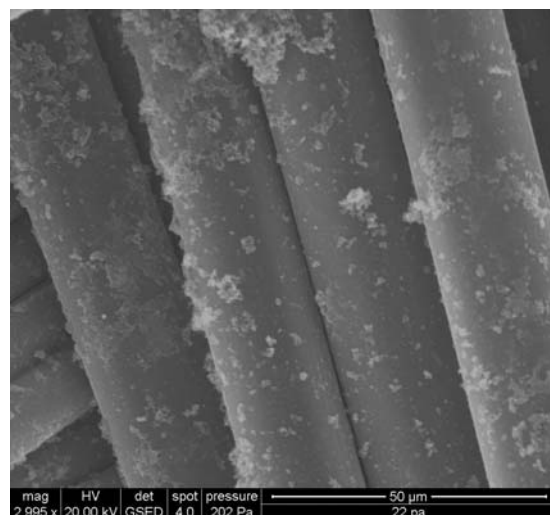
Table 2 Comparison between the main characteristic bands in FT-IR spectra of powders

B= benzenoide ring; Q = chinoide ring

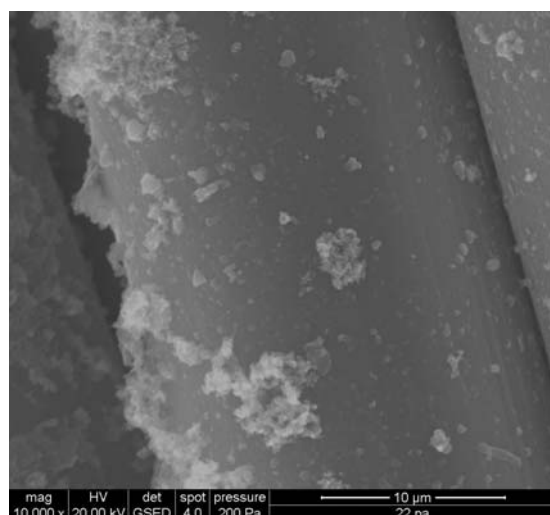
Assignment	Frequency (cm <sup>-1</sup> )		
	PANI 1	PANI 2	PANI 3
Q: C=C stretching	1570	1572	1587
B: C=C stretching	1493	1487	1490
C-N stretching	1300	1296	1290
C-N <sup>+</sup> stretching	1242	1242	1242
C-H in-plan	1116	1104	1104
C-H out-of-plan	804	799	792

### 3.2. Fabrics Characterization

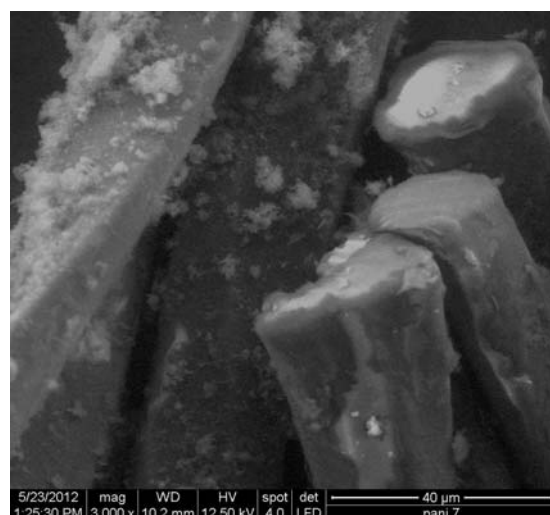
Fig. 5 shows microstructure of Nylon 6,6 fabrics coated with polyaniline by „in situ” polymerization using HCl.



a)



b)



c)

