SCIENTIFIC PAPERS
OF THE UNIVERSITY OF PARDUBICE
Series A
Faculty of Chemical Technology
18 (2012)

PREPARATION OF FUNCTIONAL PET FABRIC/POLYPYRROLE COMPOSITE

Veronika ŠAFÁŘOVÁ[a1], Jan GRÉGR[b] and Michal MARTÍNEK[c]
[a]Faculty of Textile Engineering,
[b]Faculty of Science, Humanities and Education,
[c]Faculty of Mechatronics, Informatics and Interdisciplinary Studies
Technical University of Liberec, CZ–461 17 Liberec

Received September 25, 2012

Conducting and electromagnetic shielding poly(ethylene terephthalate) (PET)/ polypyrrole (PPy) composites were synthesized by in-situ chemical polymerization of pyrrole in the presence of PET fabrics. The effects of preparation conditions on the characteristics of the composite, such as surface morphology, electrical conductivity and electromagnetic shielding efficiency were studied. The synthesized polymer composites were characterized by surface and volume resistivity, EMI shielding and SEM techniques. The most suitable medium, from the point of view of the lowest electrical volume and surface resistivity, the highest electromagnetic shielding efficiency and resultant the highest PPy content of composite fabric, was observed to be aqueous ferric chloride solution with PTSA, non-oxidizing transient tosylates and the pyrrole concentrations of 0.2 vol. %.

---

[1] To whom correspondence should be addressed (veronika.safarova@tul.cz).

Introduction

In general, textile products are electrically insulating and transparent to electromagnetic radiation, i.e., their electromagnetic shielding effectiveness is practically zero. Many of the synthetic fibers used in textile fabrics are insulating materials with a resistivity in the order of 10^{15} Ω cm^{-2} [1]. This is much higher than the resistivity desired for electromagnetic shielding applications.

In recent years, conductive fabrics have obtained increased attention for electromagnetic shielding and anti-electrostatic purposes. This is mainly due to their desirable flexibility and low weight. One way how conductive fibers can be created is by using minute electrically conductive fibers. They can be produced in filament or staple lengths and can be incorporated with traditional non-conductive fibers to create yarns that possess varying degrees of conductivity. Another way represents conductive coatings which can transform substrates into electrically conductive materials without significantly altering the existing substrate properties. They can be applied to the surface of fibers, yarns or fabrics. The most common are metal and conductive polymer coatings [2].

Theoretical

Conductive Polymers

More than 100 polymer materials with different range of electric conductance are known nowadays. A number of these polymers can be spun, which makes it useful in applications to textile structures for diverse purposes. Among the most used conductive polymers belong polyacetylene, polyaniline, polythiophene (and various polythiophene derivates), polypyrrole and polyphenylenevinylene. Structures of several conductive polymers are illustrated in Fig. 1 [3].

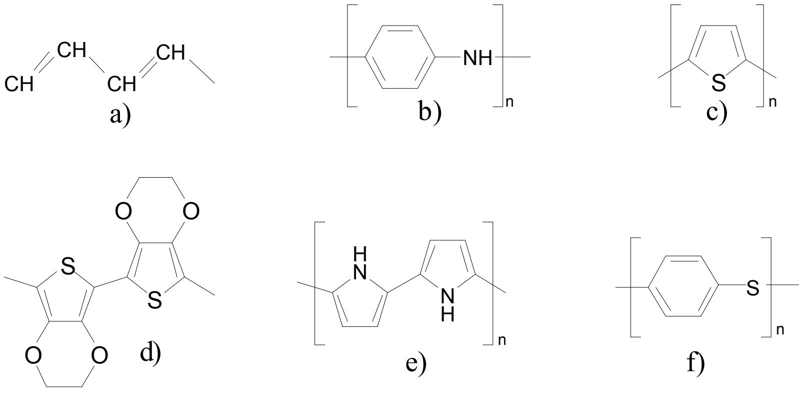


Fig. 1 Structure of: a) polyacetylene, b) polyaniline (PANI), c) polythiophene, d) poly(ehylendioxythiophene) (PEDOT), e) polypyrolle (PPy), f) polyphenylene sulfide

An advantage of conductive polymers lies in the fact that electric conductance can be significantly changed, e.g., by concentration ratio changes, temperatures of the reaction or adding a variety of oxidants and dopants. The dependence of conductance on temperature for polymers is different from that for metals or semiconductors. It generally increases with decreasing temperature for "metallic" materials, while it generally decreases with lowered temperature for semiconductors and insulators [4].

Conducting Polymer Coated Fibers

One of the most widely used approaches to fabricating electrically conductive textiles from intractable inherently conductive polymers is to use a submicron thick coating of an ICP onto an existing textile substrate. Conducting polymer-based conductive textile substrates can be fabricated by *in situ* polymerization and two-step process [5]. The *in situ* polymerization consists of adsorption of monomer on the surface of the substrate, and consequently an oxidation-polymerization process follows. This process is industrially applicable because it can be performed using a standard textile dyeing equipment using aqueous solution for both aniline and pyrrole. The *in situ* polymerization of pyrrole to form an electrically conductive textile was first reported by Kuhn and coworkers [6]. The process for forming the polypyrrole-coated textiles was based on the immersion of a fabric into an aqueous solution containing pyrrole, ferric chloride, and ammonium persulfate to initiate the polymerization reaction, and usually a sulfonated dopant anion. In dilute solutions of pyrrole (0.015-0.03 M), the polymerization reaction occurs on the surface of the fiber and leads to the formation of a precipate in the bulk liquid phase. The selection of the dopant anion affects both the surface resistivity and thermal stability of the polypyrrole-coated textiles. The surface resistivity of these PPy-coated textiles could be varied from $5\ \Omega\ \mathrm{m}^{-2}$ to $10\ \mathrm{k}\Omega\ \mathrm{m}^{-2}$ by controlling the polymerization time, the concentration of the reactants in the polymerization bath, and the type of anion used to dope the PPy coating [6,7].

