TECHNICKÁ UNIVERZITA V LIBERCI

FAKULTA TEXTILNÍ

Ing. Abdul Malik Rehan Abbasi

In-situ polymerization of pyrrole on textile substrates and characterization of their applications

AUTOREFERÁT DISERTAČNÍ PRÁCE

Název disertační práce:	**IN-SITU POLYMERIZATION OF PYRROLE ON TEXTILE SUBSTRATES AND CHARACTERIZATION OF THEIR APPLICATIONS**
Autor:	**Ing. Abdul Malik Rehan Abbasi**
Obor doktorského studia:	textilní materiálové inženýrství
Forma studia:	prezenční
Školící pracoviště:	Katedra materiálového inženýrství
Školitel:	Prof. Ing. Jiří Militký, CSc.
Školitel specialista:	

Liberec 2013

1. Objectives of the work

1.1 Characterization of EMI shielding effectiveness of PPy coated glass fabric

One of the aims of the dissertation is to develop electromagnetic interference (EMI) shield with the help of polypyrrole (PPy) coated E-glass fibre fabric through improved resistance to electromagnetic radiations while maintaining the essential characteristics imposed on textiles used in the textile industry at very low cost.

1.2 Investigation of heat generated by PPy coated glass fabric

The conversion of electricity to heat has always attracted a great attention because of applications in heaters and thermoelectric power generators. Objective is to study the amount of heat generated and dissipated to the air through convection from PPy coated glass fabric under electric field.

1.3 Study of electrothermal effect in PPy coated glass fabric

The electrons are promoted across the band gap into the conduction band by obtaining promotional energy from thermal energy. Then both this electron and the hole in the valence band can contribute to net charge flow. One of the objectives of the work is to study thermal dependence of resistance of PPy coated glass fabric in the temperature range around Tg of PPy.

1.4 Development and characterization of strain sensor

The objective is also to develop an inexpensive strain sensor based on PPy coated Latex/PA6 stretchable yarn for monitoring human body movements at very low deformations such as breathing.

2. Overview of current state of problem

Typically, metals have been used for EMI shielding and heat generating [1, 2] materials, as they have a high conductivity and dielectric constants. However, metals have disadvantages, such as their weight, corrosion properties, and poor processibility [3]. Electrically conductive polymers can be used as EMI shielding materials to avoid the disadvantages seen in metals [4,5]. Conductive polymers are insoluble and infusible, which restricts its fabrication, and it has poor mechanical properties [6]. One of the ways to avoid these problems is to prepare an electrically conductive textile composite, since these have the resiliency of a textile and excellent mechanical strength and flexibility, but also retain the electrical properties of the conductive polymer [7-10].

To prepare conductive composite fabrics, many researchers have focused on chemical oxidative polymerization and electrochemical polymerization of pyrrole in the presence of a nonconductive matrix, such as PA6 fabric, [8-11] nonwoven fabric, [12] and acryl fabric [13]. Also, using the microwave absorbance characteristics of conductive polymers, Contex®, which is chemically synthesized on PET fabric, was used as camouflage netting by the Milliken Co. [14]. However, its application to industrial scale is limited, since the substrates or matrices used have inadequate tensile strength and stability to environmental factors. This research focused on a new PPy–fabric composite with a high electrical conductivity and a high EMI shielding efficiency (EMSE).

A number of researchers and scientists have worked on Joule heating effect of PPy coated textile substrates but their development is limited to apparel and clothing application for winter garments while very limited work has been done on coating of conducting polymer on industrial fibre such as glass fibre. In this work investigation of heat generation by applying electrical field to the composite fabric was conducted.

The work has been done on the investigation of change in resistance upon the rise in temperature from absolute zero temperature to the room temperature but this work focuses on thermal dependence of the resistance of PPy coated glass fabric around the Tg of the PPy.

Electrically conducting polymer films can only withstand limited strain before breaking and cannot perform well in evaluating large strains [15]. To overcome this problem, substrates were employed to provide the necessary support and the surface for conducting polymer film deposition. Generally, fabricating a strain sensor using this approach means that the mechanical properties are highly attributed to the substrate while the conducting polymer introduces the electrical conductivity. This practice is commonly found in the research field of smart textiles which are conductive fabrics produced by coating conducting polymers onto commercial fabrics such as nylon, polyester and Lycra [16-19]. Although excellent results have been demonstrated with smart textiles using conducting polymers, the intended applications are mainly aimed at enhancing the usability of fabric beyond its current use as a protective layer. As a general purpose strain sensor, the substrate requires having some degree of rigidity and fabrics are not an ideal material due to its soft structure. Furthermore, repetitive strain can cause permanent elongation on individual fibres where the strain may not be distributed equally. This can lead to individual fibres having different mechanical properties that will affect the strain sensing performance. The proposed solution is to replace fabric with Latex/PA6 stretchable yarn, which has good combination of rigidity and elasticity. One of the studies has succeeded in fabricating a strain sensor using PPy and natural rubber substrate where PPy powder is embedded into the structure of the rubber directly [20]. Compared to the coating methods, that approach requires knowledge of rubber manufacture as well as an access to the equipment to produce rubber with consistent mechanical properties.

This work is aimed at developing a low cost, small to large strain sensor using PPy and Latex/PA6. This stretchable yarn was chosen as a substrate due to its excellent resilience and elasticity. Commercial SY strip was purchased and used to produce the strain sensor. PPy as thin film was coated onto the SY substrate by means of vapour phase polymerisation (VPP) technique that provides a good adhesion between the two components of the strain sensing element.

3. Experimental methods

3.1 Materials

For the investigation of EMI shielding effectiveness of PPy coated glass fabric, samples of two different densities is chosen. One has 410g.m^{-2} and broken twill construction is designated as “Structure 1” in the dissertation whereas other has 900g.m^{-2} and plain weave designated as “Structure 2”. For the investigation of heat generation Structure 2 and electrothermal effect Structure 1 is used.

For the development of strain sensor Latex/PA6 stretchable yarn is chosen having 42:58 PA6 and Elastodiene ratio respectively. The diameter of the latex is 0.6mm and (22x3) tex PA6 fibres are wrapped on latex. The effective diameter of the whole diameter is 0.68mm.

3.2 Sample preparation

The glass fabric sample was coated by PPy by vapour deposition technique. In order to achieve it, specimens were first washed with acetone. After drying sample was dipped in the aqueous solution of Iron (III) Chloride and tosylate (TsO$^-$) at 20°C for 1 min and squeezed at 70% pickup. Different concentration of oxidant and dopant were prepared as mentioned in

Table 1 for investigating the influence of these reagents on different characteristics of PPy coated substrates. It was then immediately exposed to the vapours of pyrrole monomer at room temperature and atmospheric pressure for 6 h. Specimen was then washed with ethanol in order to stop polymerization and subsequently with plenty of distilled water for several times to remove bi-products and un reacted monomer.