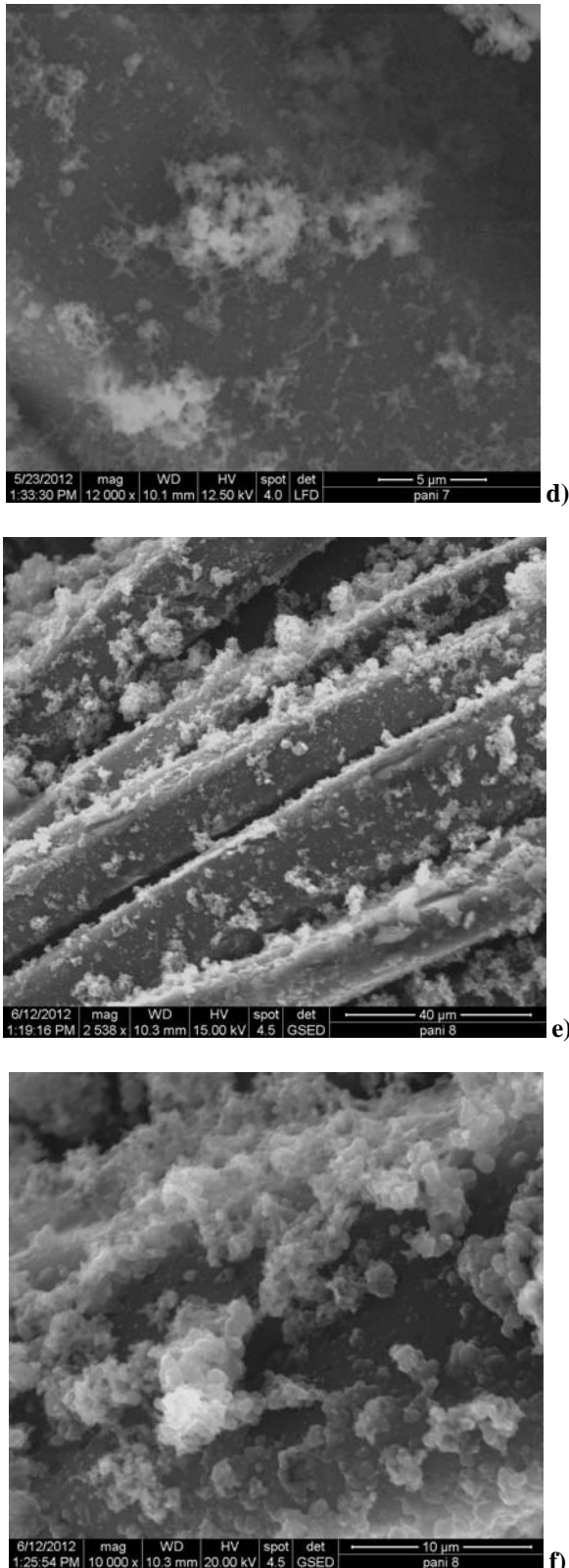


Fig.4 SEM images of polyamide fabrics covered with PANI by „in situ” polymerization: a) N-PANI 1 at 2995x magnification, b) N-PANI 1 at 10000x magnification; c) N-PANI 2 at 3000x magnification; d) N-PANI 2 at 12000x magnification; e) N-PANI 3 at 2530x magnification; f) N-PANI 3 at 10000x magnification.

In the Fig. 4c a cross section in Nylon 6,6 fibers and its uniform covering can be also seen.

Fig. 5 shows microstructure of cotton fabrics coated with polyaniline using the molar ratio into experiment 2 by „in situ” polymerization with hydrochloric acid. SEM image shows uniform coverage of cotton and Nylon 6,6 fabrics with polyaniline from "in situ" polymerization. The amount of polyaniline deposited was increased with increasing of the molar ratios aniline: oxidant and aniline: HCl.