Besides using an *in situ* polymerization of conductive polymer to form an electrically conductive textile substrate, other researchers adopted a two-step process. The major advantage of this procedure is that it can easily be adapted into a continuous process for industrial applications. Several variations to the two-step process include first immersing the textile support in a solution containing the oxidant and desired dopant anion and then exposing the impregnated textile to either conductive polymer vapor or polymer dissolved in an aliphatic solvent to initiate the polymerization reaction. Alternately, the textile support may be first exposed to polymer vapor and then immersed into an aqueous solution containing the oxidant and desired dopant anion [6,8-11].

In recent years, conductive fabrics have obtained increased attention for electromagnetic shielding and anti-electrostatic purposes.

Experimental

Polymerization of Polypyrrole on Textile Substrate

The substrate used was 100 % PETh plain weave, surface density 62.5 g m^{-2}, ends per cm 45, picks per cm 25. The conducting poly(ethylene terephthalate) (PET)/polypyrrole (PPy) composite fabrics were prepared by *in situ* chemical polymerization of pyrrole in the presence of PET fabrics using various concentrations of the monomer, the oxidant solution, the kind of the oxidant, polymerization time and the presence of surfactant (Spolion).

The *in situ* polymerization of pyrrole onto textile substrate was based on the immersion of a fabric into an aqueous solution containing pyrrole, oxidant to initiate the polymerization reaction and usually a sulfonated dopant anion. With the use of dilute solutions of pyrrole (0.1- 0.2 vol. %), the polymerization reaction occurs on the surface of the fiber and leads to the formation of a precipitate in the bulk liquid phase. The selection of the dopant anion affects both the surface resistivity and thermal stability of the polypyrrole-coated textiles. The surface resistivity of these PPy-coated textiles could be varied by controlling the polymerization time, the concentration of the reactants in the polymerization bath, and the type of anion used to dope the PPy coating.

The oxidant used was ferric chloride ($FeCl_3$), silver nitrate ($AgNO_3$), ferric tosylate ($Fe(OTS)_3$) or cupric bromide ($CuBr_2$). See equations of the reaction process

$$n\mathrm{PyH_2} + 2n\mathrm{FeCl_3} \rightarrow [\mathrm{Py}]_n + 2n\mathrm{FeCl_2} + 2n\mathrm{HCl} \qquad (1)$$

$$n\mathrm{PyH_2} + 2n\mathrm{Fe(OTS)_3} \rightarrow [\mathrm{Py}]_n + 2n\mathrm{Fe(OTS)_2} + 2n\mathrm{H{-}(OTS)} \qquad (2)$$

$$n\mathrm{PyH_2} + 2n\mathrm{CuBr_2} \rightarrow [\mathrm{Py}]_n + 2n\mathrm{CuBr} + 2n\mathrm{HBr} \qquad (3)$$

$$n\mathrm{PyH_2} + 2n\mathrm{AgNO_3} \rightarrow [\mathrm{Py}]_n + 2n\mathrm{Ag} + 2n\mathrm{HNO_3} \qquad (4)$$

The dopants used were anion *para*-toluenesulphonic acid (pTSA), sodium anthraquinone-2-sulfonic acid (AQSA) and non-oxidizing transient tosylates ($Cu(OTS)_2$, $Ni(OTS)_2$, $Co(OTS)_2$, $Cr(OTS)_2$).

A summary of sample marking and polymeric bath composition is displayed in Table I. The textile substrate before and after modification by polypyrrole is displayed in Fig. 2.

Table I Summary of sample marking and polymeric bath composition

Sample	Pyrrole ml	$FeCl_3$ g	pTSA g	Spolion ml	Another g	Polymerization h
1	0.5	2.5	1.5	-	-	3
2	0.5	2.5	1.5	-	-	96
3	0.5	-	1.5		2.5 $AgNO_3$	96
4	1	5	3	-	-	96
5	1	5	-	-	4.9 AQSA	96
6	1	5	1.5	-	-	96
7	1	-	3	-	21.2 $Fe(OTS)_2$	96
8	0.5	-	2	-	11.2 $Fe(OTS)_2$	96
9	1	-	2	-	16.74 $CuBr_2$	96
10	1	5.44	3.5	15	-	96
11	1	5.44	1.5	3	-	96
12	1	5.44	1	1	5.18 $Cu(OTS)_2$	96
13	1	5.44	1	1	5.20 $Ni(OTS)_2$	96
14	1	5.44	1	1	5.52 $Co(OTS)_2$	96
15	1	5.44	1	1	6.89 $Cr(OTS)_2$	96

