Jędrzej Banaszczyk,
Andrzej Rybak,
Mateusz Odziomek

ABB Corporate Research
Starowiślna 13A, 31-038 Kraków, Poland
E-mail: jedrzej.banaszczyk@pl.abb.com
andrzej.rybak@pl.abb.com

*AGH University of Science and Technology
Faculty of Materials Science and Ceramics
Al. Mickiewicza 30, 30-059 Kraków, Poland
E-mail: mateuszodziomek@gmail.com

Aging of Polypyrrole Coated Fabrics Potted in Epoxy

Abstract
In this article the high temperature aging of epoxy potted polypyrrole coated polyester/nylon fabrics was investigated in order to assess whether they can be used in applications where elevated temperature is common. A comparative analysis of various types of conductive fabrics was performed, including both woven and nonwoven, which were potted in epoxy resin and subjected to thermal aging. The results were compared with those obtained for polyimide/carbon ink coated quartz woven high temperature fabric. The results of the measurements were successfully approximated with analytical aging curves.

Key words: *conductive fabrics, thermal aging, PPy, polypyrrole, epoxy potting.*

Introduction

Polypyrrole (PPy) is one of the most common intrinsically conductive polymers (ICPs) employed in such applications as microwave absorption, resistive heating, electrostatic discharge protection and actuation, to name only a few. Fabrics coated with PPy are characterised by high energy efficiency, cost effectiveness and conductivity, which can be tailored and varied over several orders of magnitude [1]. However, PPy coated fabrics are generally not suitable for high temperature operations, which limits their application range.

In PPy oxygen has been shown to be the main cause of conductivity degradation. In addition, it was observed that ambient humidity causes a significant increase in the diffusion coefficients of the conductivity decay [2, 4]. For these reasons PPy will degrade slowly even at 50 °C, if exposed to humidity and oxygen. These issues have been addressed in numerous studies, where the thermal stability of polymeric coatings was enhanced by adding e.g. extra sulfonate doping agents into the polymerisation solution [2] or by the incorporation of inorganic nanoparticles (e.g. clay) by melt blending [5 - 7].

On the other hand, if the coated fabrics are protected from atmospheric moisture and oxygen, e.g. by means of potting in epoxy, their conductivity lifetime at high temperature can be significantly extended. This could be particularly interesting for power electronics applications, where high temperature is common, but the equipment is often potted in epoxy or polyurethane compounds [8]. Potting could possibly allow conductive fabric structures to perform well over extended periods of time at an operating temperature exceeding 100 °C.

In this article a long term high temperature aging investigation of five different commercially available conductive fabrics, potted in epoxy, was carried out. Four of those fabrics were PPy coated polyester and polyester/nylon woven and nonwoven fabrics, while the fifth one was a quartz woven fabric coated with polyimide/carbon ink, designed for high temperature applications. The high temperature quartz fabric provided a reference for the PPy coated fabrics.

Sample preparation

The fabrics under investigation were commercial EeonTex (USA) fabrics obtained from Eeonyx [9], whose key properties are summarized in ***Table 1***. Each fabric was given a label to facilitate its identification. The fabrics were cut into rectangular sheets of arbitrary dimensions, and four electrical contacts were attached at the vertices of the samples to enable square resistance measurements by means of the VDP method, which is discussed in detail in the next section.

The samples were subsequently potted in Epikote 05395 epoxy casting system (the Netherlands), hardened with the Epikure curing agent 04883 [10]. The curing protocol was

Table 1. *Properties of the tested fabrics.*

Label	PNNW_1	PW_1	PNNW_2	PT_1	QW_1
Substrate material	polyester /nylon	polyester	polyester /nylon	polyester	fused silica
Fabric type	nonwoven	woven pongee	nonwoven	twill	woven
Measured initial $R_{\square}$, Ω/□	18.3	536.6	41.4	108.4	183.2
Max. rated temperature, °C	80				350
Thickness, mm	0.8	0.09	0.4	0.5	0.8
Mass per m², g/m²	170	68	80	223	68

Figure 1. *PPy coated fabric sample potted in transparent epoxy, with integrated contacts for VDP measurements. Side view (left) and top view (right).*

