In order to identify the causes that led to microbiological degradation by biofouling increases a top coat painting layer applied to a railway bridge was analyzed by both FTIR and the DSC methods: the analysed painting material was that used to paint the bridge in 2013. The determinations were performed comparatively on samples of a similar painting material after 10 days of curing in a natural atmosphere at 25 ± 5 °C, after 60 days of storage under laboratory conditions (22 ± 5 °C, RH 60 ± 10 %, natural lighting), and on samples from the painting material of a certain railway bridge after approx. 4.5 years (exposed natural weathering of temperate climate with Mediterranean influences). From FTIR determinations, the amount of oxygen containing groups (C = O, C-O, C-O-C, -HO) resulted from ageing under various conditions of the painting material. From DSC determinations, the resistance of the paint to the oxidative degradation decreases with the ageing time as resulted from oxidation onset temperatures and oxidation activation energies values - which decreases with 4 kJ / mole (about 2.2 %) in only 60 days of storage in the laboratory and with 7 kJ / mole (about 3.9 %) following exposure to 100 w/m² for only 15 h and 29 kJ / mole (over 16 %) after exposure to 4.5 years of natural weathering.

Keywords: painting material, ageing, natural weathering, polyurethane, FTIR, DSC
techniques and thermal analysis of the painting material which, in exploitation, proved to be easily biodegradable, as was described in [16, 27, 32, 33].

Experimental part

In order to assess the paint thermooxidative stability applied to a railway bridge, which proved to be easily biodegradable in exploitation, paint samples were taken from the painting layer from a certain bridge painted in 2013 [32].

Similar paint samples were exposed naturally to weathering and were analysed by FTIR and DSC technics, comparatively with paint samples of the same material after 10 days of curing, and after 60 days of storage under laboratory conditions and after controlled UV exposure. The samples analysed in this study and their ageing conditions are presented in table 1.

DSC measurements were performed using a Setaram 131 EVO instrument (Setaram, France). Dynamic measurements were carried out at different heating rates of: 2.5, 5, 10, 15 °C/min, between 30-350 °C, under oxidant atmosphere (air, 50 mL/min). Samples of about 2 -3 mg were measured in aluminium pans of 30 µL with a pierced lid. Specific SETARAM software has been used for data acquisition and processing. The oxidation onset temperatures (OOT) were calculated at different heating rates from the DSC curves.

FTIR measurements were carried out using a Jasco FTIR-4200 (Jasc, JP) coupled with an ATR (Attenuated Total Reflectance) module (JASCO PRO 470 H). The carbonyl and hidroxyl indexes were calculated using the following formulas:

\[ CI = \frac{A_{C=O}}{A_{C=O}} \]

\[ HI = \frac{A_{OH}}{A_{CH_2}} \]

where:

- \( A_{C=O} \) is the absorbance of carbonyl band, measured at the maximum peak in the range of 1650-1750 cm\(^{-1}\);
- \( A_{OH} \) is the absorbance of hydroxyl band, measured at the maximum peak in the range of 3300 - 3600 cm\(^{-1}\);
- \( A_{CH_2} \) is the absorbance at 1458 cm\(^{-1}\) [34], used as internal standard.

Results and discussions

FTIR spectroscopy

FTIR analysis is a common technique used to assess the chemical changes in the polymer coatings as results of exposure to various external factors. In our case FTIR spectroscopy was used to characterize the ageing effects induced by the exposure of the paint in various environmental conditions (artificial UV, natural weathering, darkness) by observing the optical absorptions corresponding to the presence and growth of oxidative groups (carbonyl, carboxyl and hydroxyl) or the double bonds (C=C).

The absorption of natural or artificial UV radiations by polymeric materials involves the electrons excitation from the ground state to higher energy levels. These levels are unstable and induce some material structural modifications by various physico-chemical processes, known as photo degradation. This process can produce the scission (formation of low molecular weight compounds) and/or crosslinking (formation of higher molecular weight compounds) of the main polymer chain, unsaturation, photo-oxidation, photo-hydrolysis [35, 36].

Some polymeric structures, such as those containing aromatic rings, double bonds (C=C, C=O), hydroxyl and carboxyl groups or some conjugate structures could absorb by themselves the UV radiations. The photooxidation is a chained process [37, 38], with a mechanism which implies the free radicals formation due to the photon absorption by the materials. These free radicals interact with oxygen molecules forming peroxo radicals. The peroxo radicals may remove a hydrogen atom from the polymer backbone, forming a hydroperoxide and another free radical, thus accelerating the degradation of the polymeric materials [37, 39, 36].

