Comparative Studies on the Thermal Ageing of Some Painting Materials

TRAIAN RUS1, ADRIANA MARIANA BORS2, ALINA RUXANA CARAMITU3, IOSIF LINGVAY3, DANUT IONEL VAIREANU4*

1 University Politehnica of Bucharest, Faculty of Applied Chemistry and Materials Science, 1-7 Gheorghe Polizu Str., 011061, Bucharest, Romania
2 ICPE SA, 313 Splaiul Unirii, 30138, Bucharest, Romania
3 National Institute for Research and Development in Electrical Engineering INC IDEA ICPE-CA, INCIDE ICPE - CA, 313 Splaiul Unirii, 30138, Bucharest, Romania

This paper presents a comparative study with respect to the behavior of some painting materials, used mainly for decorative and protective industrial applications, exposed to a controlled accelerated ageing process by using thermal storage and successive thermal cycles. The evaluation of the structural changes, as well as those concerning the dielectric loss were carried out in a comparative manner, on the initial samples, before any exposure to thermal stresses and during the ongoing process of the thermal treatments applied. As analysis techniques coupled thermal analysis and dielectric impedance spectroscopy have been used. It was found that there is a clear correlation between the structural changes of the investigated materials, particularly in the case of the epoxy materials subjected to the applied thermal treatments and the evolution of the dielectric losses in the material. As a result of these investigations, one may determine the characteristic acceptable zones for the thermal stresses (up to 1300 h of storage and 1500 thermal cycles), anything above these boundaries leading to strong increases in the dielectric losses and hence the deterioration of the materials rendered unfit to be used for the intended purpose.

Key words: paints, epoxy-resins, polyurethanes, thermal ageing, thermal cycling

The painting materials are used both for the protection against corrosion of metallic structures mounts/assemblies and for the protection against atmospheric factors of cement-based (concrete, mortar, etc.) and/or wood constructions, as well as to ensure a pleasant appearance of the protected surfaces. Usually, by the painting materials used for surface protection are based on polymers which, under the action of stress factors, undergo various degradation / ageing processes. In the case of metallic structures exposed to atmospheric corrosion - such as metallic pillars supporting overhead power lines or various electro-energetic equipments - ageing under the influence of environmental factors of applied paint layers makes their permissivity for accelerating factors of atmospheric corrosion processes to increase (diffusivity/penetrability of humidity and O₂, CO₂, NOₓ, etc.). Thus, conditions are created for the accelerated corrosion of the metal support, which - in the absence of expensive re-painting works - can seriously affect the safety in exploitation of the metal structures [1].

In the case of reinforced concrete structures exposed to atmospheric (climatic) stress factors, concrete degradation occurs due to the simultaneous action of humidity and atmospheric CO₂, the degradation processes being accelerated by aggressive gaseous pollutants such as SO₂, NOₓ, etc. [2]. Moreover, massive degradation is recorded due to the synergic action of atmospheric factors and induced AC stray currents [2-11].

During exploitation, the painting materials suffer degradation processes due to the action of climatic factors [12-15] and UV radiation [16-21]. These degradations create conditions for establishing colonies of microorganisms - especially filamentous fungi - that contribute substantially to the global process of the paint layers degradation [22-25].

Recent studies have highlighted that electromagnetic pollution of the environment - especially with disturbing signals at 50 Hz industrial frequency - activates metabolic processes and accelerates the reproduction/multiplication of moulds [26-28] which leads to intensification of fungal attack on polymers [29-32], including painting materials [33].

It is noted that, following degradation of the paint layers due to the synergic action of environmental factors, atmospheric noxes, microbiological factors and disturbing electric fields, the processes of degradation of cement products and metal corrosion are substantially accelerated [34-41]. In this context, the issue of the development of highly resistant polymeric materials [42-46] or controlled biodegradability [47] is of great practical importance.

The lifetime of constructed structures, including those protected by paint layers, can be assessed by studies of predictive intelligent diagnostics [48,49] which involve the existence of databases regarding both the history of construction and the mechanisms and kinetics degradation processes under the actions of stressor factors of the main materials used in the construction [50, 51].

Considering the fact that during the exploitation the painting materials are exposed to both extreme atmospheric temperatures and temperature diurnal variations, the purpose of the work consists in the comparative study of the behavior of some painting materials (often used in industrial applications) exposed to accelerated ageing by thermal storage and by successive thermal cycles.