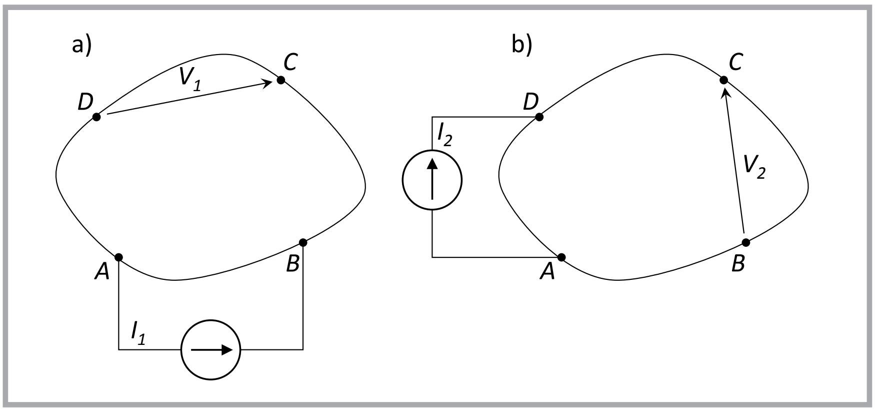

Figure 2. *VDP measurement on a sample of an arbitrary shape, with four small contacts at arbitrary positions along the circumference.*

Table 2. *Averaged increase of $R_\square$ due to three different sets of stress factors, with respect to measured initial $R_\square$, expressed in %.*

Sample	av. Δ$R_\square$, % epoxy potting	av. Δ$R_\square$, % HT and oxygen	av. Δ$R_\square$, % epoxy immersion
PNNW _1	+12.0	+44.3	+4.5
PW_1	+7.2	+46.1	+2.1
PNNW _2	+38.7	+39.6	+6.9
PT_1	+108.6	+86.2	+55.8
QW_1	+6.0	0.0	+1.1

8 hours curing at 80 °C, followed by 10 hours post curing at 120 °C. Potting of the fabrics in epoxy rendered it possible to isolate them from atmospheric moisture and oxygen. A photograph of a finished epoxy potted conductive fabric sample is depicted in ***Figure 1***.

VDP square resistance measurement method

The VDP (Van Der Pauw) method was originally introduced in [11], and it has been used in microelectronics since the 1950s to measure the square resistance of silicon wafers. Let us consider a homogenous electrically conductive sheet of uniform thickness provided with four contacts and placed at arbitrary locations along the perimeter (***Figure 2***). In the first experiment current I_1 is supplied through contacts *A* and *B*, and the voltage drop V_1 between the remaining contacts, *C* and *D,* is measured, as shown in ***Figure 2.a***. In the second experiment current I_2 is fed through *A* and *D*, and the voltage drop V_2 is now measured between contacts *B* and *C* (***Figure 2.b***). Using conformal mapping techniques, Van Der Pauw proved that the following relation holds:

$$\exp\left[-\pi \frac{V_1}{I_1 R_\square}\right] + \exp\left[-\pi \frac{V_2}{I_2 R_\square}\right] = 1 \quad (1)$$

The numerical solution of this transcendental equation immediately yields $R_\square$.

One of the main advantages of the method is that it can be applied to samples of totally arbitrary shape, provided the sample is a homogenous conducting layer. Additionally no direct access to the whole surface of the samples is required. In contrast to standard 4-point measurement methods [12], it is sufficient to provide electrical contacts at arbitrary locations on the perimeter of the samples, e.g. at the vertices, thus making the method very effective and accurate for $R_\square$ measurements of conductive fabrics, as it was proven in [13 - 15].

Results and discussion

Prior to epoxy potting, the initial average $R_\square$ of the fabrics was measured to provide reference for further tests. For each fabric, measurements were performed on three different rectangular sheets, with three independent measurements on each sheet. The results of these preliminary measurements can be found in ***Table 1***.

