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.

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.

Summary

The fabrics under investigation were commercial EeonTex (USA) fabrics obtained from Eeonxy [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 discussed in detail in the next section.
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 $R_{ce}$ due to three different sets of stress factors, with respect to measured initial $R_{ce}$, expressed in %.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Delta R_{ce}$, % epoxy potting</th>
<th>$\Delta R_{ce}$, % HT and oxygen</th>
<th>$\Delta R_{ce}$, % epoxy immersion</th>
</tr>
</thead>
<tbody>
<tr>
<td>PNNW_1</td>
<td>+12.0</td>
<td>+44.3</td>
<td>+4.5</td>
</tr>
<tr>
<td>PW_1</td>
<td>+7.2</td>
<td>+46.1</td>
<td>+2.1</td>
</tr>
<tr>
<td>PNNW_2</td>
<td>+38.7</td>
<td>+39.6</td>
<td>+6.9</td>
</tr>
<tr>
<td>PT_1</td>
<td>+108.6</td>
<td>+86.2</td>
<td>+55.8</td>
</tr>
<tr>
<td>QW_1</td>
<td>+6.0</td>
<td>0.0</td>
<td>+1.1</td>
</tr>
</tbody>
</table>

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 2a. 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 2b). Using conformal mapping techniques, Van Der Pauw proved that the following relation holds:

$$\exp\left(-\pi \frac{V_1}{t_{R_{ce}}}\right) + \exp\left(-\pi \frac{V_2}{t_{R_{ce}}}\right) = 1 \quad (1)$$

The numerical solution of this transcendental equation immediately yields $R_{ce}$.

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 $R_{ce}$ measurements of conductive fabrics, as it was proven in [13 - 15].

Results and discussion

Prior to epoxy potting, the initial average $R_{ce}$ 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 $R_{ce}$ 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 $R_{ce}$ 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 $R_{ce}$ 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 tempera-
ture 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 \( R_0 \) function in aging time can be fairly well approximated with an exponential function:

\[
R(t) = R_0 \cdot e^{-\frac{t}{\tau_a}}
\]  

(2)

where, \( R_0 \) is the square resistance, \( R_0 \) is the initial square resistance, \( t_a \) is the aging time in hours and \( \tau \) 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 \( R_0 \) given in Table 1. This decrease in \( R_0 \) 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:

\[
\frac{\sigma}{\sigma_0} = \frac{\sigma_0 - \sigma}{\sigma_0} \sim t_a^{\frac{1}{2}}
\]  

(3)

where, \( \sigma_0 \) is the initial conductivity, \( \sigma \) 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:

\[
\sigma(t_a) = \sigma_0 e^{-\left(\frac{t_a}{\tau_a}\right)^{\frac{3}{2}}}
\]  

(4)

where, \( \tau \) 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:

\[
R(t) = R_0 \cdot e^{-\left(\frac{t}{\tau_a}\right)^{\frac{3}{2}}}
\]  

(5)

directly yielding \( R_0 \). In the case of the PNNW_1 and PNNW_2 conductive nonwovens a better approximation was obtained with the expression:

\[
R(t) = R_0 (1 + c \cdot t_a^{\frac{3}{2}})
\]  

(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 \( R_0 \) 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 \( R_0 \) increased by a factor 4.25 – 7.77. This is a significant improvement with respect to the non-potted PNNW_1 nonwoven, where a comparable \( R_0 \) 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 $R_c/R_0$ of PPy coated epoxy potted polyester/nylon nonwovens aged at 140 °C.

Figure 5. Effect of high temperature aging on the $R_c/R_0$ of PPy coated epoxy potted polyester woven fabrics aged at 140 °C.

Figure 6. Effect of high temperature aging on the $R_c/R_0$ 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 $R_c$ 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.

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