In figure 2 are presented the ATR/FTIR spectra recorded on the investigated samples (table 1). The ATR/FTIR spectrum of unaged paint was used as standard. It presents the characteristic absorptions of polyurethane type coating materials (table 2).

The exposure of the polyurethane paint to various environmental conditions leads to some modifications in the ATR/FTIR spectrum, which are related to changes in

| Sample Name | Code | Remarks |
|-------------|------|---------|
| Virgin paint | S2 | Cured for 10 days at 25±5 °C and RH 60±10% |
| Paint stored in laboratory | S3 | 60 days, at 20±5 °C, RH 50±10 %, day/night cycle |
| Paint exposed to artificial UV light | S1 | Aged in a Xenotest 440 installation (Atlas Instruments, DE). Irradiance: 100 w/m² (λ: 300-400 nm). Irradiation time: 13 h; RH: 60 %; CHT: 50 °C; EST: 80 °C. |
| Paint sample taken from the bridge of the biofouling area | S3 | Natural weathering - 4.5 years |

Table 1
ANALYZED SAMPLES

Fig. 2. ATR/FTIR spectra recorded on the investigated samples
the chemical structure of the material. The most prominent modifications (fig. 2 and fig. 3) are observed for the paint exposed in natural weathering (S4), mainly in the region of –NH/-OH stretching vibrations (3100-3500 cm\(^{-1}\)) and in the spectral ranges of C=O (1600-1750 cm\(^{-1}\)) and C-O-C (1000-1200 cm\(^{-1}\)) [34, 43, 45]. These structural modifications of the C=O and C-O-C groups are mainly caused by photooxidative processes [52].

The broadening and intensity increase of the peak with maximum at 3357 cm\(^{-1}\) is due to the O-H stretching mode of a hydroperoxide (R-O-O-H), hydroxide (R-O-H), species produced in the photodegradation process of the polyurethane paint [38]. The increase in intensity of the band at 1726 cm\(^{-1}\) (fig. 3, table 2) is related to the increase of the concentration of carbonyl groups due to ß-scission of the alkoxy radical [40, 41], while the decrease of the intensity of the peak of 1684 cm\(^{-1}\) indicates chain scissions of the urethane linkages [34].

The scission of the polyurethane chain produces more oxygen containing groups as revealed by the increasing in the intensity and the broadening of the bands corresponding to C-O stretching vibrations (1000 -1200 cm\(^{-1}\), with a maximum at about 1028 cm\(^{-1}\)) [42], and by the broadening of the band between 1680-1750 cm\(^{-1}\), due to the formation of different types of carbonyl groups [43], respectively. Also, the increase in intensity of the band at 831 cm\(^{-1}\) is given the FTIR spectrum of S4 samples. This is also attributed to formation of single bond, carbon-oxygen (e.g. hydroperoxide) [44].

The exposure to artificial UV radiation (S3) does not modify significantly the paint chemical structure, as revealed by ATR/FTIR analysis, the spectrum being similar to that of S1, sample (fig. 3). This can be attributed both to the short ageing time (about 15 h) or to the fact that, firstly, the UV energy is used to finish the paint curing process, and only after that the material degradation occurs. However, a slight increase for carbonyl and hydroxyl index values (table 3) for S3 as compared to S1, is noticed.

In table 3 are presented the hydroxyl (HI) and carbonyl (CI) indexes obtained from the ATR/FTIR spectra [39, 45, 46]. These parameters reflect the influence of the various stress factors on the material, being a tool to evaluate its photodegradation state.

**Differential scanning calorimetry**

The DSC curve of virgin paint S1 recorded under oxidant atmosphere at 10 °C/min is shown in figure 4. The Onset Oxidation Temperature (OOT), also known in literature as Oxidation Induction Temperature (OIT\(^*\), [47]), is a widely used parameter in thermal analysis of polymers to monitor their degradation oxidation state under various stress factors (UV light, gamma irradiation, temperatures) [48, 39]. The OOT values recorded on the analyzed samples at different heating rates are presented in table 4. As it can be observed, as the heating rate is increased, the OOT are shifted to higher values due to heat transfer lag [49]. Also, the OOT values decrease with the ageing time from 223 °C (heating rate \(\beta=10 \, \text{°C/min}\)) for S1 to 209 °C for S3.