Table 1: Recipes for the preparation of PPy coated glass fabric specimens

Structure 1	**Structure 2**	**$FeCl_3$ [mol/L]**	**TsO^- [mol/L]**
T1	D1	0.3	0.15
T2	D2	0.4	0.2
T3	D3	0.5	0.25
T4	D4	0.6	0.3

Table 2: Recipes for developing strain sensor based on latex/PA6 stretchable yarn (SY)

Latex/PA6 specimen label	**$FeCl_3$ [mol/L]**	**TsO^- [mol/L]**
SY1	2.0	1.0
SY2	0.6	0.3
SY3	0.1	0.05

With the aim of coating PPy on SY, pre-treatment with acetone was not carried out in order to preserve the resilience and elastic properties of the latex. The rest of the method for preparing the samples was same as described above. Different samples were prepared by varying concentration of oxidant and dopant in order to coat polypyrrole on the substrates as tabulated in Table 2

3.3 Characterization of samples

For evaluation of electrical properties of fabrics, two parameters were selected, namely the surface and volume resistivity. These parameters can be calculated from the information of surface and bulk resistivity, the dimensions of the electrodes, and/or the thickness of the sample. For this purpose, concentric electrode system was used conforming to DIN EN 1149-1, EN 100 015, EN 61340-5-1 together with Agilent 53131A digital multimeter. Measurements of electrical resistance were performed in the climatic conditions, *temperature* = (20 ± 2) °C and *Relative humidity* = (40 ± 2) % which is in accordance with the standard ČSN 80 0059.

For measuring EMSE, specimen holder EM-2107A from Electro-metrics® USA along with ZNC3-Vector Network Analyser from Rohde & Schwarz® GmbH & Co. Germany, were used. The fixture is an enlarged section of coaxial transmission line and complies fully with the requirements of ASTM test method D4935-1.

The thickness of polypyrrole coating on glass fibers was characterized by Scanning Electron Microscope (SEM) Carl Zeiss® Ultra plus, Confocal Laser Scanning Microscope Olympus® Japan and optical microscope Carl Zeiss AXIO Imager M2.

For the purpose of evaluating heat generation by polypyrrole coated glass fabric samples 5V, 10V, 15V and 20V DC electromotive force by DC voltage supplier NZ-2229.2 from Statron® Czech Republic, were applied via stainless steel clamp type electrodes. Meanwhile DC current passing through substrate was measured by connecting Agilent 53131A digital multimeter in series. The rise in temperature was determined by Infra-Red thermal camera by

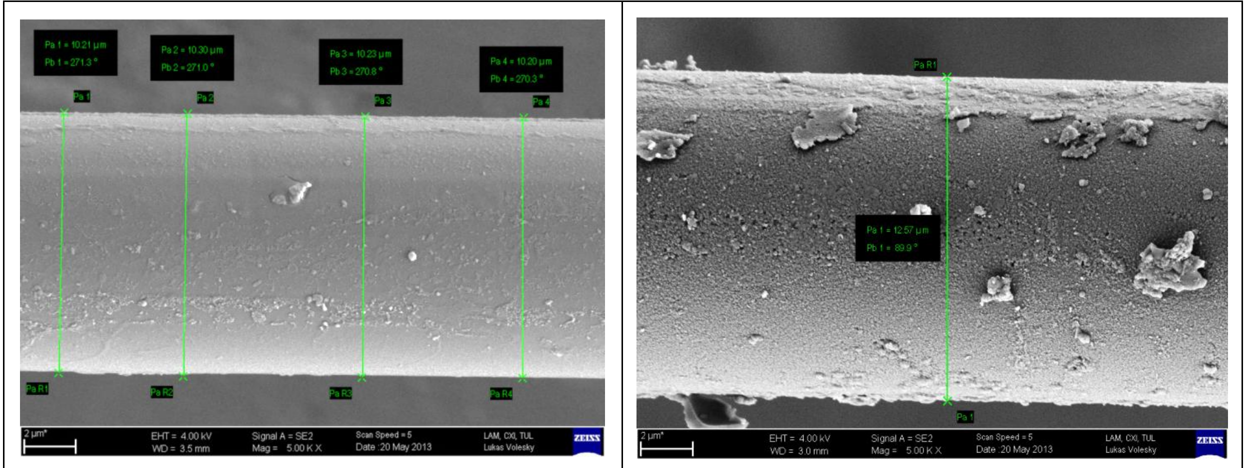
Fluke® together with k-type thermo couples in connection with ART® data acquisition module. Infra-Red thermal camera was helpful to figure the homogeneity of the specimen out.

With the intention of investigating electrothermal feedback in PPy coated glass fabric, specimen was placed between two stainless steel clamp type connector and then in MMM laboratory oven Venticell® at 30, 60, 90, 120 and 150°C for approx. 5 h and change in electrical resistance was measured through Agilent® 53131A digital multimeter.

With the objective of characterizing sensitivity of strain sensor based on PPy coated SY under cyclic loading, substrate was subjected to tensile testing machine Labtest from LaborTech® Ltd Czech Republic. The cycle was set for 2% strain at 100mm/min with rest of 1 second at relaxed position to simulate normal human breathing rhythm. One set of measurement includes 40 cycles, therefore in this way 5 sets of readings were recorded and compiled.

4. Results and discussion

The formation of the PPy coating on the textile substrate starts from deposited oligomers, which form islands in the initial stage and finally grow and cover the surface of the substrate completely. The surface morphology of the E-glass fibre coated with PPy was analysed by Scanning Electron Microscope (SEM) Carl Zeiss® Ultra plus after gold coating. The average thickness of coating of PPy on E-glass fibre was measured as 1.165±0.052μm as shown in Figure 1. It can also be perceived that through vapour deposition technique PPy covers each individual fibre in the fabric very well



(a)

(b)

Figure 1: SEM micrographs (a) E-glass control (b) E-glass coated with PPy

4.1 Dependence of resistivity on doping concentration

There is linear decrease in surface ρ_s as well as volume resistivity ρ_v of the specimens was observed in case of structure 1 as shown in Figure 2 and these expressions can be written as Equation 1 and 2 having R^2= 0.9936 and 0.9985 respectively.