During epoxy potting, the PPy coatings are subjected to both contact with the epoxy in which the fabrics are immersed and high temperature, which is necessary to carry out the curing process itself. The combination of these two factors is likely to cause coating degradation, and for this reason the conductivity measurements were repeated after the samples were potted in epoxy. The results of these measurements can be found in the second column of ***Table 2***, and it is clear that epoxy potting caused an increase in the $R_\square$ of the conductive fabrics.

In order to find the dominant factor affecting the deterioration of the PPy coatings during potting, additional aging tests were performed. A set of fabrics was subjected to a temperature cycle of 8 hours at 80 °C, followed by 10 hours at 120 °C in oxygen atmosphere conditions, inside a regular laboratory oven, following the temperature profile of the epoxy curing protocol. A second set of samples was immersed in uncured epoxy and stored at room temperature (22 °C) for a period of 6 days. The measured average increase of the $R_\square$ of these samples is presented respectively in the third and fourth column of ***Table 2***.

It is clear from the measurement results gathered in ***Table 2*** that epoxy immersion itself had a limited impact on the coating stability. The only exception is the PT_1 fabric, where the observed $R_\square$ increase was indeed significant. The contact of the fabrics with epoxy was expected to cause conductivity degradation. For instance, alkaline atmosphere is known to cause deprotonation of the chains, as well as deintercalation of dopant ions that are responsible for conductivity [16 - 18]. However, the combination of high temperature with immersion in epoxy, which takes place during the potting process, had a much more considerable adverse effect on the stability of the coatings. The high curing temperature accelerated the rate of the reaction and contributed to the loss of conductivity.

Still, in the case of the PNNW_1 and PW_1 fabrics a much more significant conductivity degradation was caused by exposure to high temperature in oxygen atmosphere than by epoxy potting. As far as the PNNW_2 is concerned, the conductivity loss measured after both experiments was comparable. The PT_1 twill fabric, turned out to be the least resistant one, and it was the only investigated PPy coated fabric for which epoxy potting caused a higher conductivity loss than exposure to high temperature in oxygen atmosphere. The polyimide/carbon ink coated quartz fabric proved resistant to oxidation, while immersion in epoxy caused only a slight coating degradation, which was aggravated by high temperature during epoxy curing. The results of the initial tests showed that epoxy potting can enhance the stability of PPy coatings at elevated temperature.

In the next series of tests the PPy coated PNNW_1 nonwoven was subjected to aging in a climatic test chamber at 90 °C and at controlled relative humidity of 72%, 60% and 50% RH for 288 hours. The results of the square resistance measurements, taken at time intervals of 20 – 70 hours, are plotted in ***Figure 3***. The coatings exposed to oxygen, humidity and elevated temperature aged rapidly and their $R_\square$ in function of aging time canbe fairly well approximated with an exponential function:

$$R_\square = R_0 \cdot e^{\tau \cdot t_a} \quad (2)$$

where, $R_\square$ is the square resistance, R_0 is the initial square resistance, t_a is the aging time in hours and τ is the characteristic time for the degradation reaction, which depends on the relative humidity, and aging temperature. It must be mentioned that R_0 is slightly lower than the measured initial $R_\square$ given in ***Table 1***. This decrease in $R_\square$ is attributed to temperature induced hopping [19, 20].

The last series of tests consisted in aging sets of the epoxy potted conductive fabric sheets for 160 days at a constant elevated temperature of 140 °C. An attempt was made to approximate the measurement results with analytical curves. In general, for diffusion-controlled kinetics, the relation:

$$\frac{\sigma_0 - \sigma}{\sigma_0} \propto t_a^{\frac{1}{2}} \quad (3)$$

where, σ_0 is the initial conductivity, σ is the conductivity and t_a is the aging time, leads to a good fit of the experimental data for short aging times and for $\sigma/\sigma_0 > 0.5$ [2, 20]. However, since here we deal with long aging times and $\sigma/\sigma_0 < 0.5$, this expression does not provide an accurate approximation. In our case fitting with the expression:

$$\sigma(t_a) = \sigma_0 e^{-(t_a/\tau)^{\frac{1}{2}}} \quad (4)$$

where, τ is the characteristic time for degradation reaction, leads to a much better approximation, especially for the PW_1 and PT_1 woven textiles [21]. ***Equation 4*** is known to give a good fit on a wide time scale and can be transformed to the form:

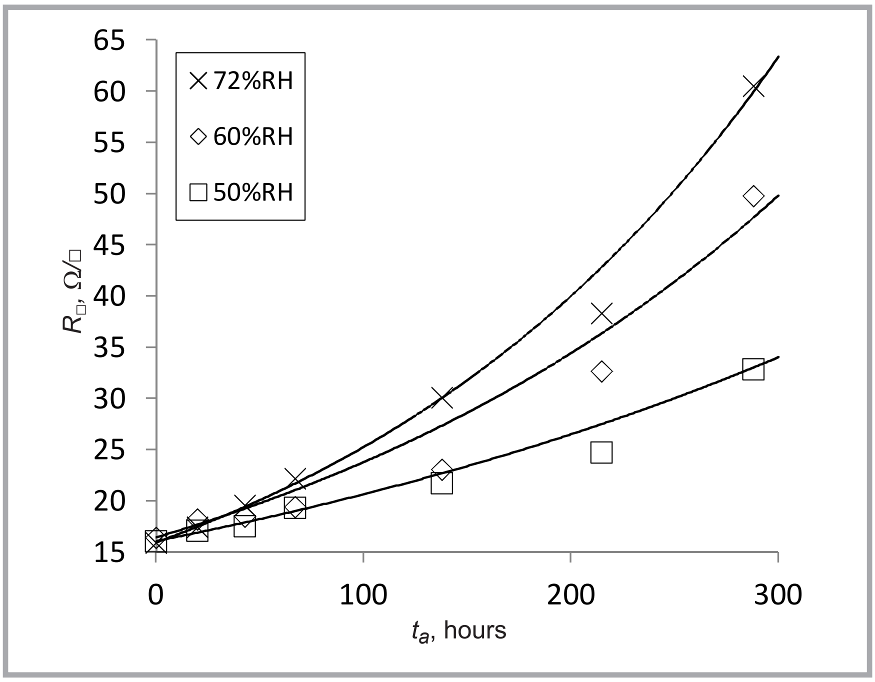

Figure 3. *$R_\square$ of PPy coated PNNW_1 nonwoven, aged in oxygen atmosphere at varied relative humidity at 90 °C.*

Table 3. *Total average change of the $R_\square$ of the resin potted fabrics subjected to aging at 140 °C for 160 days.*

Sample	av. R_0, Ω/□ potted fabric	av. $R_\square$, Ω/□ HT aging	av. $R_\square/R_0$
PNNW _1	20.5	32.3	1.57
PW_1	575.5	2746.6	4.77
PNNW _2	60.2	163.9	2.72
PT_1	226.2	962.3	4.25
QW_1	194.3	209.9	1.08

$$R_\square = \frac{R_0}{e^{-(t_a/\tau)^{\frac{1}{2}}}} \quad (5)$$

directly yielding $R_\square$. In the case of the PNNW_1 and PNNW_2 conductive nonwovens a better approximation was obtained with the expression:

$$R_\square = R_0(1 + c \cdot t_a^{\frac{1}{2}}) \quad (6)$$

where, c is an experimental coefficient.

The measurement results are gathered in ***Table 3*** and are plotted together with the fitting curves in ***Figures 4 – 6*** (see page 82), where Fit 1 is the ***Equation 4*** and Fit 2 is the ***Equation 6***.

Conclusions

The thermal stability of PPy coated conductive fabrics can be significantly enhanced by potting in epoxy resin. During epoxy curing the conductivity of the coatings is likely to degrade, especially if high curing temperature is required, but by isolating the fabrics from ambient humidity and oxygen the stability of the coatings at elevated temperature is improved, as can be seen by comparing ***Figure 3*** with ***Figure 7*** (see page 82).

We have tested different kinds of PPy coated fabrics, including nonwovens and woven fabrics. After 160 days of aging at 140 °C the $R_\square$ of the nonwovens increased by a factor 1.57 – 2.72 with respect to the initial value R_0, while in the case of the woven fabrics the $R_\square$ increased by a factor of 4.25 – 4.77. This is a significant improvement with respect to the non-potted PNNW_1 nonwoven, where a comparable $R_\square$ increase was observed after only 10 day aging at 50% RH at 90 °C.