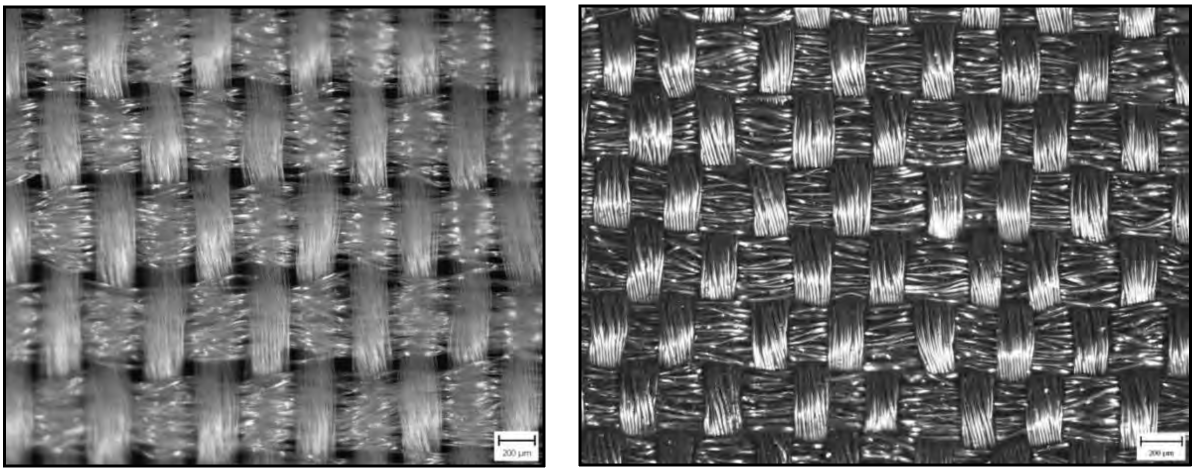


Fig. 2 Microscopic image of a) 100 % PET weave before modification, b) PET fabric/ polypyrrole composite

The characterization of conducting composite fabric was performed by evaluation of fixed PPY weight per unit area (m_{PPY}), testing surface (ρ_S) and volume resistivity (ρ_V), EMI shielding effectiveness (*SE*) by waveguide method and SEM techniques.

The volume and surface resistivity was measured according to the standard ČSN 34 1382, at the temperature of 22.3 °C and relative humidity $RH = 40.7$ %. The volume resistivity was measured by applying a voltage potential across opposite sides of the sample and measuring the resultant current through sample. The volume resistivity ρ_V [Ω cm] was calculated from the relation

$$\rho_V = R_V \frac{S}{h} \tag{5}$$

where R_V [Ω] is volume resistance reading, h is thickness of fabric [cm], S is surface area of electrodes [cm^2]. The surface resistivity was measured by applying a voltage potential between two electrodes of specified configuration that are in contact with the same side of a material under the test. The surface resistivity ρ_S [Ω] was calculated from the relation

$$\rho_S = R_S \frac{2\pi}{\ln \frac{R_2}{R_1}} \tag{6}$$

where R_S [Ω] is surface resistance reading, R_1 is outer radius of the center electrode [m], R_2 is inner radius of the outer ring electrode [m]. The mean values of ρ_S and ρ_V are listed in Table II.

The electromagnetic shielding was characterized by the attenuation of the electromagnetic field power density by using of a simple device. Basic parts of the device are two waveguides. One waveguide is connected with a receiving wire (antenna). The textile sample is placed on the entrance of the second waveguide. The end of this waveguide is filled with a foam saturated with carbon absorbing the electromagnetic field passed through sample. The sample is oriented perpendicularly to the electromagnetic waves. The transmitting antenna is placed in front of the first waveguide input. The used source of electromagnetic field was the ZigBee module working at the frequency of 2.4 GHz. The total shielding effectiveness *SE* [dB] was calculated from Eq. (7), where P_1 [W m^{-2}] is input power density and power P_2 is power density after passing through the sample. The mean values of *SE* are given in the next to last column of Table II.

$$SE = -10 \log \frac{P_2}{P_1} \tag{7}$$

Table II Mean values of surface and volume resistivity, electromagnetic shielding efficiency and weight of PPY fixed per unit area

Sample No.	ρ_S, Ω	ρ_V, Ω cm	*SE*, dB	m_{PPY}, mg dm^{-2}
untreated sample	1.23×10^{12}	4.89×10^{12}	0	0
1	2.65×10^{6}	1.11×10^{9}	1.60	-
2	5.18×10^{5}	1.05×10^{8}	5.65	-
3	1.22×10^{7}	1.59×10^{9}	1.07	-
4	1.52×10^{5}	2.37×10^{7}	17.73	219.90
5	2.61×10^{8}	5.75×10^{9}	1.46	-
6	6.91×10^{5}	2.04×10^{8}	14.57	-
7	3.24×10^{3}	1.29×10^{6}	18.17	196.70
8	5.10×10^{5}	1.22×10^{7}	13.37	115.10
9	2.58×10^{6}	1.84×10^{8}	0.07	33.80
10	2.27×10^{4}	7.15×10^{6}	11.40	324.20
11	7.93×10^{3}	4.24×10^{6}	21.28	466.90
12	2.56×10^{3}	6.69×10^{5}	20.26	209.20
13	3.50×10^{3}	7.56×10^{5}	19.45	170.70
14	1.97×10^{3}	6.99×10^{5}	19.02	178.50
15	3.33×10^{3}	8.12×10^{5}	18.28	167.60