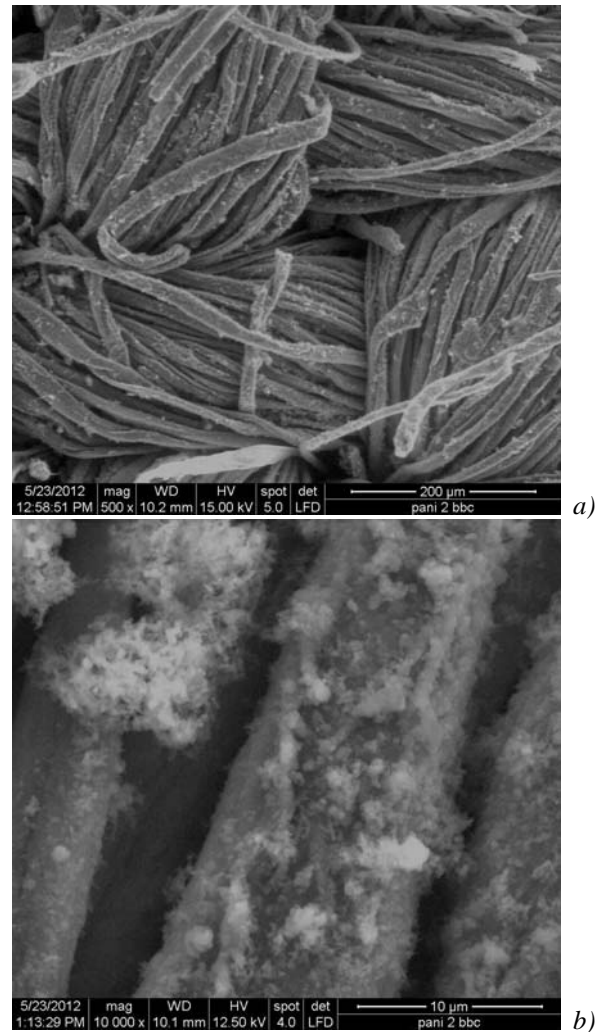


Fig.5 SEM images of cotton fabrics covered by „in situ” polymerization in the experiment 2: a) C-PANI 2 at 500x magnification, b) C-PANI 2 at 10000x magnification;

Structural characterization by ATR of textile materials after polyaniline deposition was presented in the figure 6.

In the spectra of N-PANI 1 and N-PANI 2 the intensities of bands characteristic to stretching of benzenoid ring (B:C=C) and bands characteristic to stretching of chinoid ring (Q:C=C) are similar, so the emeraldine is 50% oxidized. In the spectrum of N-PANI 3 the difference in intensities is higher.

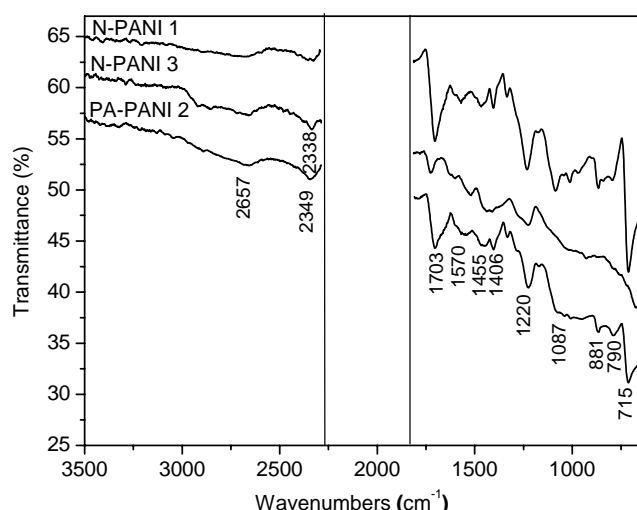


Fig.6 ATR spectra of polyaniline coated Nylon 6,6 fabrics.

Table 3 The main characteristic bands in FT-IR spectra of covered Nylon 6,6

B= benzenoide ring; Q = chinoide ring

Assignment	Frequency (cm <sup>-1</sup> )		
	N-PANI 1	N-PANI 2	N-PANI 3
-CH=O stretching	2698	2657	2657
=NH <sub>2</sub> <sup>+</sup> stretching	2354	2349	2338
C=O stretching	1706	1703	1726
Q: C=C stretching	1572	1570	1520
B: C=C stretching	1474	1455	1438
C-N stretching	1408	1406	1417
C-N <sup>+</sup> stretching	1232	1220	1233
C-H in-plan	1088	1087	1032
C-H out-of-plan	795, 713	790, 715	682

The cotton fabrics have a similar behaviour with Nylon 6,6 fabrics showing a 5% decrease in transmittance values. For exemplification in Fig. 7 the ATR spectrum of C-PANI 2 is presented.

