Failure investigation of a protective epoxy coating by means of crosscheck between infrared spectroscopy and thermal analysis

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Highlights

- an epoxy coating applied on the inner walls of a heat exchanger failed
- IR spectroscopy, thermal analysis and optical microscopy were carried out
- thermo-oxidative degradation of the coating was identified as cause of failure

Abstract

This paper reports the failure of an epoxy coating that was applied for corrosion prevention on the inner walls of a heat exchanger. The coating became brittle and detached from the walls of the exchanger after one year of service. An investigation was performed in order to evaluate the failure cause by means of thermal analysis, optical microscopy and infrared spectroscopy. Thermal analysis excluded an incomplete curing of the detached paint. Optical microscopy highlighted sediments, pores and cracks over the detached coating surface; infrared spectroscopy revealed vibrational bands associated with thermo-oxidative phenomena. A thermo-oxidative simulation was performed on fresh coating samples, pointing out that epoxy coating starts degrading around 100-120 °C. Taking into account the temporary malfunction of the cooling system reported by the user, the failure cause was identified in an overheating that induced a thermo-oxidative degradation of the coating and its subsequent embrittlement and detachment.

Keywords

epoxy protective coating; heat exchanger; FT-IR spectroscopy; thermo-oxidation; thermal analysis

1. Introduction

Organic coatings are widely used for protection against corrosion and erosion of critical equipment's components such as heat exchangers tubing [1–3]. Among others, epoxy-based paints allow for rapid, in-situ application and generally provide long-term protection [2,3]. This paper reports the failure of an epoxy coating that was applied for corrosion prevention on the inner walls of a heat exchanger conveying seawater. After one year of service, the plant was stopped for ordinary maintenance and the piping system was inspected. The user noticed that coating was detached from the inner walls of heat exchanger. Detached coating flakes appeared brittle and dark-colored. About four months before the failure, the user reported also a temporary interruption in the water cooling supply inside the piping. Fourier-Transform infrared spectroscopy (FT-IR) was used to detect molecular by-products typical of thermo-oxidative degradation (such as carbonyl and amide groups), while simultaneous thermal analysis (STA) to gather information about oxidative and thermal stabilities and to assess the initial decomposition temperature. As already reported [4], a crosscheck between FT-IR and STA has been successfully applied to investigate the weathering effect on coatings degradation.

2. Experimental

Tubing material is an Al-Brass (JIS C687T – Cu 76-79%, Al 1.8-2.5%, Mn <0.2%, Pb <0.05%, Fe <0.05%, Ni 0.2-1.0%, Zn rem.); pipe outer diameter is 22 mm and wall thickness 0.5 mm; inner pipe wall was painted with a protective epoxy coating. First coating layer (bonded to the inner pipe wall) was a red-colored epoxy paint (bisphenol-A diglycidyl ether, amine hardening agent); second coating layer (facing the conveyed fluid) was a green-colored epoxy paint (bisphenol-A diglycidyl ether, amine hardening agent). Conveyed cooling fluid inside the heat exchanger was seawater (inlet temperature 18-25°C, outlet temperature 38-40 °C); outer fluid water vapor (temperature: up to 130°C). A schematic of the heat exchanger pipe section and the coating layers location is represented in Figure 1. Two detached coating samples (sample "A" and "B", originated from different pipe areas) were sent back for analysis. Detached samples were observed by optical microscopy (Optika SZN-2 stereo microscope) and analyzed via Fourier-Transform infrared spectroscopy (FT-IR). FT-IR spectra were acquired via a Thermo-Nicolet Nexus 470 spectrometer, equipped with a diffused reflectance accessory (DRIFT). Abrasion-Drift technique was used: an abrasive paper was used to collect samples from the coatings; a background spectrum was first collected on the abrasive paper, then a diffuse reflectance spectrum of the sample was recorded. Y-axis of FTIR spectra (% Reflectance) have been inverted for clarity. Differential Scanning Calorimetry (DSC) measures were carried out by means of a Netzsch DSC 200 F3 Maia in calm air both on fragments detached form the pipe in order to determine the possible presence of unreacted material and / or residual solvent. The thermal cycle was set as follows: initial stand-by at 20°C for 10 min; heating from 20°C to 200°C at 10 K/min. In order to understand the reasons of coating embrittlement and failure, fresh coating samples were prepared in laboratory. Specimens were obtained after mixing "green epoxy" or "red epoxy" with the amine hardening agent in a 77:23 ratio, as suggested by technical data sheet. Coatings were cured at room temperature for 24 hours, and then heated at 50°C for 4 hours. Thermogravimetry (TGA) and Differential Thermal Analysis (DTA) were performed on these samples in order to characterize the degradation phenomena. Materials were heated from 25°C to 1000°C, with a heating rate of 10K/min, in dynamic air, using a Netzsch STA 409 EP instrument. Fresh epoxy coatings were finally