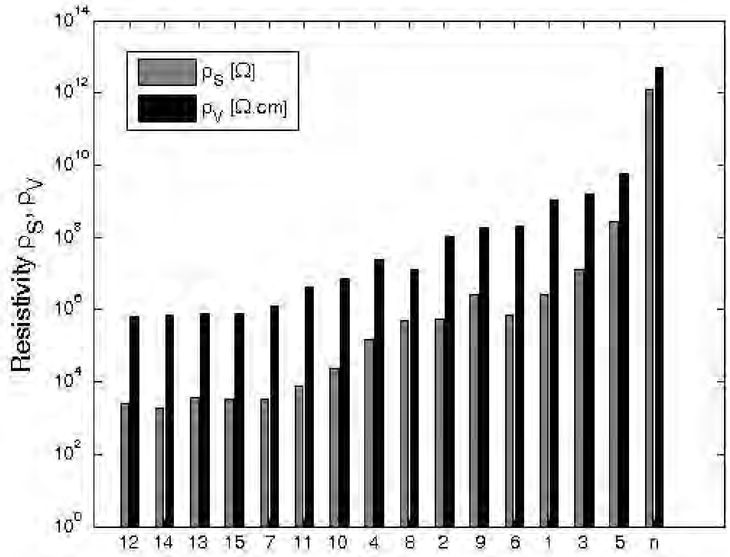


Fig. 3 Comparison of volume and surface resistivities of PET fabric/polypyrrole composites

Results and Discussion

Electrical Properties

From the point of view of the lowest values of electrical resistivities, the most suitable activator for polypyrrole seems to be *para*-toluenesulphonic acid (pTSA) together with chosen non-oxidizing transient tosylates, see samples no. 12, 14. In this case, electrical resistivities increased by about 7 and 9 orders for volume and surface resistivity, respectively, when compared with the untreated sample (marked with letter n). In both cases, the concentration of the monomer was 0.2 vol.%, and the oxidant was ferric chloride. We can generally say that a higher concentration of the monomer can improve electrical properties of the treated samples. The comparison of surface and volume resistivities of the prepared composite samples is displayed in Fig. 3.

Polymerization Time

Synthesis time can significantly affect the conductivity of the composite textile. In Fig. 4 we can see a dependence of natural logarithm of surface and volume resistivity on polymerization time (t) for samples no. 1 and 2. These samples were prepared according to the following recipe: the concentration of monomer 0.1 vol. %, oxidizing agent pTSA, $FeCl_3$ was used to create an acid medium. A composite sample gets a more intense black colour with an increasing polymeric time and decreases in surface and volume resistivities can be observed (see Fig. 3). The dependence of the individual resistivity can be approximated by the following formula

$$\rho = P_1 + (\rho_C - P_1)\exp(-P_2 t) \tag{8}$$

where: ρ is the volume or surface resistivity, P_1 and P_2 are constants, and ρ_C is the volume or surface resistivity of untreated sample. It was calculated: $P_1 = 51.8\times10^4$, $P_2 = 4.88$ for surface resistivity. $P_1 = 1.05\times10^8$, $P_2 = 2.37$ is valid for the dependence of the volume resistivity on polymerization time.

Study of Oxidation Reduction Potential During Polymerization

In situ polymerization consists of adsorption of monomer on the surface of the substrate and consequent oxidation polymerization process with a suitable oxidizing agent. The oxidizer is referred to as chemical compounds that readily transfer oxygen atoms or a substance that gains electrons in a redox chemical reaction. The oxidizing agent is “reduced” by taking electrons on itself and the

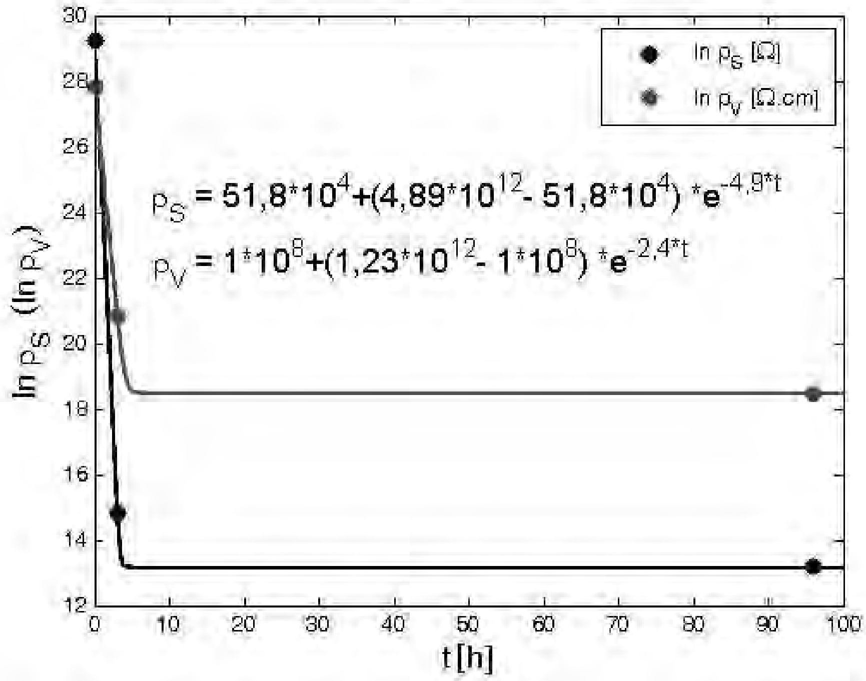


Fig. 4 Dependence of natural logarithm of surface and volume resistivity on polymerization time for samples no. 1 and 2