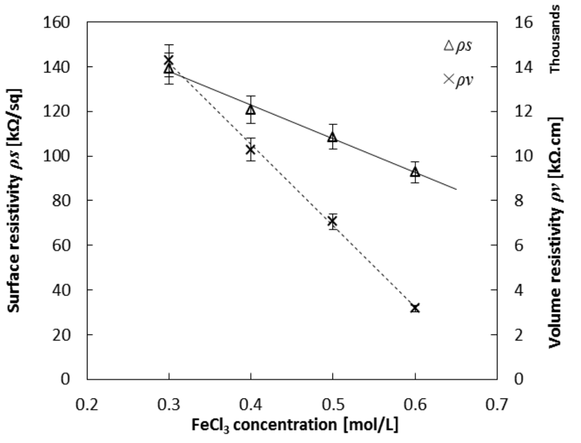
$$\rho_s = -151.53 \cdot C + 183.54 \quad (1)$$

$$\rho_v = -36529 \cdot C + 25136 \quad (2)$$

Here, C is the concentration of $FeCl_3$ in [mol/L]. By taking structure 2 into account the decrease in resistivity follow power function of concentration of $FeCl_3$ as presented in Figure 3 that can written as Equation 3 and 4 with R^2=0.993 and 0.927 respectively;

$$\rho_s = 0.32 \cdot C^{-1.893} \quad (3)$$

$$\rho_v = 4.32 \cdot C^{-3.718} \quad (4)$$



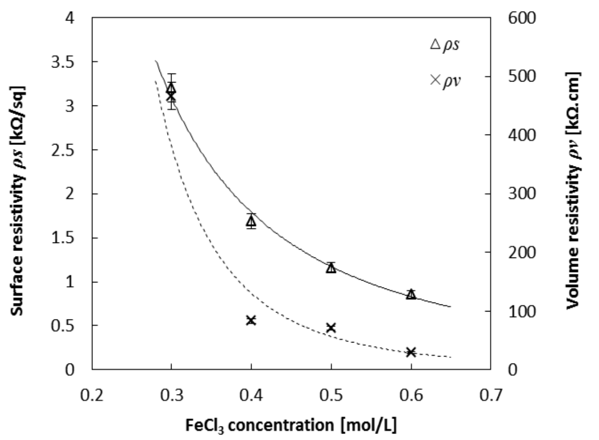


Figure 2: Dependence of resistivity of PPy coated glass fabric of structure 1 on concentration of FeCl$_3$

Figure 3: Dependence of resistivity of PPy coated glass fabric structure 2 on concentration of FeCl$_3$

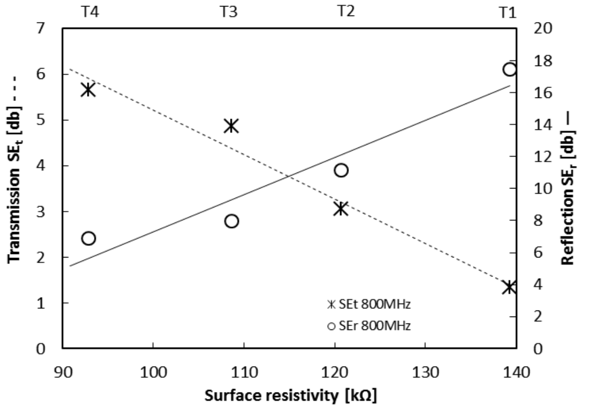
5.2 EMSE of PPy coated glass fabric

The dependence of EMSE for transmission SE_t and reflection SE_r of glass fabric on the concentration of oxidizing and doping agent was investigated that can be seen in Figures 4 and 5. The EMSE for transmission improves by increasing PPy concentration which ultimately decrease electrical resistivity, at the same time performance against reflection of EMR was also observed to be enhanced. In glass fabric structure 1 (light) the dependence of EMSE for both transmission and reflection is found to be a linear function to resistivity whereas EMSE follows power function when plotted against resistivity in case of structure 2 (heavy) glass fabric samples which is clear from the Figure 5.

The relationship between EMSE and surface resistivity of structure 1 (light) for transmission and reflection can be expressed as Equation (5) and (6) with R^2=0.97 and 0.92 respectively.

$$SE_t = -0.0971 \cdot \rho_s + 14.92 \tag{5}$$

$$SE_r = 0.23 \cdot \rho_s - 15.96 \tag{6}$$



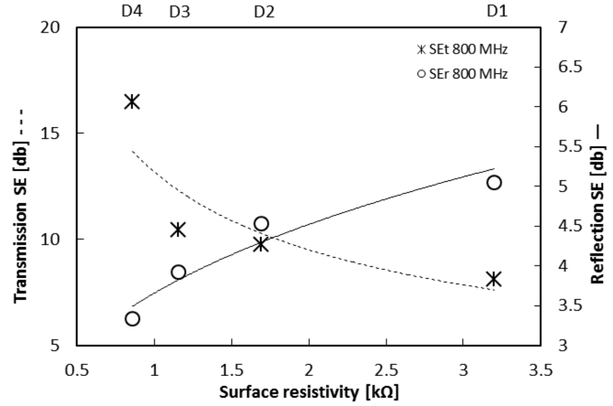


Figure 4: Dependence of SE_t and SE_r on surface resistivity of PPy coated glass fabric sample of structure 1

Figure 5: Dependence of SE_t and SE_r on surface resistivity of PPy coated glass fabric sample of structure 2

Similarly the relationship between EMSE and surface resistivity of structure 2 (heavy) for transmission and reflection can be expressed as Equation (7) and (8) with R^2=0.79 and 0.93 respectively.

$$SE_t = 13.18 \cdot \rho_s^{-0.472} \tag{7}$$

$$SE_r = 3.66 \cdot \rho_s^{0.306} \tag{8}$$

And it can be used as grade 3 (good) for general use or grade 1 (fair) for professional use [21].

5.3 Heat generation by PPy coated glass fabric

Sharp increase in temperature was observed in first 3 min which was then stabilized after reaching to maximum temperature as shown in Figure 6. Power density (volume specific power) is the amount of power (time rate of energy transfer) per unit volume. It is then also called volume power density which is expressed as [W/m^3]. Volume power density is sometimes an important consideration where space is constrained. In this study power density P_D is extremely linear function of voltage supplied to the PPy coated glass fabric as illustrated in Figure 7 and expressed in Equation 9.

$$P_D = 82.58V - 245.83 \tag{9}$$

However, temperature rise in fabric sample at equilibrium (after 3 min) follow exponential function of voltage with coefficient of determination R^2= 0.9717 that can be written as;

$$T = T_0 e^{0.0795V} \tag{10}$$

Here, T is the temperature in [°C] measured at equilibrium at applied DC V and T_o is the temperature of fabric at ambient conditions, which in this study was 22.3°C.