thermally aged in ventilated oven (temperature variation: ±2°C) to simulate a thermo-oxidative degradation. Aging tests were performed for 2 hours, at 90°C, 100°C, 120°C, 140°C and 200°C, and at 120°C for 16 hours. Afterwards, samples were characterized by means of FT-IR spectroscopy: a comparative evaluation among spectra of new, aged and detached samples was carried out.
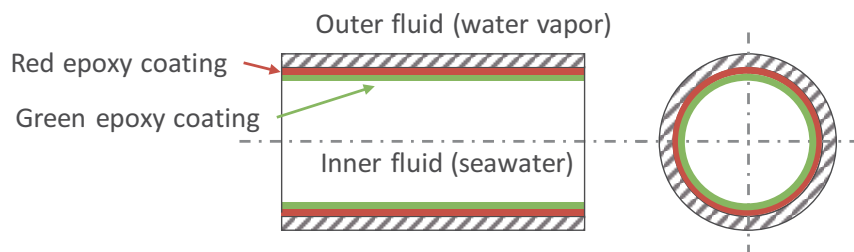

Figure 1. Schematic of heat exchanger pipe section and location of red and gren coating layers.

3. Results

3.1. Visual inspection and optical microscopy

Visual inspection of green coating on sample A shows some surface sediments and pores all over sample surface (Figure 2). At optical microscope observation (Figure 4a), many cracks can be seen; cracks are spread all over sample surface.
On red coating there are no evident porosities, but some sediments can be seen (Figure 4b), with colors ranging from ochre (lower part), to brown (central part) up to white (upper part). These deposits, probably already attached on pipe walls before coating application, were embedded inside the red coating.
Green coating on sample B (Figure 3a, Figure 5a) appears brown-tarnished and it is characterized by many surface sediments. Some small pores are noticeable, even if less abundant than in sample 1. Red coating on sample 2 (Figure 3b, Figure 5b) is characterized by large dark areas; in other areas the red coating does not show deposits or cracks.
Figure 6 shows a visual comparison of color change induced by simulated thermal aging on coatings: all samples were kept at the respective temperatures for 2 hours, except for samples at 120°C (which were left in the oven for 2 and 16 hours). Samples up to 120°C - 2h do not show significant color change, whereas for higher temperatures (or longer time at 120°C), an overall darkening effect is noticeable.
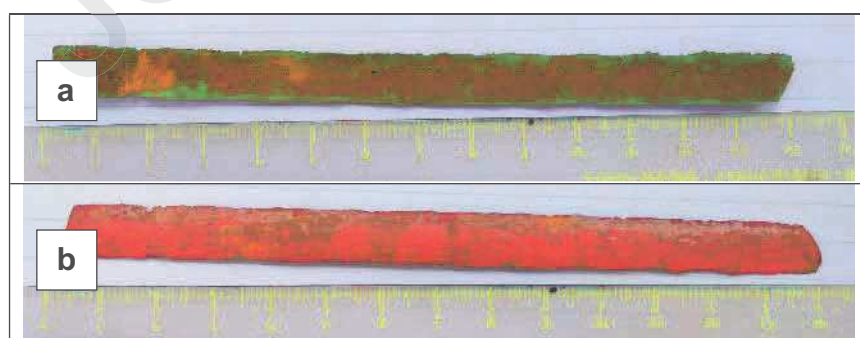