* email: di_vaireanu@chim.upb.ro
Experimental part

Materials and methods

The behavior under the influence of prolonged thermal stress and some cyclic and rapid temperature variations on 2 materials type: epoxy resins and polyurethane resin paints often used in industrial applications (table 1) was studied.

<table>
<thead>
<tr>
<th>Samples code</th>
<th>Brand name</th>
<th>Resin type</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-1</td>
<td>Sigmaprime 200</td>
<td>Epoxy</td>
</tr>
<tr>
<td>S-2</td>
<td>Intergard 410</td>
<td>Modified epoxy</td>
</tr>
<tr>
<td>S-3</td>
<td>Intertane 990</td>
<td>Acrylic polyurethane</td>
</tr>
<tr>
<td>S-4</td>
<td>Sigmadur 550H</td>
<td>Polyurethane</td>
</tr>
</tbody>
</table>

Table 1

THE INVESTIGATED PAINT MATERIALS

were made by coupled techniques of thermal analysis and by impedance dielectric spectroscopy.

The thermal analysis determinations were performed by progressively heating samples of 10 - 30 mg, in static air, from ambient temperature to 600 °C with a heating rate of 10 K/min using a dedicated data processing software, STA 409PC Produced by Netzsch (Germany). Determination of dielectric impedance spectroscopy was performed at 20 ± 2°C and a 3V voltage, applied to the paint sample foils fixed between two 25 mm electrodes - equipment type 1296 Dielectric interface / AMTEK, from Solartron Analytical.

Results and discussions

The TG, DTA and DTG thermograms recorded by progressive heating in the presence of oxygen (static air) of the S-1 sample before thermal treatments are shown in figure 2.

Analyzing figure 2, it is noted that to the progressive heating of the initial S-1 epoxide material (unexposed to thermal treatments) between approx. 50 °C and approx. 150°C, a process occurs with the formation of volatile products when the material suffers a mass loss of $\Delta m_V = 3.45\%$. The material shows no endothermic peak (minimum DTA) characteristic of the melting processes. These findings suggest that up to approx. 150°C, the polymerization process continues (curing), and then it is soaked through vitreous transition (glass transition).

The first exothermic process of oxidation with the formation of O1 solid peroxide products is slightly pronounced (distinguishable only by the DTA curve inflection at 265 °C) since it is covered by the exothermic process of oxidation O2 with maximum at $T_{MaxO2} = 355°C$. The O2 process is followed by oxidation processes with the...
formation of volatile products $O_3$ and $O_4$ ($T_{\text{Max}O_3} = 409.9$ °C and $T_{\text{Max}O_4} = 468.9$ °C and a mass loss of $\Delta m_{O_3} = 24.1 \%$) respectively $O_7$ with $T_{\text{Max}O_7} = 547.8$ °C and $\Delta m_{O_7} = 10.31 \%$.

During thermal storage at 100 °C, the epoxy material S-1 undergoes structural changes as a result of which, the recorded thermograms change accordingly. Thus, in figure 3 it can be noticed that during the progressive heating of S-1 material by storing at 100 °C for 720 h until at 200°C, it does not suffer mass losses by volatilization (as in the initial case fig. 2). It is also observed that the main thermooxidation processes are the same as in figure 2 - but on the DTA curve there is an extra exothermic peak - corresponding to $O_5$ - which suggests that after the heat treatment applied the structure of the material suffers changes that made the thermooxidation processes more complex.

As a result of these modifications, the characteristic temperatures $T_{\text{Max}}$ of the $O_1 - O_7$ thermooxidation processes and the related $\Delta m$ mass losses have changed. At the extension of the applied thermal treatment, the structural changes are accentuated and the thermooxidation processes with the formation of volatile compounds are complicated and changed accordingly, as shown in figure 4 in which the thermograms obtained are presented for sample S-1 after 1392 hours of thermal storage at 100°C.

In figure 5 it is observed that during the 800 applied thermal cycles, the material structure is stabilized, respectively up to 200°C there are no decomposition processes with formation of volatile products (process V - fig. 2). It is also noted that, after application of the thermal cycles, the polymer exhibits a tendency of ordering the structure, respectively increasing the crystallinity of the material, which leads to the appearance of a DTA endotherm minimum corresponding to melting at $T_M = 264°C$.