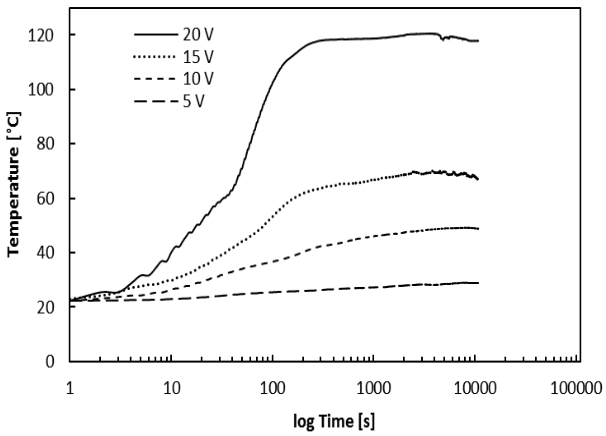


Figure 6: Escalation of temperature of PPy coated glass fabric specimen D4 with increase in time and different DC voltage *V*

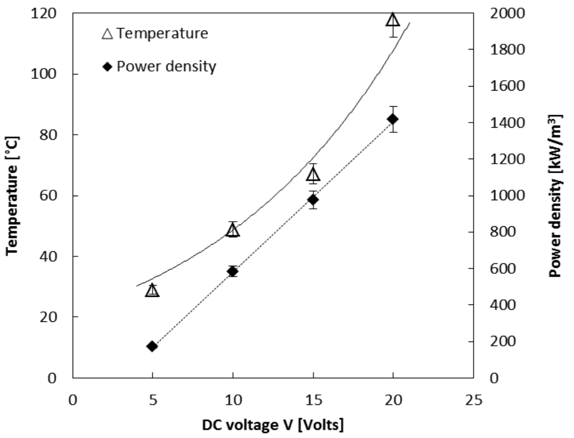


Figure 7: Rise in power density and temperature of sample D4 as a function of DC voltage.

By calculating dimensionless numbers Reynolds Number Re = 9.1·103, Prandtl Number Pr = 0.683, Nusselt Number Nu = 55.8 and Heat Transfer Coefficient h = 23.3 W.m^{-2}K^{-1} from some known parameters, heat transfer to air by convection was determined. The relationship between heat generated $\left(\dot{E}_{gen,element}\right)$ by the PPy coated glass fabric and heat transfer to air $\left(\dot{Q}\right)$ can be written as follows;

$$\dot{Q} = 0.8559 \cdot \left(\dot{E}_{gen,element}\right)^{0.8638} \tag{11}$$

That shows heat generated at low voltages is transferred approximately all to the air through convection but thermal energy generated due to comparatively high voltage transfer partial energy to the air.

5.4 Electrothermal effect in PPy coated sample

With the help of thermo couple it was found that sample attains the temperature of preheated oven in 180s therefore data were collected after each second from **180s to 12600s**. By using surface response method of analysis, a model is proposed to estimate the approximate change in resistance due to change in temperature at different time intervals as mentioned in Table 9 and surface plot is presented in Figure 8.

Table 3 Estimates of the regression coefficients

Effect	Coefficient	Standard Error	t-value	p-value
CONSTANT	0.841	0.169	4.971	0.000
T	2.010	0.150	13.388	0.000
t	1.170	0.140	8.353	0.000
*T*T*	1.908	0.223	8.544	0.000
*t*t*	0.385	0.266	1.446	0.150
*T*t*	2.605	0.214	12.162	0.000

Coefficient of multiple determinations R^2= 0.858, Squared Multiple R= 0.737, Adjusted Squared Multiple R= 0.728, Residual Standard Deviation= 1.117

It is clear from the Figure 8 that resistance of PPy coated fabric sample decreases with the increase in temperature till 80°C beyond which slight increase in resistance can be observed. The Tg of PPy was found to be 76.1°C by DSC analysis which is very near to this temperature. Above Tg significant increase in resistance was recorded which increases continuously with the passage of time.

As the loss in conductivity of PPy is permanent above Tg, Kaynak [22] explained the fact in terms of permanent degradation or damage of polymer structure upon heating and this degradation becomes more pronounced with the increase in temperature.

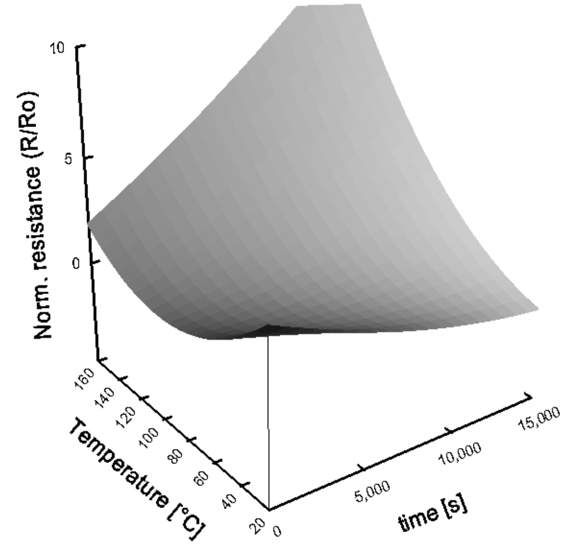


Figure 8: Surface plot of thermal influence of temperature and time on resistance of sample (T4)

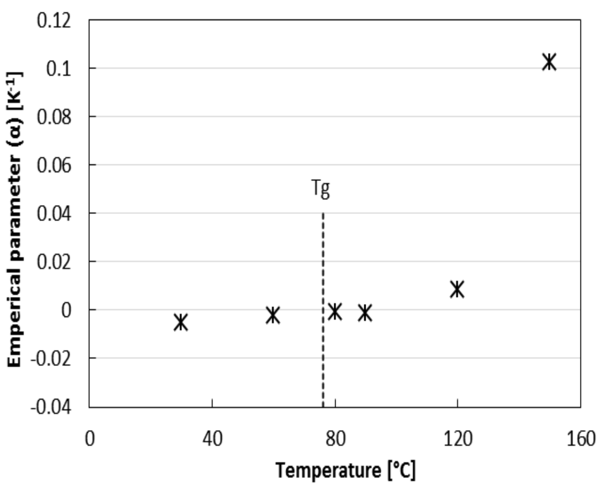


Figure 9: The dependence of empirical parameter α on the temperature of sample (T4)

The electrical resistivity ρ of most materials changes with temperature T. If the temperature T does not vary too much, a linear approximation is typically used:

$$\rho = \rho_0 \left[1 + \alpha (T - T_0)\right] \tag{47}$$

Here, α is called the temperature coefficient of resistivity in [K^{-1}], T_o is a fixed reference temperature in [K] (usually room temperature) and ρ_o is the resistivity at temperature T_o. Negative values of α shown in Figure 9 the typical behaviour of semiconductors whereas the positive temperature coefficient (PTC) after crossing Tg refers to the material that experiences an increase in electrical resistance with increase in their temperature such as conductors [23].