Figure 2. Visual survey of sample A: (a) inner surface of the coating, facing conveyed fluid; (b) outer surface of the coating, facing the pipe wall.
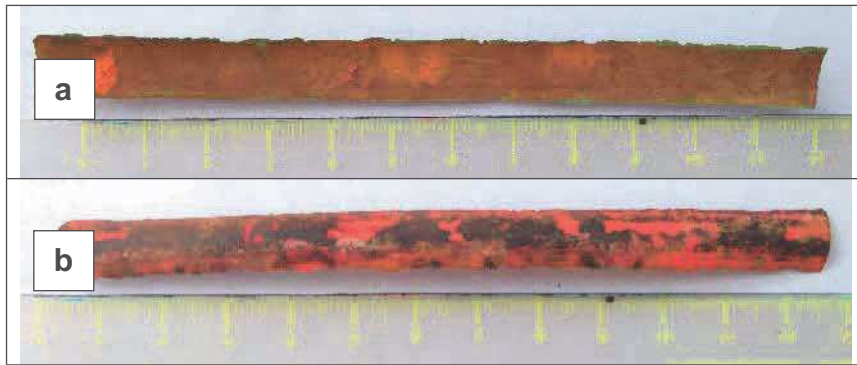
Figure 3. Visual survey of sample B: (a) inner surface of the coating, facing conveyed fluid; (b) outer surface of the coating, facing the pipe wall.
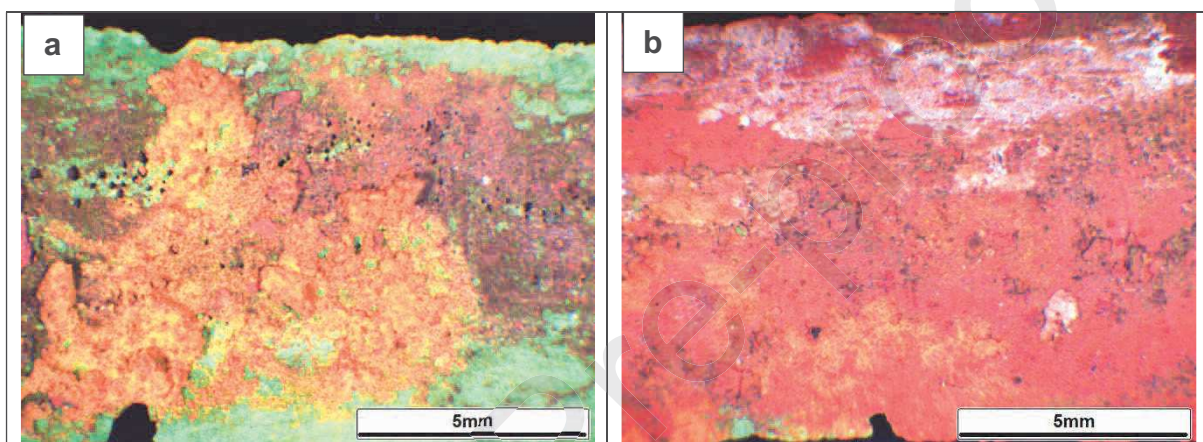

Figure 4. Optical microscopy of sample A: (a) inner surface of the coating, facing conveyed fluid; (b) outer surface of the coating, facing the pipe wall (right).
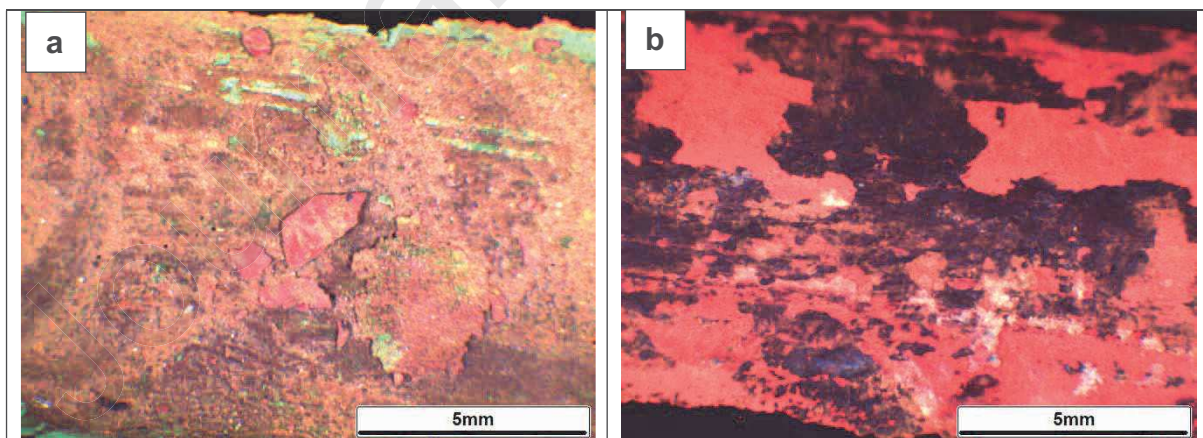

