Assessment of Paint Layers Quality by FTIR and DSC Techniques

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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/m^2 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

In the sustainable development perspective ensuring a secure transport infrastructure is a priority issue. In this context, the development and use of efficient painting materials for the anticorrosion protection of metal structures related to transport infrastructure - such as bridges and viaducts - is a complex theoretical theme that has special practical (technical, economic and ecological) implications. Modern painting materials are composites based on polymeric material (usually polyurethanes, epoxy, etc.) with fillers of inorganic powders and various ingredients such as antioxidants, colour pigments etc. During exploitation, the painting layers are exposed to several stress factors specific to the exposure environment. Under the simultaneous and concerted action of stress factors, often with synergistic effects, paint layers aged and lose their anticorrosion protection capability.

In the paints case, stress factors usually act on the polymer matrix causing its degradation / ageing. In general, polymer degradation is a complex process in which a thermooxidation reaction [1-9] plays a determining role, which in the painting layers case is initiated by solar radiation in the IR spectrum and especially UV [10-12] and accelerated by climatic conditions specific to the operating environment [11, 13-15].

On the painting layers with degraded polymer the microorganisms, especially filamentous moulds (fig. 1) are fixed, which cause the polymeric protective layers biodegradation [5, 16-26].

The penetration of mycelial hyfes into the anticorrosion protection layers results in moisture retention and diffusivity increase of corrosive agents from the environment towards the metal support, so the polymeric layer loses its anticorrosion protection capability.

It is noted that in the paints case in which inorganic powders containing soluble salts (soluble salts of K, Na, Mg etc.) have been used as filler, the growth of filamentous moulds is accelerated, as reported in [27].

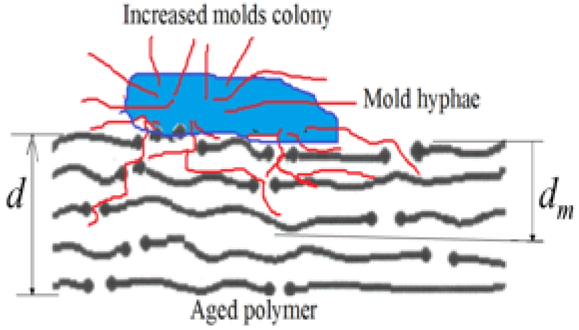

Fig. 1. Polymeric protective layers biodegradation: **d** - physical layer thickness; **d_m** - the thickness of the biodegradation layer [16]

Both the painting materials manufacture and the metal painting operations have a negative impact on the environment (dispersion of various organic and inorganic noxes [28-30]), so it is desirable that the painting materials used are suitable for the application, and to provide highest stability and sustainability under the exploitation conditions, aiming at preserving and protecting the environment [31].

In the metal structures case related to transport infrastructures, particularly those operating in protected environments such as Natura 2000, the suitable painting material choice with high durability in operation is a complex issue.

Recently, a case of unexpectedly rapid biodegradation of the paint on a newly repainted railway bridge section has been reported [32].

Microbiological studies have shown the fact that filamentous moulds have a major contribution to the growth a complex fouling (filamentous moulds, moss, algae and lichens) [33] and to a significant decrease in the paint layer anticorrosion protection [16, 32].

In this context, the paper aim is to analyse the thermooxidative behaviour by means FTIR (DSC)

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Table 1
ANALYZED SAMPLES

Sample		Remarks
Name	Code	
Virgin paint	S_1	Cured for 10 days at 25±5 °C and RH 60±10%
Paint stored in laboratory	S_2	60 days, at 20±3 °C, RH 60±10 %, day/night cycle
Paint exposed to artificial UV light	S_3	Aged in a Xenotest 440 installation (Atlas Instruments, DE). Irradiance: 100 w/m² (λ: 300-400 nm); Irradiation time: 15 h; RH: 60 %; CHT: 50 °C; BST: 80 °C.
Paint sample taken from the bridge of the biofouling area	S_4	Natural weathering - 4.5 years