5.5 Characterization of PPy coated Latex/PA6 yarn

5.5.1 Linear dependence of resistance on length

It was found that resistance of PPy coated Latex/PA6 stretchable yarn is a linearly increasing function of the distance between the electrodes holding the yarn as shown in Figure 10 and this relationship can be expressed as;

$$R = ZD + r \tag{49}$$

where, R is the resistance [kΩ] of PPy coated Latex/PA6 yarn sample, D the distance between measuring electrodes and r the resistance of the electrodes found to be 0.0001kΩ approx. in this work. However the slope Z is the directly proportional to the resistivity ρ in [kΩ.cm] of the PPy coated Latex/PA6 yarn samples as shown in the Figure 11 for this experiment and can be calculated as;

$$Z = 275.63 \cdot \rho - 0.0769 \tag{50}$$

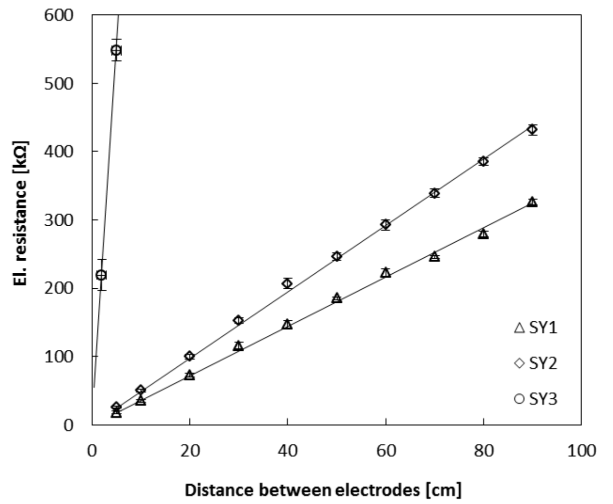


Figure 10: Dependence of electrical resistance of PPy coated Latex/PA6 yarn samples on length

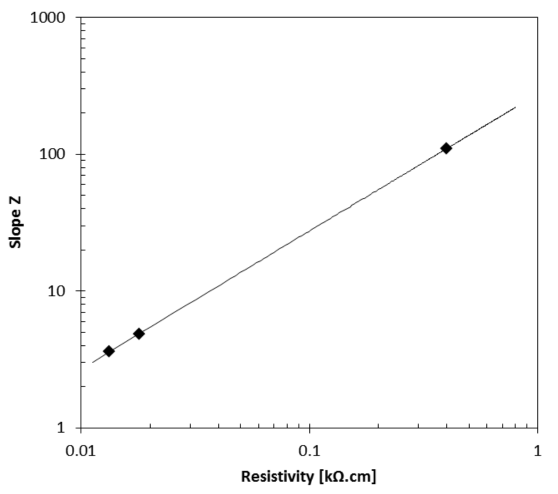


Figure 11: Relationship between slope Z and resistivity of the samples

5.5.2 Sensitivity of strain sensor against cyclic loading

The response of resistance of the samples on 2% deformation and relaxation during 40 cycles are plotted in Figure 12. it can be observed that SY1 gives almost equal response dR against deformation in terms of magnitude but this response is not consistent with the number of cycles. The SY2 gives neither an equal response against deformation (decreases with number of cycles) nor the consistency of the response. Whereas SY3 is the best among all the samples and it gives not only an equal response upon deformation but also the level of consistency of the response after each cycle is outstanding.

The average response in terms of change in resistance against deformation has been calculated from 40 cycles and named as sensitivity $\left(dR/_{d\varepsilon}\right)$ of each sample. The sensitivity levels of all PPy coated Latex/PA6 samples are shown in Figure 13.

Although SY3 has the highest resistivity among all three samples under study, however it outperformed SY1 and SY2 in terms of response against small extension. The sample SY2 has been found as the worst in terms of sensitivity and its deviation in the results. The standard deviations of the specimens were calculated as 0.182, 0.315 and 4.49 [kΩ.cm] for SY1, SY2 and SY3 respectively.

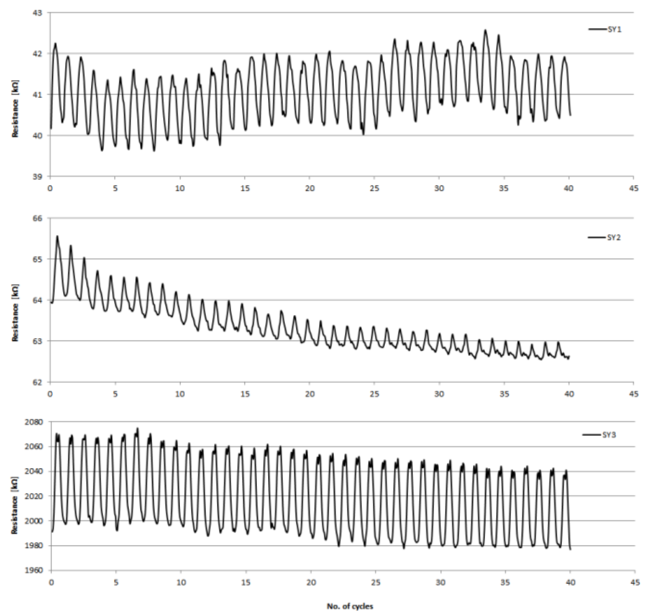


Figure 12: Response of PPy coated Latex/PA6 samples at 2% deformation for 40 cycles

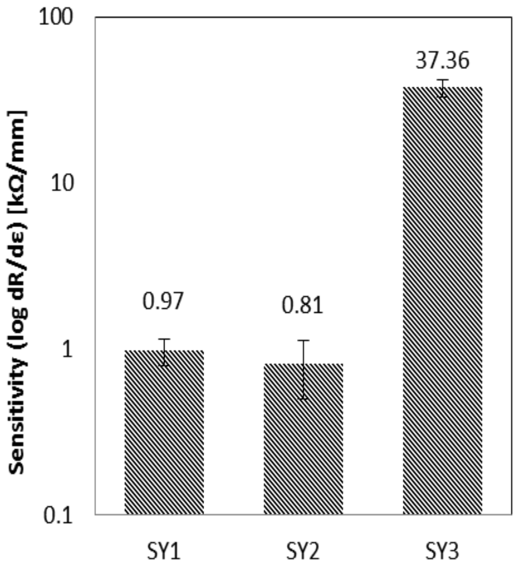


Figure 13: Dependence of sensitivity of the strain sensor on longitudinal deformation

5.5.3 Mechanical properties

During cyclic loading of PPy coated Latex/PA6 yarn samples, change in mechanical behaviour was also studied and average force-elongation curve, during 40 cycles of elongation and relaxation is plotted as shown in the Figure 14. It can be observed that SY1 and SY2 were affected most due to the presence of more quantity of PPy on the surface of each individual fibre. Whereas SY3 was found to be least affected and hence kept the resilience of original yarn. A tangent was drawn on the initial linear portion of the average curves and initial modulus was calculated as shown in Figure 15.