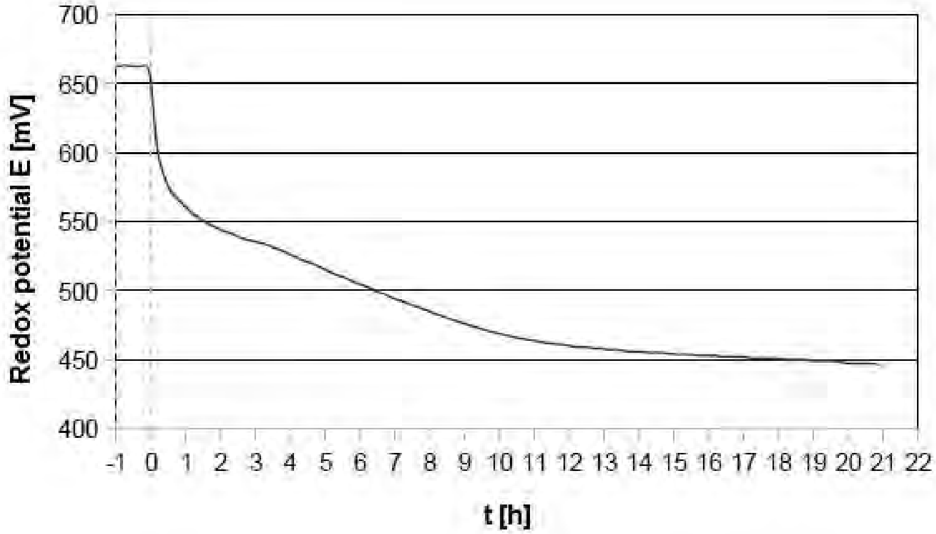


Fig. 5 Dependence of redox potential on polymerization time

reactant is “oxidized” by having its electrons taken away. These redox changes during polymerization can be observed. The basic bath (5.44 g $FeCl_3$ and 3 g pTSA dissolved in 500 ml water) was prepared for this experiment. The measurement of redox potential proceeded 21 hours at the temperature of 4 °C. In Fig. 5 we can see a dependence of redox potential on polymerization time. The highest redox potential (ORP) 663 mV was measured in the freshly prepared polymerization bath before addition of pyrrole. A fast exponential drop of ORP came after the addition of monomer. A strong decrease in redox potential can be observed during the first stage of polymerization, which in this case lasted about one hour.

Electromagnetic Shielding Efficiency

From the point of view of obtaining the highest electromagnetic shielding, the use of *para*-toluenesulphonic acid (pTSA) for activating polypyrrole seems to be optimal. With the application of this procedure, the electromagnetic shielding effectiveness of samples gets over about 20 dB, which is in agreement with requirements for electromagnetic shielding textiles [12]. In this case, the concentration of the monomer was 0.2 vol. %, and ferric chloride was used as the oxidant. We can generally say that a higher concentration of the monomer can improve electromagnetic shielding ability of the treated samples. The comparison of shielding effectiveness of PET fabric/polypyrrole composites is shown in Fig. 6.

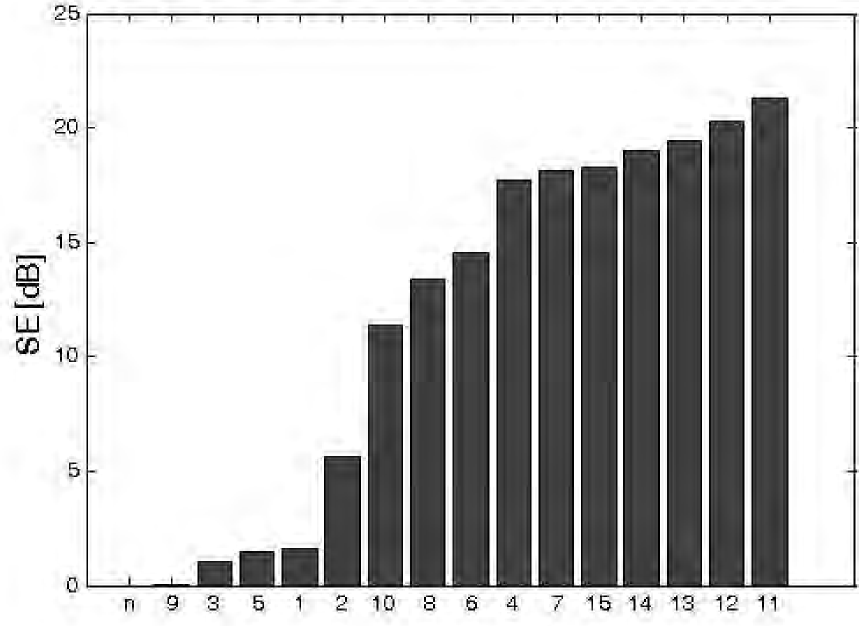


Fig. 6 Comparison of shielding effectiveness of PET fabric/polypyrrole composites

Quantity of Polypyrrole Fixed on Textile Substrate

The quality and quantity of conductive polymeric layer have essential effect on electromagnetic shielding of the composite. A relationship between fixed PPy weight per unit area and electromagnetic shielding efficiency and/or electric properties (Fig. 7) was observed. It is clear that electromagnetic shielding is increasing with an increasing quantity of PPy fixed on the textile substrate. At the same time, electric resistivity is decreasing and/or electric conductivity is increasing is with an increasing amount of PPy on textile.