In the spectrum of C-PANI 2 the difference between intensities of characteristic bands to stretching of benzenoid ring (B:C=C) and bands characteristic to stretching of chinoid ring (Q:C=C) was smaller than 10% and the emeraldine was ~ 50% oxidized.

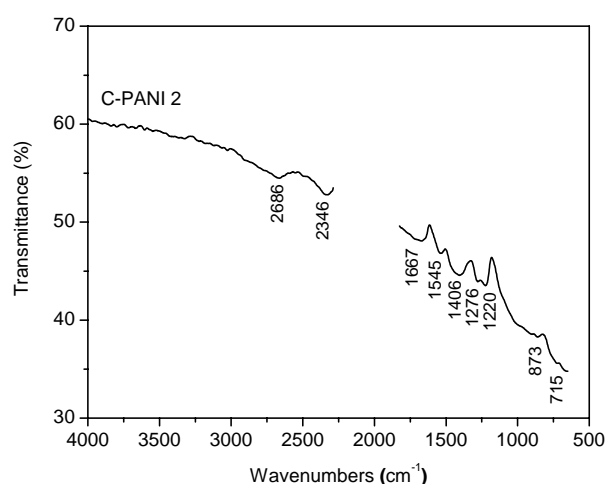


Fig.7 ATR spectrum of polyaniline coated cotton fabric.

In the Table 5 the results of electrical resistivity measurements on coated fabrics according to standard SR-EN 1149-1:2006 were presented.

Table 5 Materials characteristics of PANI coated fabrics

	Electrical resistivity (Ωcm) SR EN 1149-1:2006	Aspect/ color
N-PANI 1	2.4*10 <sup>2</sup>	Dark green
N-PANI 2	1.3*10 <sup>2</sup>	Dark green
N-PANI 3	8.2*10 <sup>5</sup>	Green -black
C-PANI 1	3.8*10 <sup>2</sup>	Dark green
C-PANI 2	1.2*10 <sup>2</sup>	Dark green
C-PANI 3	2.1*10 <sup>6</sup>	Green-black

All fabrics prepared by „in situ” polymerisation were coated uniformly and showed good electrical resistivities of 10<sup>2</sup> -10<sup>6</sup> Ωcm. The best resistivities were obtained for molar ratio aniline: oxidant: HCl of 2.2:1:3 and 1:1:3.

When molar ration aniline:HCl was 1:3 the good electrical properties were obtained in one step reaction. When the molar ration increased the electrical properties decreased.

The N-PANI 1 and N-PANI 2 fabrics presented comparable results with the data obtained of Hirase [9] and Nouri [15].

The C-PANI fabrics have better electrical properties then those published in the literature data.

In the Table 6 the diameter of yarns in the fabrics before and after covering with polyaniline according standard SR 13152: 1993 are presented.

When aniline was added in excess the layer of polymer on fiber was thicker. Bonds formed between N-H from polyamide and chloraniline can decide this behaviour.

Table 6 the diameter of yarns in the fabrics before and after covering with polyaniline

Fabrics	Diameter ( $\mu\text{m}$ )	
	Warp	Weft
Nylon 6,6	18	11
N-PANI 1	19.5	13
N-PANI 2	21.4	21.4
N-PANI 3	31	29
Cotton	18	18
C-PANI 1	20	20.4
C-PANI 2	23	23
C-PANI 3	28	30

The thickness of deposited layer increased with the excess of aniline and excess of HCl.

## 5. Conclusions

All fabrics prepared by „in situ” polymerisation were coated uniformly and showed good electrical resistivities of  $10^2$  - $10^6$   $\Omega\text{cm}$ . The best resistivities were obtained for molar ratio aniline: oxidant:HCl =2.2:1:3 and 1:1:3.

When aniline was added in excess the layer of polymer on fiber was thicker and the values of electrical resistivity on surface increased. Bonds formed between N-H from Nylon 6,6 and aniline hydrochloride can decide this behaviour.

By using an excess amount of HCl good electrical properties were obtained in one step of reaction.

In all reactions the resistivity values obtained were similar or better than the data reported in the literature.

Elimination of re-doping process can decrease the cost of fabrication.

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