The DTA peak corresponding to the first exothermic process of formation a solid peroxide products $O_1$, with $T_{\text{Max}O_1} = 284°C$ is slight by pronounced because it is masked by the thermooxidation process with formation $O_2$ volatile products which begins at approx. 280°C and has $T_{\text{Max}O_2} = 368.9°C$. This behavior, respectively process disappearance and structural ordering - the increase of crystallinity and the occurrence of the melting process after applying thermal cycles is similar to the behavior of epoxy materials exposed during thermal storage.

![Fig. 3. The thermograms obtained on S-1 sample after 720 h of thermal storage at 100°C](image1)

![Fig. 4. The thermograms obtained on S-1 sample after 1392 h of thermal storage at 100°C](image2)
The thermal analysis determinations performed on the S-2 epoxy material both on the initial sample and those heat-treated by storage were similar to those obtained on S-1 sample, the differences recorded being the process characteristic temperatures and the related mass losses.

Table 2 shows the characteristic data obtained on S-1 sample at various thermal storage times at 100 °C and during thermal cycles. Table 3 shows these data for the S-2 epoxy material.

By analyzing the values presented in table 2 and table 3, it is found that the two epoxy materials investigated behave the similar from a thermal point of view.

At the thermal ageing of two materials - both by exposure to rapid temperature variations (thermal cycling between -38 and 85 °C) and by storage at 100°C at the beginning of the treatment there are processes of decomposition with volatile products formation, processes that are finalized in the case of thermal storage after approx. 700 h of treatment at 100 °C (Δm_tends to zero) respectively after 600-800 thermal cycles (according to fig. 1).
In the case of thermal storage it was found that the temperature characteristic of the first $T_{MaxO1}$ thermooxidation process, respectively the formation of solid peroxide products, up to 1392 h of exposure $T_{MaxO1}$ is approximately constant, suggesting that there are no significant changes in the structure of the material.

Starting with 1392 h of storage, $T_{MaxO1}$ shows a decreasing trend indicating that the thermooxidative stability of the investigated materials decreases due to structural changes - perhaps shortening polymer chains and increasing the share of tertiary and quaternary (more reactive) carbon atoms in the structure. This hypothesis is supported both by the complication/multiplication of the thermooxidation processes with volatile products formation in the temperature range of 380-530°C ($O3-06$) and by the increasing trend of the total mass losses at 600°C of the samples stored thermally at 100°C more than 1392 h. Between -38 and 85°C), the degree of structural ordering of the material (crystallinity) increases which provides a melting process distinct at $T_M$. When cycles continues, $T_M$ increases and $T_{MaxO1}$ decreases, indicating that a cross-linking process of the material occurs. These structural changes of the epoxy materials investigated following the thermal treatments applied are also reflected in the evolution of dielectric losses in material - as shown in figure 6 (dielectric loss evolution following thermal storage at 100°C) and figure 7 (dielectric loss evolution following thermal cycles).

In the case of thermal cycles, there is a different behavior compared to ageing through thermal storage. Thus, after the completion of the decomposition processes with $V$ volatile compounds formation (after about 800 fast cycles between -38 and 85°C), the degree of structural ordering of the material (crystallinity) increases which provides a melting process distinct at $T_M$. When cycles continues, $T_M$ increases and $T_{MaxO1}$ decreases, indicating that a cross-linking process of the material occurs. These structural changes of the epoxy materials investigated following the thermal treatments applied are also reflected in the evolution of dielectric losses in material - as shown in figure 6 (dielectric loss evolution following thermal storage at 100°C) and figure 7 (dielectric loss evolution following thermal cycles).

For epoxy material S-2 the curves shape of figure 6 and figure 7 are similar, with the difference that the systematically recorded values were higher by 5-10% than for S-1.

From the analysis of figure 6 and figure 7 it is noted that, at the beginning of the applied thermal treatments (up to 700 hours of storage and 800 thermal cycles respectively) the dielectric losses in S-1 decrease (more pronounced to 50 Hz), indicating that, following volatile products elimination processes $V$, the polar groups weight, especially of the -OH groups) decreases in the material structure.