Figure 5 – optical microscopy of sample B: (a) inner surface of the coating, facing conveyed fluid; (b) outer surface of the coating, facing the pipe wall.
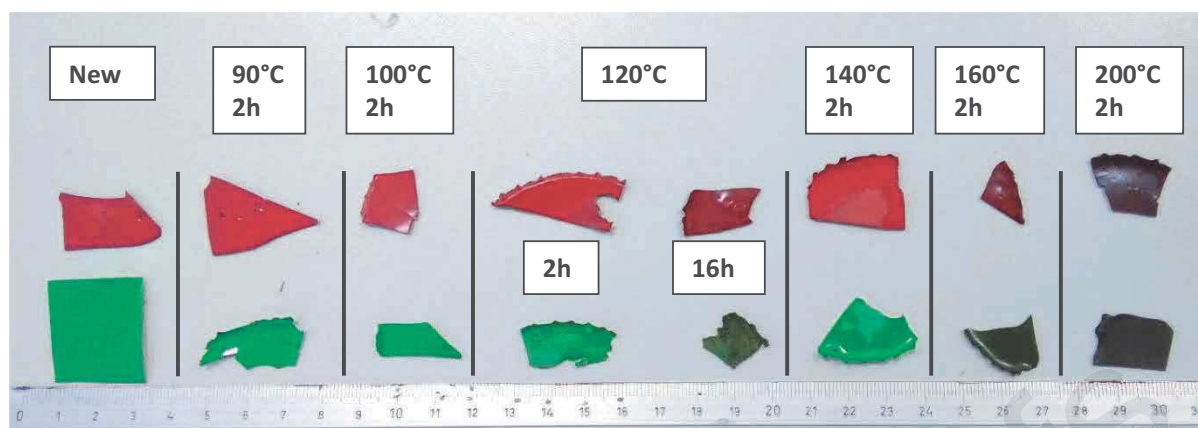
Figure 6 – Color change in samples subjected to thermal treatments.

3.2. FT-IR spectroscopy

FT-IR spectra of detached coating were compared with spectra of new samples realized in laboratory. From FT-IR data analysis, new coatings show vibrational bands compatible with an epoxy resin derived from mixed aliphatic-aromatic chains and an amine hardener [5–7]. Identified vibrational bands are summarized in Table 1.

Table 1. FT-IR bands of coating obtained in laboratory and coating detached from pipe walls.

Band (cm^{-1})		Assignment
New coating	Detached coating	
~ 3420	~ 3420	OH stretch
3050	3050	arom CH stretch
2960	2960	CH stretch
2925	2925	CH_2 stretch (asym.)
2870	2870	CH_2 stretch (sym.)
-	1730	C=O stretch
-	1650	Amide - I
1605	1605	
1580	1580	
1512	1512	arom. C=C stretch
1470	1470	
1440	1440	CH_2 bending deformation
1292	1292	C-O-C stretch
1250	1250	C-N stretch
1271	1271	C=O deformation
1185	1185	C-O stretch
1040	1040	C-O-C stretch

From the comparison (Figure 7) between the spectra of fresh green coating and detached green sample two additional peaks (at 1730 cm^{-1} and 1650 cm^{-1}) can be noticed in the latter one. The first peak, related to carbonyl stretch, is usually associated with generic thermo-

oxidative degradation of polymers, while the second band is related to an "amide-I" vibration (carbonyl and C-N vibration overlap), typically linked to amine group oxidation [7–9]. Fresh red coating shows the same vibrational bands already seen for green paint; the only difference consists in a small peak linked to carbonyl group, most likely due to the presence of a filler or a dye. Spectra comparison (Figure 7) between new and detached red samples shows an extra peak at 1650 cm^{-1} (amide-I) and an increase in intensity of 1730 cm^{-1} peak (carbonyl stretch). These peaks, already examined in the previous case (green coating), are linked to thermo-oxidative degradation phenomena of epoxy resins [8–10].