In general, the PPy coating conductivity decreased less for the nonwovens than for the woven fabrics. This result could be caused by the fact that the nonwovens had higher initial conductivities than the woven fabrics, but it may also be related

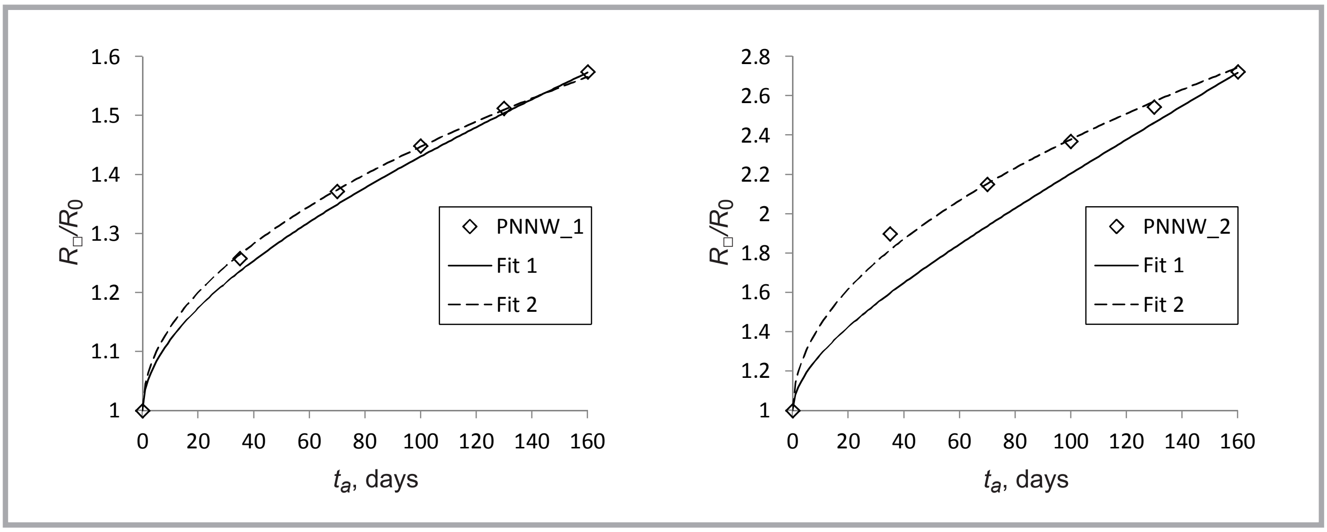

Figure 4. *Effect of high temperature aging on the $R_{\square}/R_0$ of PPy coated epoxy potted polyester/nylon nonwovens aged at 140 °C.*