### Table 3: The Results Obtained by Thermal Analysis on Thermally Treated Epoxy Materials S-2

<table>
<thead>
<tr>
<th>Thermal stress</th>
<th>$\Delta M$</th>
<th>$T_M$</th>
<th>$T_{MaxO1}$</th>
<th>$T_{MaxH1}$</th>
<th>$T_{MaxO1}$</th>
<th>$T_{MaxH1}$</th>
<th>$T_{MaxO1}$</th>
<th>$T_{MaxH1}$</th>
<th>$T_{MaxO1}$</th>
<th>$T_{MaxH1}$</th>
<th>$T_{MaxO1}$</th>
<th>$T_{MaxH1}$</th>
<th>$T_{MaxO1}$</th>
<th>$T_{MaxH1}$</th>
<th>$T_{MaxO1}$</th>
<th>$T_{MaxH1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>3.63%</td>
<td>266.6</td>
<td>355.5</td>
<td>7.09</td>
<td>410.5</td>
<td>466.8</td>
<td>-</td>
<td>-</td>
<td>24.21</td>
<td>552.3</td>
<td>8.87</td>
<td>43.81</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>48</td>
<td>2.92%</td>
<td>260.4</td>
<td>352.3</td>
<td>7.96</td>
<td>402.5</td>
<td>461.3</td>
<td>-</td>
<td>-</td>
<td>26.21</td>
<td>541.4</td>
<td>9.98</td>
<td>47.07</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>144</td>
<td>1.98%</td>
<td>266.9</td>
<td>351.2</td>
<td>8.95</td>
<td>398.8</td>
<td>443.6</td>
<td>-</td>
<td>-</td>
<td>24.03</td>
<td>538.9</td>
<td>10.98</td>
<td>49.94</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>408</td>
<td>0.75%</td>
<td>267.2</td>
<td>348.9</td>
<td>10.32</td>
<td>381.1</td>
<td>409.1</td>
<td>-</td>
<td>-</td>
<td>22.05</td>
<td>537.8</td>
<td>12.54</td>
<td>45.66</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>720</td>
<td>0.18%</td>
<td>266.9</td>
<td>344.8</td>
<td>11.53</td>
<td>371.2</td>
<td>388.1</td>
<td>440.4</td>
<td>-</td>
<td>19.21</td>
<td>537.1</td>
<td>14.23</td>
<td>45.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1152</td>
<td>0</td>
<td>264.4</td>
<td>346.5</td>
<td>12.12</td>
<td>377.9</td>
<td>390.3</td>
<td>441.8</td>
<td>-</td>
<td>18.06</td>
<td>538.4</td>
<td>14.76</td>
<td>44.94</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1392</td>
<td>0</td>
<td>264.4</td>
<td>346.3</td>
<td>12.67</td>
<td>383.4</td>
<td>400.1</td>
<td>443.9</td>
<td>449.5</td>
<td>16.46</td>
<td>541.5</td>
<td>15.12</td>
<td>44.25</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1776</td>
<td>0</td>
<td>263.7</td>
<td>346.5</td>
<td>13.77</td>
<td>384.2</td>
<td>401.3</td>
<td>444.5</td>
<td>450.5</td>
<td>16.87</td>
<td>542.9</td>
<td>15.38</td>
<td>46.53</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1968</td>
<td>0</td>
<td>263.5</td>
<td>346.6</td>
<td>14.83</td>
<td>384.9</td>
<td>403.9</td>
<td>445.2</td>
<td>451.3</td>
<td>17.88</td>
<td>544.6</td>
<td>16.12</td>
<td>48.83</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In the case of thermal storage, ageing through thermal storage. Thus, after the completion of the decomposition processes with $V$ volatile compounds formation (after about 800 fast cycles
When prolonging the applied thermal treatments - at over approx. 1300 h of storage and more than 1500 thermal cycles - $t_g\delta$ values increase what suggests that the material suffers degradation processes (as shown in table 2).

Fig. 8. Thermograms obtained on the S-3 polyurethane material before applied the thermal treatments

Fig. 9. Thermograms obtained on S-3 polyurethane material after storage for 1152 h at 100°C

Fig. 10. The thermal diagrams obtained on S-3 sample after exposure to 1000 thermal cycles
The TG, DTA and DTG thermograms recorded by the progressive heating in oxygen presence (static air) of the S-3 polyurethane material sample before the thermal treatments applied are shown in figure 8.

By analyzing the thermograms in figure 8, it is observed that on progressive heating of sample S-3 up to approx. 180°C a decomposition process occurs by the volatile products formation ($\Delta m_V = 1.98\%$) followed by the endothermic process $M$, when the material melts with $T_M = 270.1\, ^\circ C$.

Upon the progressive heating of the material over $T_M$ up to 600°C several complex oxidation processes occur (some of them to overlap on the DTA curve), the first pronounced endothermic peak being recorded at $T_{\text{MaxO}_1} = 407\, ^\circ C$. The total loss of recorded mass up to 600°C was $\Delta m_T = 69.69\%$.