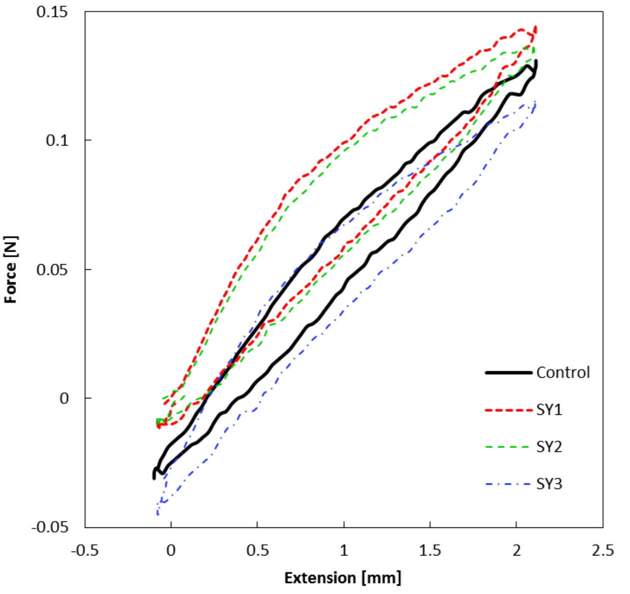


Figure 14: Average Force-elongation curve of control and PPy coated Latex/PA6 samples

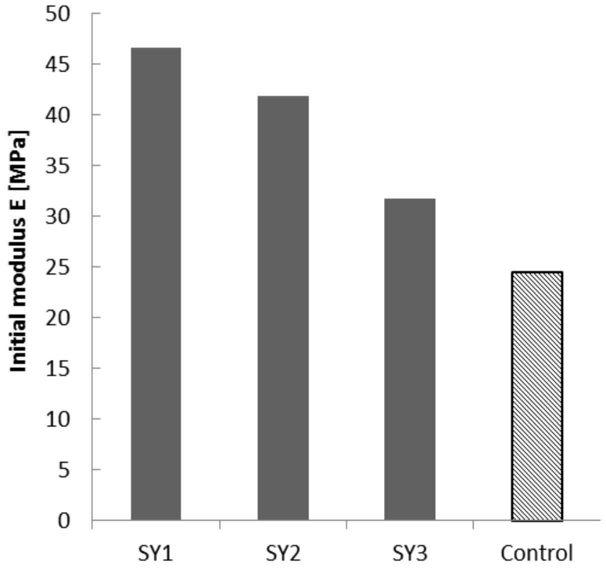


Figure 15: Initial modulus of control and PPy coated Latex/PA6 samples

Major changes occurred in the case of SY1 and SY2 which is practically undesirable on the basis of application point of view.

5.5.4 Decay of conductivity with time and commercial washing

In order to monitor this decay, PPy coated Latex/PA6 yarn samples was kept under temperature of 20±2°C and relative humidity for 40±2% for 21 weeks. Figure 16 illustrates the change in resistivity ρ of each sample after every four weeks during storage. It is worth noting that the resistivity increases significantly in the first week and this rise is more pronounced in the case of SY2 and SY3 whereas there is a continuous rise found in case of SY1 being as most conductive sample.

As the conducting polymers adhere to the surface of the fibre substrate only during polymerization and they are not absorbed in the fibre structure therefore smaller amount can be detached during washing cycle. When the samples of PPy coated Latex/PA6 were washed according to ISO 105-C06:2010, it was observed that resistivity increases significantly in all the samples as expected that can be seen from Figure 17. Only the first wash increases resistivity up to 70 % in SY1, 65% in SY2 and 20% in SY3. The change in resistivity continues in subsequent washing cycles and becomes manifold after five washing cycles.

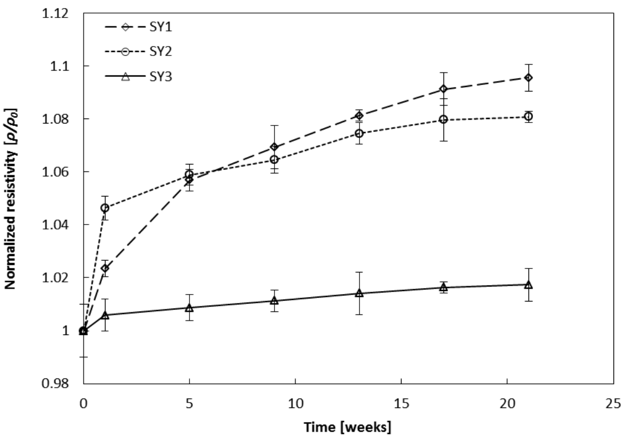


Figure 16: Aging behaviour of PPy coated Latex/PA6 samples at ambient conditions

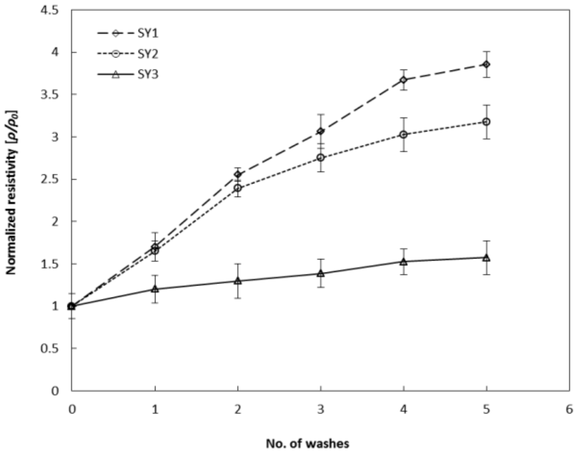


Figure 17: Dependence of resistance on commercial washing cycles

It is noted that the presented strain sensor is sensitive to environmental conditions such as humidity and temperature. Resistivity increases with rise in humidity whereas decreases with the increase in temperature. The sample of high resistivity found to be least affected by the humidity and temperature.

6. Author's publications on the topic

6.1 List of publications in international journals

[1] Abbasi, A. M. Rehan, Militky, J. and Gregr, J. Heat generation by polypyrrole coated glass fabric, *Journal of Textiles,* (Accepted).

[2] Abbasi, A. M. Rehan, Ramadan, M. A., Wiener, J., Baheti, V. and Militky, J. Electrothermal feedback in polypyrrole coated cotton fabric, *Journal of Textile Engineering,* (Accepted).

[3] Abbasi, A. M. Rehan, Wiener, J. and Militky, J. Cotton fabric coated by polypyrrole: effect of temperature on conductivity, *Melliand International,* **19,** 2013, pp. 21.

[4] Abbasi, A. M. Rehan, and Militky, J. EMI Shielding Effectiveness of polypyrrole coated glass fabric, *Journal of Chemistry and Chemical Engineering,* **7,** 2013, pp. 256-259.

[5] Abbasi, A. M. Rehan, Marsalkova, M.and Militky, J. Conductometry and Size Characterization of Polypyrrole Nanoparticles Produced by Ball Milling, *Journal of Nanoparticles,* **2013**, 2013, (published online).

[6] Abbasi, A. M. Rehan, Mangat, M. M., Baheti, V. and Militky, J. Thermal properties of cotton fabric coated with polypyrrole, *Journal of Fiber Bioengineering and Informatics,* **5,** 2012, pp. 163-168.

[7] Ramadan, M. A., Abbasi, A. M. Rehan, Wiener, J., Baheti, V. and Militky J. Polypyrrole coated cotton fabric: The thermal influence on conductivity, *Vlakna a Textil,* **19**(3)**,** 2012, pp. 41-49.