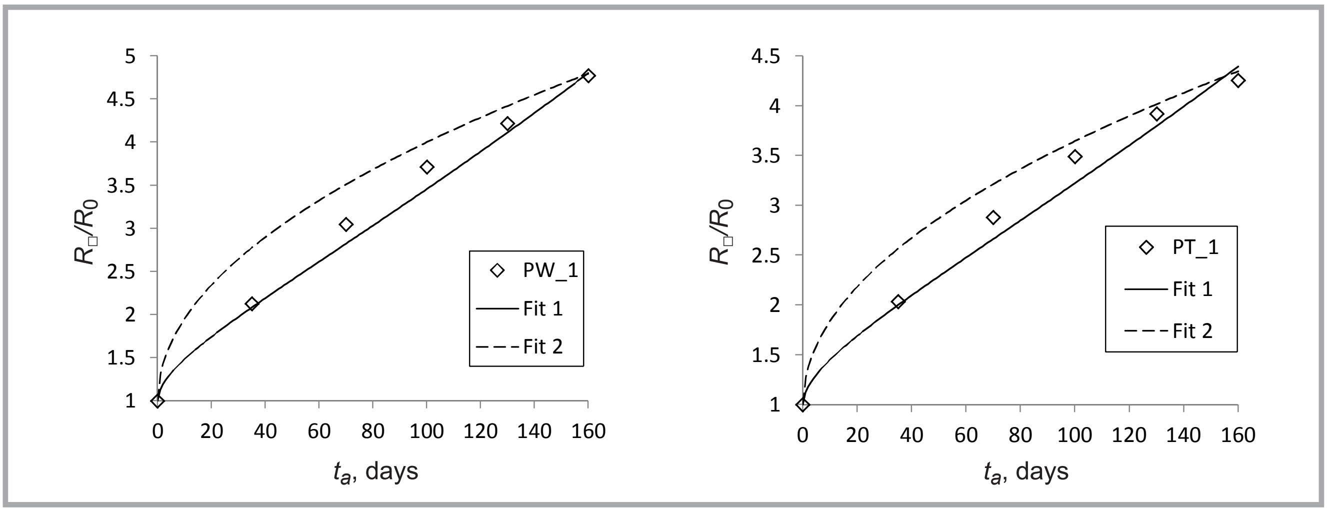

Figure 5. *Effect of high temperature aging on the $R_{\square}/R_0$ of PPy coated epoxy potted polyester woven fabrics aged at 140 °C.*

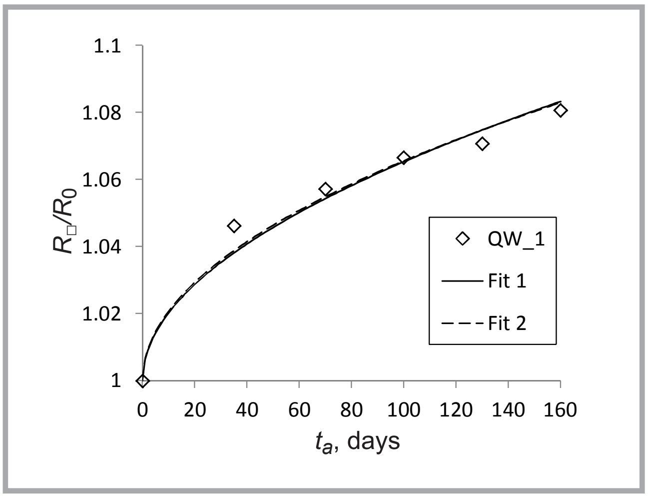

Figure 6. *Effect of high temperature aging on the $R_{\square}/R_0$ of polyimide/carbon ink coated epoxy potted quartz woven fabric aged at 140 °C.*

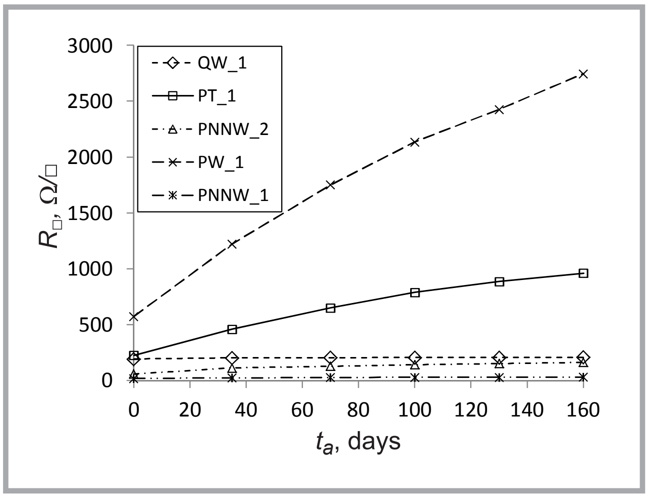

Figure 7. *Comparison of the aging curves for all epoxy potted conductive fabrics aged at 140 °C.*

to the structural differences between the two kinds of fabric. Aging of the woven fabrics is more accurately approximated with ***Equation 5***, while aging of the nonwovens follows ***Equation 6*** more closely.

The resin potted high temperature quartz woven fabric coated with the polyimide/carbon conductive ink performed best, and its $R_{\square}$ increased only by a factor of 1.1 with respect to the initial value. However, such materials are relatively expensive, and PPy coated polyester/nylon nonwovens and woven fabrics can be considered as substitutes in certain applications, where potting the fabric or coating it with epoxy or other protective film is possible.