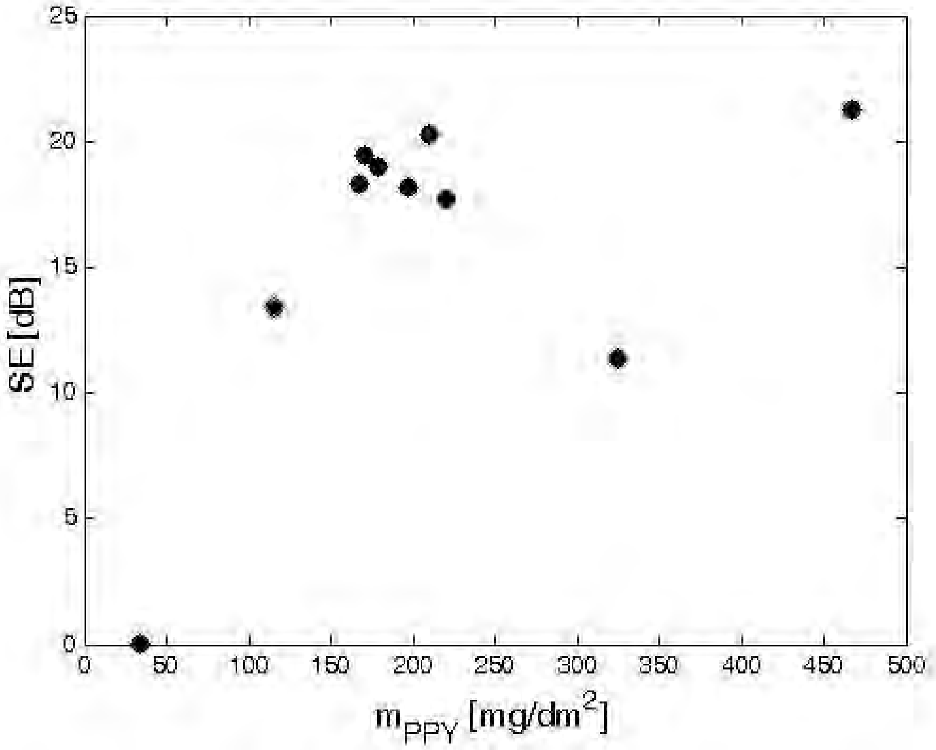


Fig. 7 Dependence of shielding effectiveness on PPY weight per unit area

Correlation Between Volume and Surface Resistivity

The correlation between volume and surface resistivity of the treated samples is shown in Fig. 8. When comparing the volume and surface resistivity, we can say that surface resistivity is always about 2.5 orders of magnitude lower than volume resistivity. This effect can be caused by a more dense presence of PPy on the surface of the sample. The approximate linearity is visible. The solid lines in this graph correspond to the linear model with the parameters obtained by minimizing the sum of squared differences.

Correlation Between Electric Resistance and Electromagnetic Shielding

The dependence of the total shielding effectiveness *SE* on logarithms of surface resistivity ln (ρ_S) and volume resistivity ln (ρ_V) of the modified samples is shown in Figs 9a and 9b. It is clear that electromagnetic shielding increases with an increasing electric conductivity and/or decreasing electric resistivity of PET/polypyrrole composites.