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:

$$CI = \frac{A_{C=O}}{A_{CH2}} \qquad (1)$$

$$HI = \frac{A_{OH}}{A_{CH2}} \qquad (2)$$

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_{CH2} 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 groth 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 peroxy radicals. The peroxy 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

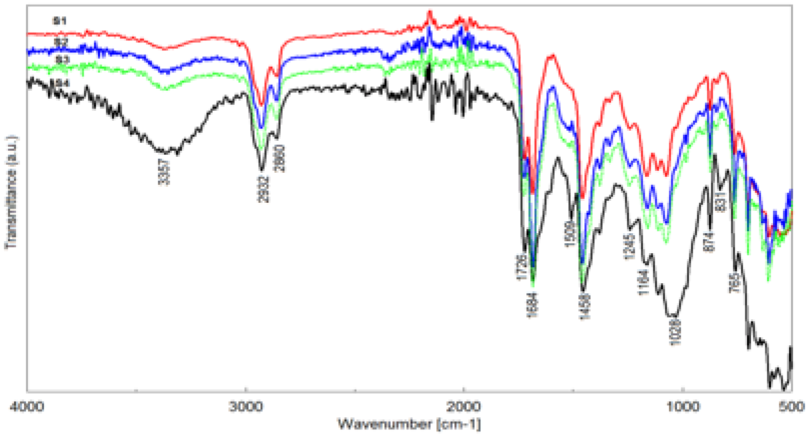

Fig. 2. ATR/FTIR spectra recorded on the investigated samples

Table 2
CHARACTERISTIC ABSORPTION BANDS OF S1 [34, 43, 52, 44, 55]

Wavenumber [cm^{-1}]	Assignment
3357	-OH/-NH stretching vibration
2932, 2860	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
1458, 1378	Scissoring and bending of $–CH_2–$ group
1426	-OH deformation
1330	NCO deformation/CH_2
1245	(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]
765	C-N stretch

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}) [45] 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 â-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 (***S**$_3$*) does not modify significantly the paint chemical structure, as revealed by ATR/FTIR analysis, the spectrum being similar to that of ***S**$_2$* 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 ***S**$_3$* as compared to ***S**$_2$* 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.

Table 3
CARBONYL AND HYDROXYL INDEXES

Sample	CI_{1726}	CI_{1684}	HI_{3357}
S1	0.86	1.81	0.13
S2	1.06	1.62	0.15
S3	1.07	1.58	0.15
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.

Differential scanning calorimetry

The DSC curve of virgin paint S 1 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 β=10 °C/min) for S1 to 209 °C for S3.

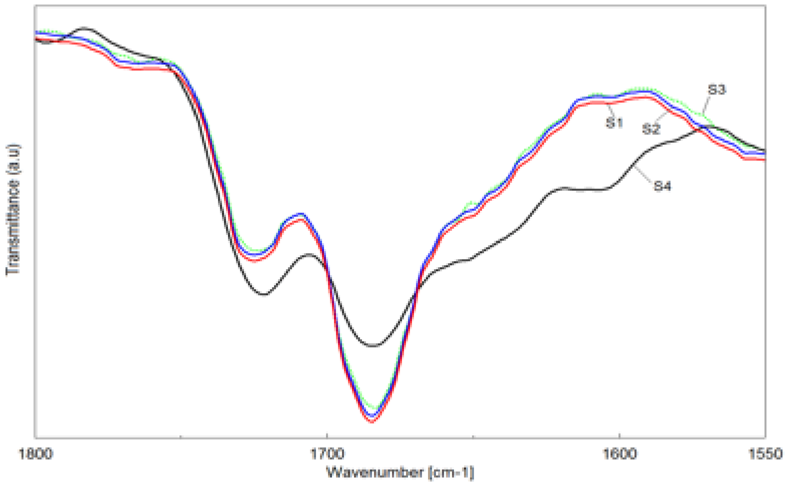

Fig. 3. ATR/FTIR spectra recorded on the carbonyl groups region of the investigated samples