Aged coating spectra, if compared to new coating ones (Figure 8 and Figure 9), show the already mentioned extra peaks (1730 cm^{-1} and 1650 cm^{-1}). These peaks start emerging around 100-120°C. Intensities of degradation-related peaks rise with the aging temperature. The same peaks are visible in the spectrum acquired from coating detached from pipe walls, although the relative intensity ratio is different. The comparison between spectra of coatings aged for 2 hours at 120°C with those belonging to coatings aged for 16 hours at the same temperature (Figure 9, Figure 10 and Figure 11) shows how the degradation-related peaks (1730 cm^{-1} and 1650 cm^{-1}) intensities increase for longer aging times.
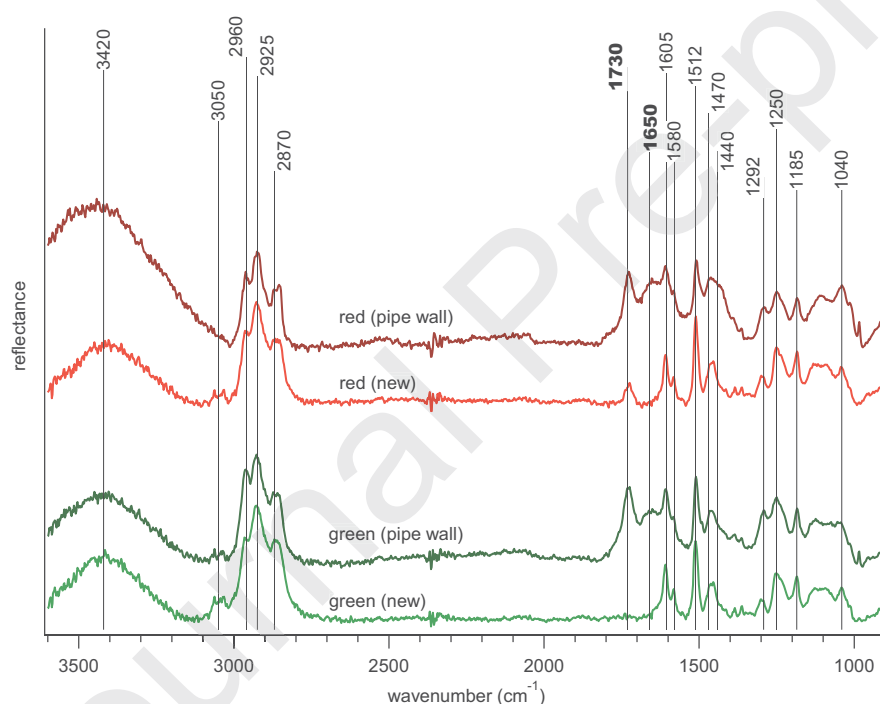

Figure 7. FT-IR spectra of new coatings and coatings detached from the pipe wall, from bottom to top: fresh green paint, detached green sample, fresh red paint and detached red sample.
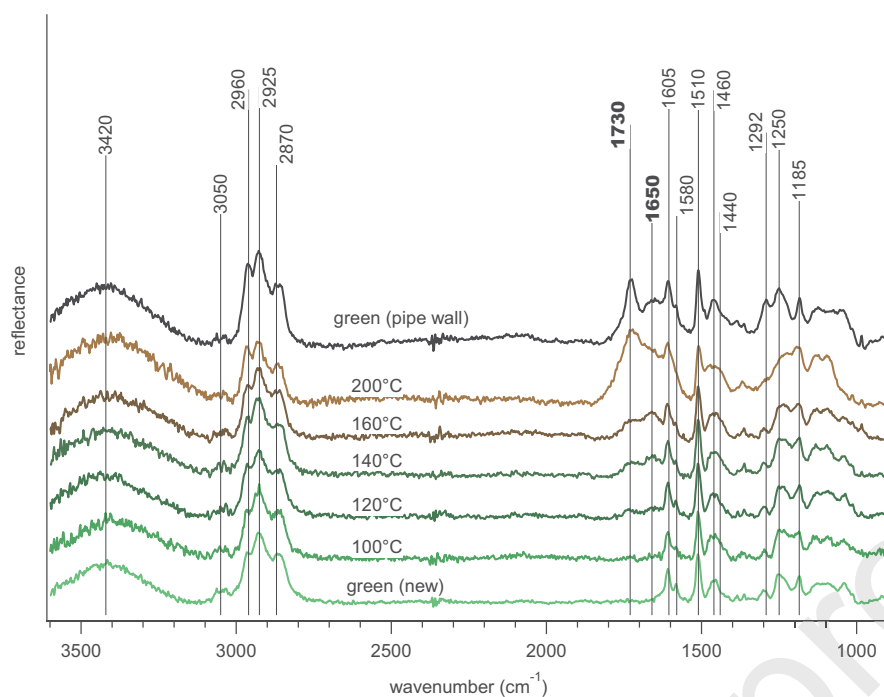
Figure 8. FT-IR spectra comparison of laboratory aged green sample with fresh green coating and detached green coating, from bottom to top: new green coating, aged green coatings (aging temperature above the curves) and green coating detached from the pipe wall.
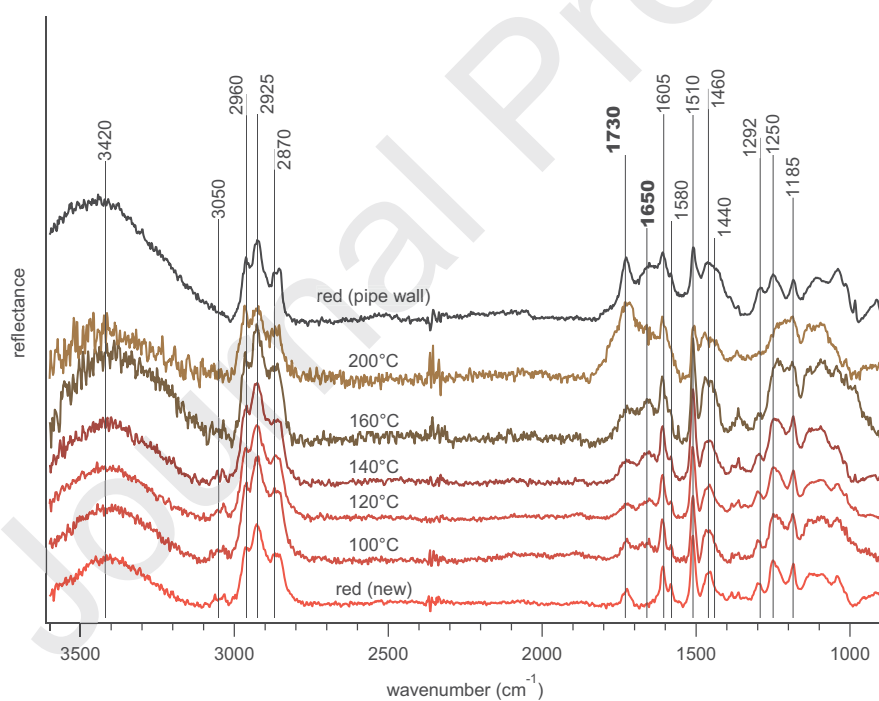