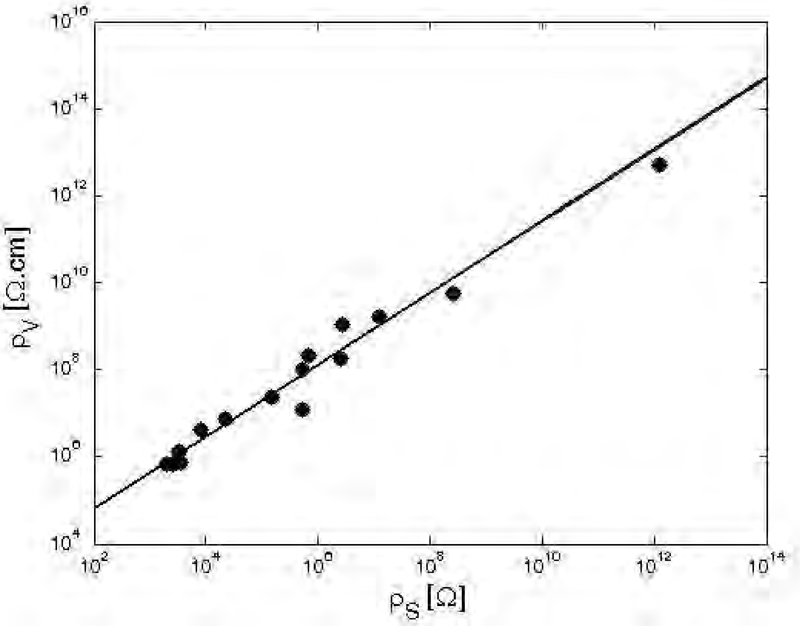
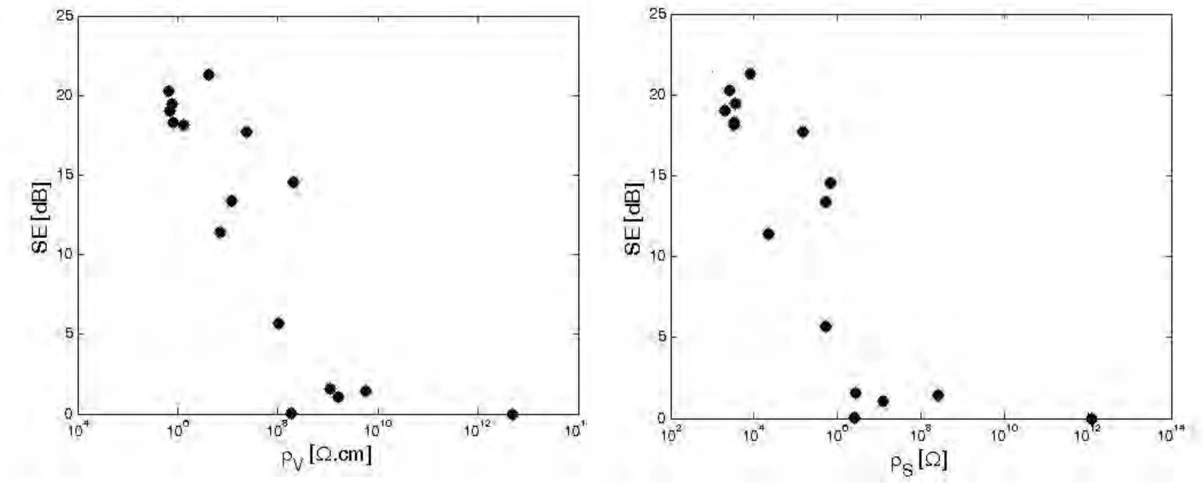


Fig. 8 Correlation between volume and surface resistivity of treated samples

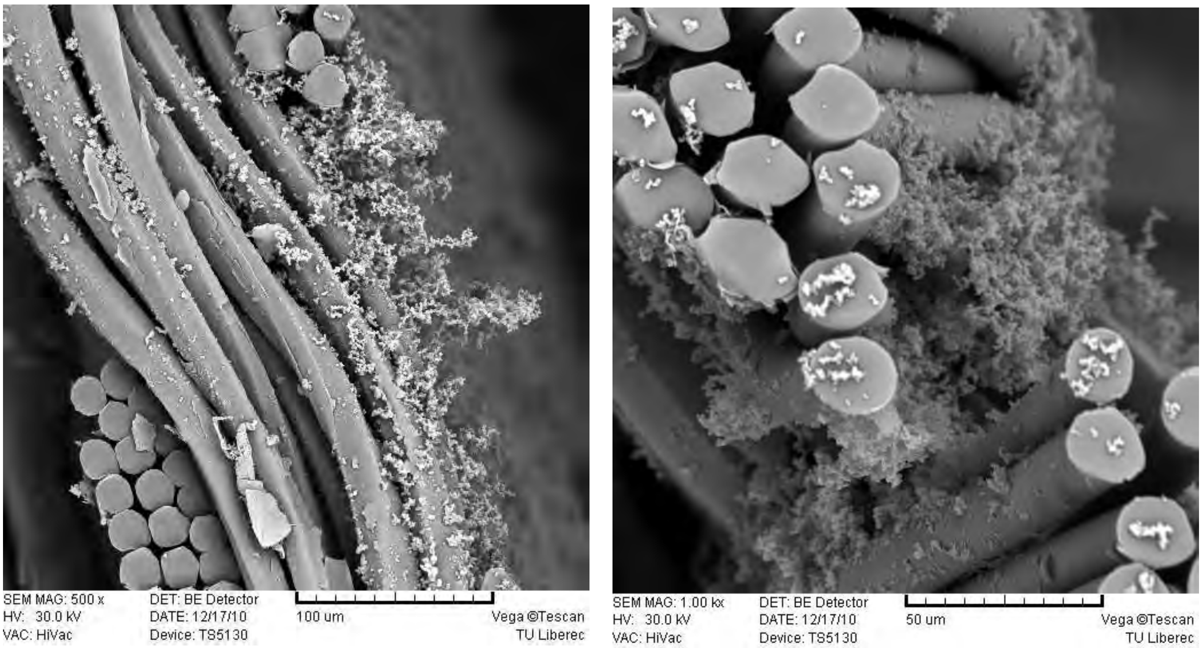


a) b)

Fig. 9 Dependence of electromagnetic shielding efficiency on a) volume resistivity, b) surface resistivity of PET fabric/ polypyrrole composite