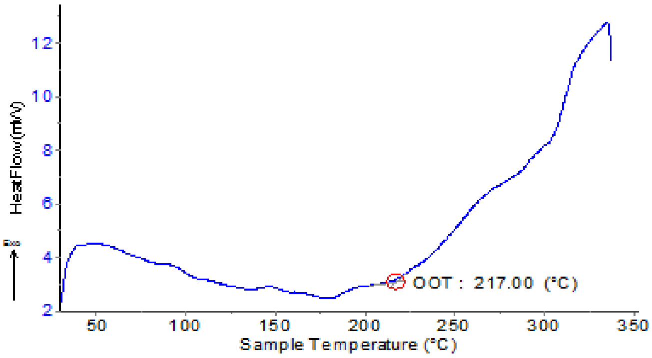

Fig. 4. DSC curve (10 °C/min)

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^2/β) vs. 1/OOT (β is xx 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/β) 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.

Table 4
HEATING RATES AND AGEING CONDITIONS INFLUENCE ON OOT VALUES

Heating rate [°C/min]	OOT [°C]			
	S1	*S2*	*S3*	*S4*
2.5	208	207	207	197
5	217	216	214	204
10	223	221	220	209
15	227	227	226	218

Table 5
ACTIVATION ENERGY OBTAINED FOR **S$_1$**

β* [K min^{-1}]	OOT [°C]	OOT [K]	1/OOT [K^{-1}]	OOT^2/β [K·min]	ln(OOT^2/β)	*E$_a$/R* [K]	*E$_a$* [kJ mole^{-1}]
2.5	208	481.15	0.002078	92602.1	11.44	21673	180
5	217	490.15	0.002040	48049.4	10.78		
10	223	496.15	0.002015	24636.3	10.11		
15	227	500.15	0.001999	16683.3	9.72		

* conventionally, the heating rate β is expressed as K min^{-1}

Table 6
ACTIVATION ENERGIES **E$_a$** OBTAINED FOR ALL ANALYZED SAMPLES USING DSC OOT VALUES AND KISSINGER [51] METHOD

Sample	*E$_a$/R* [K]	*E$_a$* [kJ mole^{-1}]
S$_1$	21673	180
S$_2$	21159	176
S$_3$	21012	173
S$_4$	18946	151

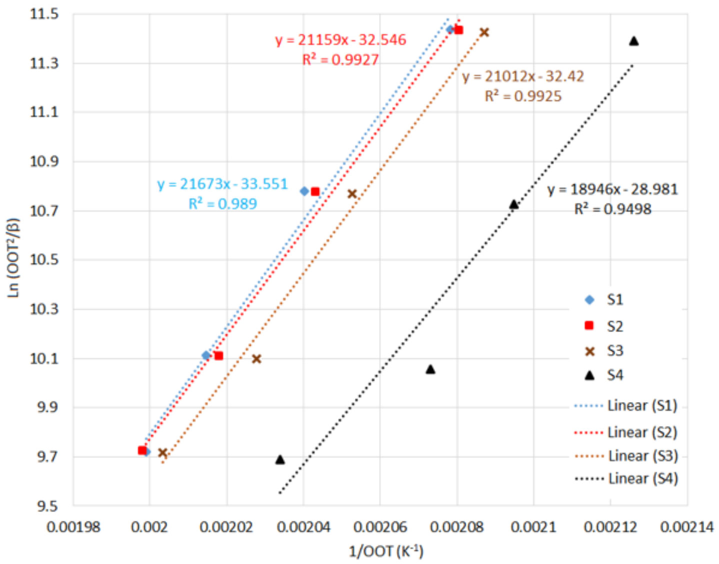

Fig. 5. Plots of ln(OOT^2/â) vs. 1/OOT (Kissinger [51] method)

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/m^2 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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