[8] Abbasi, A. M. Rehan, Mangat, M. M., Baheti, V. K. and Militky J. Electrical and thermal properties of polypyrrole coated cotton fabric, *Vlakna a Textil,* **19**(1)**,** 2012, pp. 48-52.

[9] Abbasi, A. M. Rehan, Marsalkova, M., Baheti, V. K.and Militky. J. Polypyrrole nanoparticles prepared by planetary ball milling and its conductivity, *Journal of Nanocomposites and Nanoceramics* **2,** 2011, pp. 1-4.

6.2 List of contributions in international conferences

[1] Abbasi, A. M. Rehan, Militky, J. Joule heating in polypyrrole coated glass fabric, *8th International Conference – TEXSCI,* Liberec, 23-25 Sep 2013.

[2] Abbasi, A. M. Rehan, Militky, J. and Mazari, A. Heat generation by polypyrrole coated glass fabric, *21st ICCE Proceedings,* Tenerife, Spain, 21-27 July 2013

[3] Abbasi, A. M. Rehan, Gregr, J., Baheti, V. and Militky, J. Heat generation by polypyrrole coated glass fabric, *19th International Conference STRUTEX Proceedings,* Liberec: Livox s.r.o Liberec, 2012.

[4] Abbasi, A. M. Rehan, and Militky, J. EMI shielding effectiveness of polypyrrole coated glass fabric, *International Technical Textile Conference,* Izmir: Meta Basim Press, 2012, pp. 29-30.

[5] Abbasi, A. M. Rehan, Mangat, M. M.and Militky, J. Thermal properties of cotton fabric coated with polypyrrole, *5th Textile Bioengineering and Informatics Symposium Proceedings,* Ueda: TBIS, Hong Kong China, 2012, pp. 757-761.

[6] Abbasi, A. M. Rehan, Ramadan, M. A. and Militky, J. The influence of temperature on polypyrrole coated cotton fabric, *41st Textile Research Symposium Proceedings,* Guimaraes, Portugal: Universidade Minho, 2012, pp. 280-285.

[7] Abbasi, A.M. Rehan, Marsalkova, M., Baheti, V. K. and Militky J. Development of polypyrrole coated glass fabric composite as EMI shield, *12th AUTEX World Textile Conference,* Zadar: University of Zegreb, Croatia, 2012, pp. 1529-1532.

[8] Abbasi, A. M. Rehan, Baheti, V. K. and Militky J. Production of nanoparticles of polypyrrole by ball milling, *2nd Nanomaterials and Nanotechnology Meeting Proceedings,* Ostrava: Repronis, 2011, pp. 93-94.

[9] Abbasi, A. M. Rehan, Marsalkova, M., Baheti, V. K.and Militky. J. Optimization of milling conditions for the production of polypyrrole nanoparticles, *18th international conference STRUTEX,* Liberec: Livox s.r.o., 2011, pp. 237-241.

[10] Abbasi, A. M. Rehan, Marsalkova, M.and Militky, J. Rheological and electrical properties of polypyrrole nanocomposites, *18th international conference STRUTEX,* Liberec: Livox s.r.o., 2011, pp. 401-404.

[11] Abbasi, A. M. Rehan, Militky, J.and Baheti. V. K. Production of nanoparticles of polypyrrole by ball milling, *40th Textile Research Symposium,* Kyoto, 2011.

[12] Abbasi, A. R., and Militky, J. Production of PPy nanoparticles by ball milling and electrical conductivity of their composite with polyurethane. *Workshop pro doktorandy FS a FT TUL,* 2011, Svetlanka: Vysokoskolsky podnik Liberec, spol. s.r.o. pp. 8-12.

[13] Abbasi, A. M. Rehan, EMI shielding effectiveness of polypyrrole coated textile fabric, *Workshop pro doktorandy FS a FT TUL,* 2012, Svetlanka: Vysokoskolsky podnik Liberec, spol. s.r.o. pp. 8-11.

7. References

[1] Hao, L. et al. Development and characterization of flexible heating fabric based on conductive filaments, *Meas.: J. the Int. Meas. Conf.*, 45, 2012, pp. 1855-1865.

[2] Hamdani, S. T. A. et al. Thermo-mechanical behavior of textile heating fabric based on silver coated polymeric yarn, *Materials,* **6,** 2013, pp. 1072-1089.

[3] Oh, K. W. et al. Adhesion improvement of electroless copper plated layer on PET film - effect of pretreatment conditions, *Polymer (Korea),* **25,** 2001, pp. 302-310.

[4] Joo, J. et al. Electromagnetic radiation shielding by intrinsically conducting polymers, *App. Phys. Lett.*, **65,** 1994, pp. 2278-2280.

[5] Kuhn, H. H., et al. Toward real applications of conductive polymers, *Synth. Met,* **71,** 1995, pp. 2139-2142.

[6] Wang, L. X. et al. Preparation, properties and applications of polypyrroles, *Reac. & Func. Polym.*, **47,** 2001, pp. 125-139.

[7] Li, H. H. et al. Polypyrrole carbon fiber composite film prepared by chemical oxidative polymerization of pyrrole, *J. App. Polym. Sci.*, **64,** 1997, pp. 2149-2154.

[8] Kim, S. H. et al. Electrical properties and EMI shielding characteristics of polypyrrole–nylon 6 composite fabrics, *J Appl. Polym. Sci.*, **87,** 2003, pp. 1969-1974.

[9] Oh, K. W. et al. Improved surface characteristic and the conductivity of polyaniline nylon fabrics by plasma treatment, *J Appl. Polym. Sci.*, **81,** 2001, pp. 684-694.

[10] Oh, K. W. et al. Electrically conductive textiles by in situ polymerization of aniline, *J Appl. Polym. Sci,* **74,** 1999, pp. 2094-2101.

[11] Im, S. S. and Byun, S. W. Preparation and properties of transparent nylon6-based composite films, *J Appl. Polym. Sci,* **51,** 1994, pp. 1221-1229.

[12] Lee, C. Y. et al. Conductivity and EMI shielding efficiency of polypyrrole and metal compounds coated on (non) woven fabrics, *Synth. Met.*, **119,** 2001, pp. 429-430.

[13] Lee, Y. K. and Cho, J. C. Preparation and Physical Properties of Conductive Poly(acrylonitrile) Fabrics Containing Polypyrrole, *Polymer (Korea),* **24,** 2000, pp. 276-280.

[14] Heisey, C. L. et al. Surface and adhesion properties of polypyrrole-coated textiles, *Tex. Res. J.*, **63,** 1993, pp. 247-256.

[15] Murray, P. et al. Electrochemical induced ductile–brittle transition in tosylate-doped (pTS) polypyrrole, *Synth. Met.*, **97,** 1998, pp. 117-121.

[16] Li, Y. et al. A flexible strain sensor from polypyrrole-coated fabrics, *Synth. Met.*, **151**, 2005, pp. 89-94.