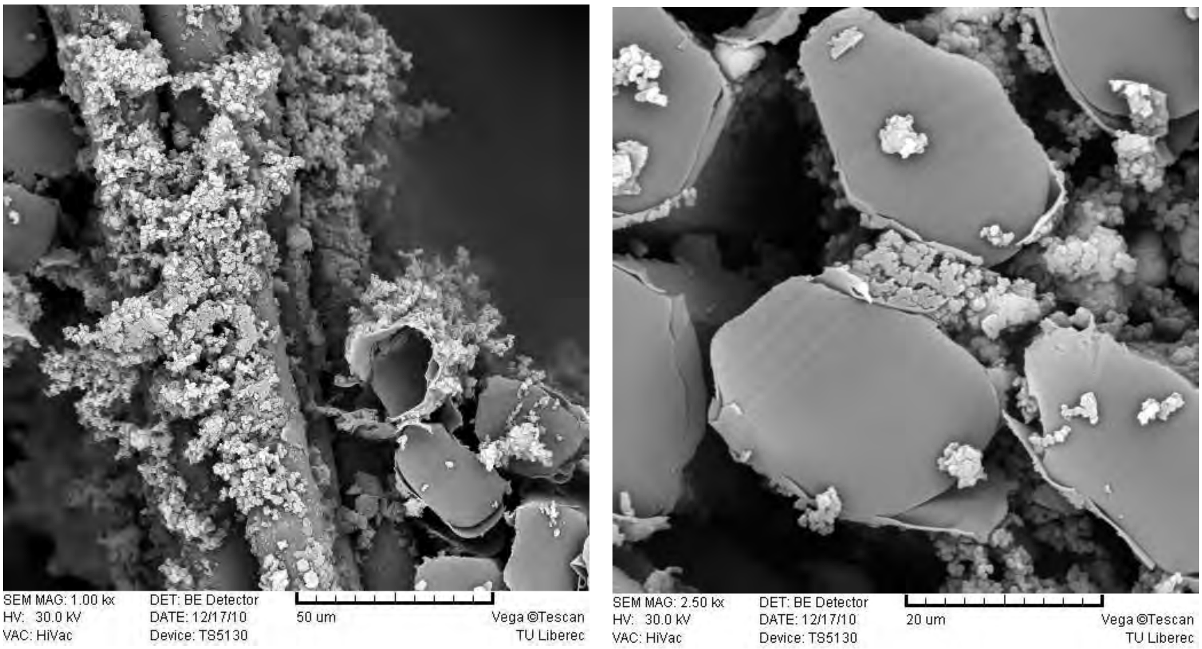
Analysis of Fabricated Conductive Layer by SEM

It is clear from the microscopic images (Figs 10 and 11) that the continuous polypyrrole layer was created on the PET fibers. We can observe from the cross section images that this layer adheres to the PET fibers by only weak forces and rips off in some places.



a) b)

Fig. 10 Microscopic image of PET fabric / polypyrrole composite zoomed a) 500×, b) 1000×



a) b)

Fig. 11 Microscopic image of PET fabric / polypyrrole composite zoomed a) 1000×, b) 2500×

It was found that addition of surfactant (Spolion) can strengthen the doping process. From this point of view, the best results seem to be achieved in samples no. 12-15 where Spolion enhanced the function of dopants used in this experiment. In this case, 1 ml Spolion solution (50 g l^{-1}) in 500 ml polymeric bath was used.

Conclusion

The electrically conductive samples with electromagnetic shielding ability were created by modifying the nonconductive textile substrate by means of conductive polymer. The most suitable medium, from the point of view of the lowest electrical volume and surface resistivity, the highest electromagnetic shielding efficiency and the highest resultant PPy content of composite fabric, was observed to be aqueous ferric chloride solution with pTSA, non-oxidizing transient tosylates ($Cu(OTS)_2$, $Ni(OTS)_2$, $Co(OTS)_2$, $Cr(OTS)_2$) and the pyrrole concentrations about 0.2 vol. %.

Acknowledgement

This work was supported by the research project TIP – MPO VaV 2009 "Electromagnetic field protective textiles with improved comfort" of the Czech Ministry of Industry and student project 2012 "Effect of porosity on electromagnetic shielding effectiveness of textile structures" of Technical university of Liberec.

References

[1] Perumalraj R., Dasaradan B. S.: Fibers Text. East. Eur. **18**, 74 (2010).
[2] Šafářová V., Militký J.: AUTEX 2011 Book of Proceedings, 1123 (2011).
[3] The Nobel Prize in Chemistry, 2000: Conductive polymers [online]. c2009 [cit. 2012-8-26]. Available from WWW: <http://nobelprize.org/nobel_prizes /chemistry/ laureates/2000/chemadv.pdf>.
[4] Kiess H.: *Conjugated Conducting Polymers*, Springer-Verlag, Berlin, 1992.
[5] Wan M.: *Conducting Polymers with Micro or Nanometer Structure*, Springer, Berlin Heidelberg, Berlin, 2008.
[6] Heisy C.L., Wightman P., Pitman E.H., Kuhn, H.H.: Text. Res. J. **63**, 247 (1993).
[7] Chandran A.S, Narayanakutty S. K.: J. Mater. Res. **24**, 2728 (2009).
[8] Xue P., Tao X.M., Kwok K.W.Y., Leung M.Y., Yu T.X.: Text. Res. J. **74**,

929 (2004).
[9] Wang L.J., Lin T., Wang X.G., Kaynak A.: Fibers Polym. **6**, 259 (2005).
[10] Najar S.S., Kaynak A., Foitzik, R.C.: Synthetic Met. **157**, 1 (2007).
[11] Kaynak A., Najar S.S, Foitzik, R.C. Synthetic Met. **158**, 1 (2008).
[12] Committee for Conformity Assessment on Accreditation and Certification of Functional and Technical Textiles [online]. 01.08.2010 [cit. 2012-09-14]. Specified Requirements of Electromagnetic Shielding Textiles. Available from WWW: <http://www.ftts.org.tw/images/fa003E.pdf>