Thermograms recorded on S-3 material exposed to thermal treatments - as shown in figure 9 and figure 10 are similar to those of figure 8.

Table 4 shows synthetically the main characteristic data of the results obtained by thermal analysis of S-3 and S-4 material samples exposed to applied thermal treatments.

The analysis of the data in table 4 shows that the two investigated epoxy materials exhibit slightly different thermal behavior - respectively at the beginning of the thermal treatments applied, volatile product formation $V$ process being more pronounced in the case of S-3 sample than for S-4 sample.

It is also noted that, in the case of S-3 sample, the temperature characteristic of the first T $\text{MaxO}_1$ thermo-oxidation process and the total mass losses $\Delta m_T$ at 600°C are systematically higher than at S-4 sample. These findings indicate that S-4 material has a higher thermal stability than S-3.

For both materials it is noted that in the beginning of the applied thermal treatments (up to 1392 h of storage at 100°C or 1000 applied thermal cycles) the material structure stabilizes. Continuing the treatments applied on both materials, there is a decrease in $T_M$ and $T_{\text{MaxO}_1}$, respectively an increase of $\Delta m_T$, which suggests that the material degrades by breaking the polymer chains. This explanation is also supported by the evolution of dielectric loss $\tan \delta$.
during applied thermal treatments (fig. 11 for S-3 sample and fig. 12 for S-4 sample).

Dielectric loss evolutions during thermal treatments applied to S-4 sample was similar to that for S-3 sample, with the difference that values recorded at S-4 sample were systematically lower by 10-15% as compare to S-3 sample, indicating a higher thermal stability and sustainability in case of S-4 sample.

Considering the thermal behavior of the materials investigated above as well as the results of the investigations on the evolution of the thermal and dielectric characteristics following exposure to various doses of UV [16], it is considered appropriate to continue the research in order to show the synergistic effects at UV action simultaneous exposure and repeated thermal cycles (more accurate simulation of the actual operating conditions) of epoxy and polyurethane paint materials.

Conclusions
The thermal analysis of the unexposed materials to thermal treatments subjected to a progressive heating process between 50 and 150 °C has shown that there is a stage of volatile products formation of less than 3.5%, but the material has no endothermic characteristic point, (minimum DTA) associated with the melting processes, suggesting in fact that up to 150°C, the curing process continues up to a glass transition phase.

The investigated epoxy materials, stored at 100°C, suffer structural changes, reflected in the associated thermograms. However, if these materials are further subjected to a progressive heating, after storing them at 100°C for 720 h, they will suffer little or no mass loss, which suggests that after the applied heat treatment the material structure is somehow stabilized making it less prone to further thermooxidation processes, within the material degradation limits. It has been found that there is a clear correlation between the structural changes of the investigated materials subjected to the applied thermal treatments and the evolution of the dielectric losses in the material.

Dielectric losses have a minimum zone between 600 and around 1300 h, for the thermal storage at 100°C, and a similar minimum zone for the thermal cycling, between 600 and 1500 cycles, regardless of the applied frequency, suggesting that the investigated materials can cope with thermal stresses within these limits and may be used safely in industrial applications. If one extends the applied thermal treatments above 1300 h of storage and more than 1500 thermal cycles - $\tan \delta$ increases sharply (a strong increase in dielectric losses), indicating clearly that the materials undergo various degradation processes, and, consequently they are no longer fit to be used for the intended purpose.

Acknowledgment: This work was financially supported by the UEFISCDI of Romania, under the scientific Programme NUCLEU 2016 - 2017, contract PN 16 11 02 11 /2016.

References
43. PICA, A., FICAI, A., Rev.Chim. (Bucharest), 67, no. 1, 2016, p. 34
44. PANAITE, V., BOICIUC, S., MUSAT, V., Rev. Chim. (Bucharest), 66, no. 2, 2015, pp. 231
47. BRIA, V., CIRCIUMARU, A., BIRSAN, I.G., Mat. Plast., 48, no. 2, 2011, p. 189
51. ISOC, G., ISOC, T, ISOC, D., Studies in Computational Intelligence (SCI), 486, 2013, pp. 53-64.
52.*** Sigmaprim 200: https://docs.td.ppgpmc.com//download/428/428/sigmaprime-200-series
56.CIOBOTARIU, O.R., BRIA, V., GRAUR, I., VONESCU, D.C., Rev. Chim. (Bucharest), 66, no. 11, 2015, p. 190

Manuscript received: 8.01.2018