**Table 2**

| Wavenumber [cm\(^{-1}\)] | Assignment |
|--------------------------|------------|
| 3357                     | –OH/-NH stretching vibration |
| 2932, 3860               | Symmetric and antisymmetric stretch of CH\(_2\) |
| 1726                     | C=O stretch from urethane |
| 1684                     | H bond C=O stretch/tertiary urethane C=O/C=O bonded |
| 1509                     | –NH deformation and antisymmetric stretch of C-N |
| 1478, 1378               | Scissoring and bending of –CH\(_2\) – group |
| 1426                     | –OH deformation |
| 1330                     | NCO deformation/CH\(_4\) |
| 1245                     | (O=O-C-O-C stretch/Urethane C-O stretch |
| 1200-1000                | C-O-C stretching vibrations |
| 1164                     | C-N-C asymmetric stretch |
| 874                      | C-N-C symmetric stretch |
| 831                      | C-O (Hydroperoxide) [44] |
| 65                       | C-N stretch |

**Table 3**

| Sample | CI\(_{1726}\) | CI\(_{1028}\) | HI\(_{3357}\) |
|--------|---------------|---------------|--------------|
| S1     | 0.86          | 1.81          | 0.13         |
| S2     | 1.06          | 1.62          | 0.15         |
| S3     | 1.07          | 1.38          | 0.13         |
| S4     | 1.57          | 1.55          | 0.74         |

As expected, the paint exposed in natural conditions (UV light, variable temperatures and humidity) present higher values for carbonyl and hydroxyl indexes. The paint stored for 60 days in laboratory conditions with partial access at the light seems to be also a little bit more degraded than the unaged paint.
These results are in good agreement with the ATR/FTIR, revealing that with the increase of the ageing time of the paint the carbonyl and hydroxyl indexes increase, simultaneously with an OOT decrease.

The activation energy is a parameter used to investigate different transformations into the polymeric materials such crystallization, degradation/oxidation, decomposition, etc. [50]. The environmental factors effect on physico-chemical behavior of polymeric system can be also evaluated in terms of activation energies. In oxidation terms of a polymeric material, the activation energy is the minimum amount of energy necessary to start the oxidation process.

In our case, the oxidation activation energies were calculated using the Kissinger method [51], from the slope of \( \ln(OOT/\beta) \) vs. \( 1/OOT \) (\( \beta \) is \( \alpha \) the heating rate?; the slope is in fact as \( Ea/R \), were \( Ea \) is activation energy, expressed in Kelvin (K) degrees, and \( R \) – the gas constant; \( R = 8,314 \) J K\(^{-1}\) mole\(^{-1}\); OOT is expressed also in K degrees). An example for obtaining the oxidation activation energy for the unaged sample \( (S_1) \) is given in table 4. The plots of the \( \ln(OOT^2/\beta) \) vs. \( 1/OOT \) are shown in figure 5 and in table 5 are given the activation energies for all analyzed samples.

As can be observed (table 5) the activation energy for the oxidation process decreases as the ageing time increases.

The decrease by 4 kJ/mole (about 2.2 %) in only 60 days of laboratory storage and by 7 kJ/mole (about 3.9 %) following exposure to 100 w/m\(^2\) for only 15 hours indicates a low thermal stability of the material, which is confirmed by the substantial decrease of 29 kJ/mole (over 16 %) after the exposure of 4.5 years to natural weathering.

The low thermal stability of the polymer, also confirmed by the SEM image (with major bumps and cracks) of the top coat exposed at 4.5 years in natural weathering presented in [27], correlated with the content in chlorine, phosphorus, potassium, sodium and magnesium of the painting material [27] can explain the weak resistance to microorganisms action of the investigated paint layer.
Conclusions
The ATR/FTIR and DSC techniques were used to assess the degradation state of some polyurethane coating at different ageing times and conditions.

The exposure of polyurethane coating samples to environmental conditions for different period of times leads to the increase of the amount of oxygen containing groups (C=O, C-O, C-O-C, -HO), to the appearance of some UV induced scission processes on the polymer chains, as compared to the unaged sample.

The resistance of the paint to the oxidative degradation decreases with the ageing time as resulted from OOT and oxidation activation energies values.

The decrease by 4 kJ/mole (about 2.2 %) for only 60 days of laboratory storage and 7 kJ/mole (approximately 3.9%) following exposure to 100 W/m² for only 15 h and 29 kJ/mole (over 16 %) after 4.5 years exposure to natural weathering, are values indicating reduced thermooxidative stability of the investigated painting material.

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