[17] Xue, P. et al. In situ SEM studies on strain sensing mechanisms of PPy-coated electrically conducting fabrics, *Applied Surface Science,* **53,** 2007, pp. 3387-3392.

[18] Wu, J. et al. Conductive polymer coated lycra, *Synth. Met.*, **155**, 2005, pp. 698-701.

[19] Molina, J., et al. Chemical and electrochemical polymerisation of pyrrole on polyester textiles in presence of phosphotungstic acid, *Europ. Polym. J.*, **44**, 2008, pp. 2087-2098.

[20] Bunsomsit, K. et al. Polypyrrole-coated natural rubber latex by admicellar polymerisation, *Coll. and Polym. Sci.*, **280,** 2002, pp. 509-516.

[21] *Committee for Conformity Assessment on Accreditation and Certification of Functional and Technical Textiles* [online]. Sep 2003. Specified Requirements of Electromagnetic Shielding Textiles, Available at http://www.ftts.org.tw/images/fa003E.pdf

[22] Lin, T. et al. A. Polymerising pyrrole on polyester textiles and controlling the conductivity through coating thickness, *Thin Solid Films,* **479,** 2005, pp. 77-82.

[23] Alenitsyn, A. G. et al. Concise Handbook of Mathematics and Physics, 1997, CRC Press, pp. 331-332.

8. Summary

The main aim of this research work is to study few different applications of PPy coated textile substrates. In this context pyrrole was polymerized on two kinds of glass fabric and a stretchable yarn (Latex wrapped with PA6) by vapour deposition technique. Anhydrous Iron(III) Chloride as an oxidizing agent and tetraethyl ammonium p-toluene sulfonate as a doping agent were used in the polymerization. The concentration of polypyrrole was controlled by varying the concentration of oxidizing and doping agents whereas the rest of the process parameters such as time, temperature, pressure etc. were kept constant.

SEM and LSCM micrographs show that during vapour phase polymerization PPy is deposited on the surface of the fibres and covers them very well. The average thickness of the PPy produced on glass fibre by using 0.6mol/L Iron(III) Chloride and 0.3mol/L p-toluene sulfonate is calculated as 1.165±0.502µm from SEM image analysis and 1.372±0.223µm from LSCM analysis. Meanwhile FTIR analysis of PPy coated substrates also confirms the completion of polymerization of pyrrole through characteristic absorbance peaks.

Weight gain by glass fabric substrate after PPy deposition was found to be linear increasing function of concentration of Iron(III) Chloride (which is responsible for the oxidation of pyrrole monomer and hence regulate the yield). The electrical resistivity and EMI shielding effectiveness of PPy coated glass fabric having areal density of 410g.m^{-2} was found to be decreased linearly depending on the concentration of Iron(III) Chloride whereas the fabric having 900g.m^{-2} follows a power function. It can be inferred from the cross-sectional view of the coated fabric specimens that PPy develops on each individual fibre of the fabric structure mentioned former while later structure does not allow pyrrole vapours to access fibres in the core of yarn and hence PPy is not formed there. Due to this circumstance PPy is deposited on the fibres which are well exposed. It was also resolved that density of the fabric also makes a great influence on EMI shielding effectiveness and found to be significantly increased for higher density fabric.

The tensile strength of PPy coated glass fabric considerably decreases with the increase in concentration of PPy on fabric substrate regardless of the density of the fabric whereas elongation at break increases in terms of high density and decreases in low density fabric structure. The reason might be the presence of friction between more numbers of PPy coated fibres in the denser fabric structure.

When DC voltage is supplied to PPy coated glass fabric, it produces heat instantly mainly depending upon the time and potential of voltage being supplied. The temperature rises very sharply within 300 to 400s and level off after reaching to plateau. The thermal power density produced in the fabric follows a linear function of the voltage supplied whereas temperature follows a power function. With the help of dimensionless numbers and equation of heat transfer by convection, it was calculated that the amount of heat transferred to air follows a positive power function to the heat being converted from electrical energy. This interprets that ratio between heat conducted to air by convection and heat produced does not remain constant at different levels and that the remaining amount of heat conducted within fabric itself more than conducted out at higher voltage.

Thermal treatment at elevated temperatures affects the electrical conductivity and electroactivity of PPy. The rate of thermal degradation of conductivity is also very much dependent on temperature and duration of heating. During the series of experiments conducted in this dissertation it was observed that conductivity of PPy coated glass fabric increases as the temperature increases till it reaches to Tg of PPy which determines the common behaviour of semiconductors. While thermal treatment above Tg cause a loss in conductivity and this loss is permanent. The reason for this fact could be the lattice vibrations in the amorphous regions which do not allow charge to flow easily.

The strain sensor was developed by deposition of PPy on Latex wrapped with PA6 fibres through a vapour deposition technique. With the aim of studying dependence of resistance on the length of the conductor, extensive experimental analysis was carried out and concluded that resistance follows an extremely linear function of length and a model has been proposed to calculate the resistance at a particular length. The slope of this said function can be calculated from resistivity of the sample.

PPy coated Latex/PA6 samples were subjected to cyclic deformation of 2% and corresponding change in resistance was analysed. It was found that samples with more amount of PPy coating on them perform worse than sample with least amount of PPy. It means that high resistive sample gives higher level of sensitivity and consistency of response against small deformations.

PPy being as a brittle polymer changes the mechanical properties of the textile substrate on which it has been coated. In case of Latex/PA6 samples, PPy increases the friction between the PA6 fibres and consequently tangent modulus increases. More amount of PPy on the fibres make a larger change in the modulus that is utterly undesirable compared to fewer amount.

Conductivity of conducting polymers is highly dependent on the time of storage in a particular environment. Latex/PA6 samples coated with PPy were kept under ambient conditions for several weeks. All the samples drop conductivity within couple of weeks more pronouncedly which continues to be dropped in case of relatively high conductive sample whereas the drop is not so significant in the case of least conductive sample.

Commercial and domestic laundering plays an important role if the characteristic component of the garment loses its property such as colour, softness and conductivity etc. PPy coated Latex/PA6 samples were tested under standard commercial laundering procedure for few times and found to lose conductivity constantly on every cycle. Similarly, in the case of time decay property, more conductive samples lose conductivity more drastically than the one with least conductivity.

The effect of humidity and temperature of environment on resistivity of PPy coated Latex/PA6 samples was also found to be imperative. The resistivity decreases with the increase in temperature from 10°C to 50°C, clearly reflects the general behaviour of semiconductors. However, humidity causes an increment in resistivity which is a typical phenomenon in intrinsically conducting polymers only.

In the context of sensitivity, uniformity of the response, effect of environmental conditions and decay properties, among all three samples of PPy coated Latex/PA6, highly resistive sample is considered to be a best suitable for the practical application of strain sensing. While the total cost of manufacturing of this strain sensor is less than 1Kč per meter.

VydalaTextilní fakulta, Technické univerzity v Liberci jako interní publikaci pod pořadovým číslem DFT/5/2013 v počtu 20 výtisků