References

1. Sparavigna A, Florio L, Avloni J, Henn A. Polypyrrole coated PET fabrics for thermal applications. *Materials Sciences and Applications* 2010; 13: 253-259.
2. Tansley TL, Maddison DS. Conductivity degradation in oxygen-aged polypyrrole. *J. Appl. Phys.* 1991; 69: 7711-7713.
3. Thiéblemont JC, Planche MF, Petrescu C, Bouvier JM, Bidan G. Stability of chemically synthesized polypyrrole films. *Synth. Met.* 1993; 59: 81-96.
4. Erlandsson R, Inganas O, Lundstrom I, Salaneck WR. Thermal stability of polythiophene and polypyrrole. *Synth. Met.* 1985; 10: 303-318.
5. Varesano A, Tonin C, Ferrero F, Stringhetta M. Thermal stability and flame resistance of polypyrrole-coated PET fibres. *J. Therm. Anal. Cal.* 2008; 94: 559-565.
6. Ribeiro SPS, Estevão LRM, Nascimento RSV. Brazilian clays as synergistic agents in an ethylenic polymer matrix containing an intumescent formulation. *J. Therm. Anal. Cal.* 2007; 87: 661-665.
7. Yu-Chuan L, Chenh-Jung T. Enhancements in Conductivity and Thermal and Conductive Stabilities of Electropolymerized Polypyrrole with Caprolactam-Modified Clay.*Chem Mater* 2003; 15: 320-326.
8. Hewitt DA, Stone DA, Foster MP. An experimental evaluation of thermally conductive filler loaded encapsulant composites. In: *7th IET International Conference onPower Electronics, Machines and Drives (PEMD 2014),* Manchester, UK,8-10 April 2014, pp. 1-6.
9. www.eeonyx.com
10. www.momentive.com
11. Van Der Pauw LJ. A method of measuring the specific resistivity and Hall effect of discs of arbitrary shape. *Philips Res. Repts* 1958; 13: 1-9.
12. MR-1 surface resistance meter. http://www.schuetz-messtechnik.com/de/pdf/Kde-MR1.pdf (accessed: 03 June 2014).
13. Banaszczyk J, De Mey G, Schwarz A, Van Langenhove L. The Van Der Pauw method for sheet resistance measurements of polypyrrole coated woven fabrics. *J. Appl. Polym. Sci.* 2010; 117: 2553-2558.
14. Banaszczyk J. Theoretical and experimental investigation of thermal and electrical properties of electroconductive fabrics. PhD Thesis, Ghent University, Belgium, 2010.
15. Kazani I, Hertleer C, De Mey G, Schwarz A, Guxho G, Van Langenhove L.Electrical Conductive Textiles Obtained by Screen Printing. *FIBRES & TEXTILES in Eastern Europe* 2012; 1: 57-63.
16. Patil AJ, Deogaonkar SC. Conductivity and atmospheric aging studies of polypyrrole-coated cotton fabrics. *J. Appl. Polym. Sci.* 2012; 125: 844-855.
17. Pei Q, Qian R. Protonation and deprotonation of polypyrrole chain in aqueous solutions. *Synth. Met.* 1991; 45: 35-48.
18. Hwang J, Pyo M. pH-Dependent Mass and Volume Changes of Polypyrrole/Poly(styrene sulfonate). *Bull Korean Chem. Soc.* 2006; 27: 2067-2070.
19. Mott NF, Davis EA. *Electronic Process in Non-Crystalline Materials*. Oxford: Clarendon Press, 1979.
20. Sixou B, Mermilliod N, Travers JP, Temperature and Aging Time Dependence of the Conductivity in a Conducting Polymer: a Unified Picture. *Europhys. Lett.* 1995; 30:157-162, 1995.
21. Dalas E, Sakkopoulos S, Vitoratos E. Thermal degradation of the electrical conductivity in polyaniline and polypyrrole composites. *Synth. Met.* 2000; 114: 365–368.

Received 13.12.2013 Reviewed 17.07.2014