Figure 9. FT-IR spectra of aged red coating compared with new and detached red coatings, from the bottom: new red coating, aged red coatings (aging temperature above the curve) and red coating detached from the pipe wall.
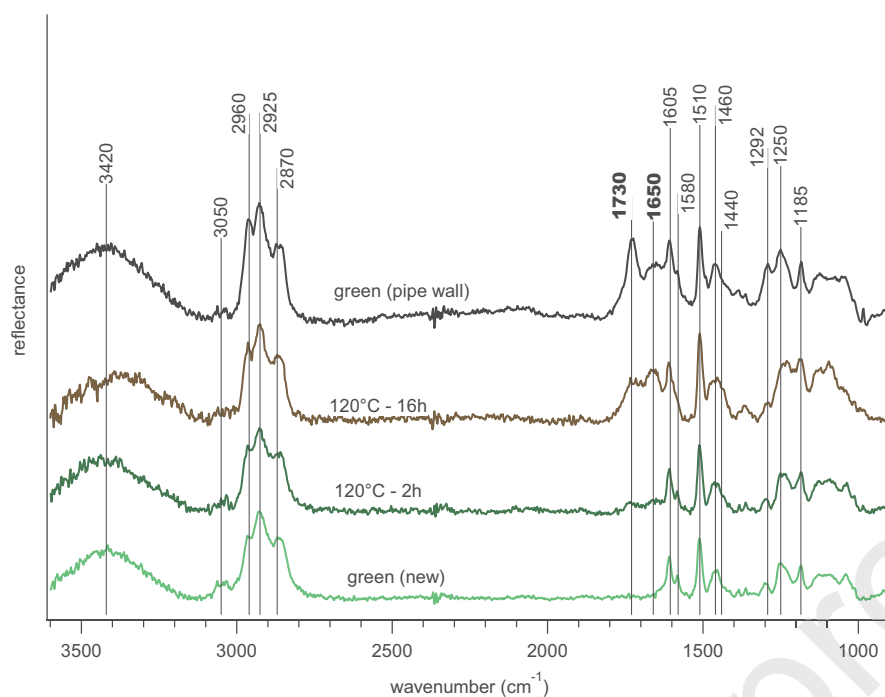
Figure 10. FT-IR spectra of aged green coatings at 120°C 2h (dark green curve) and 16h (brown curve), new green coating (bottom green curve) and green coating detached from the pipe wall (black curve).
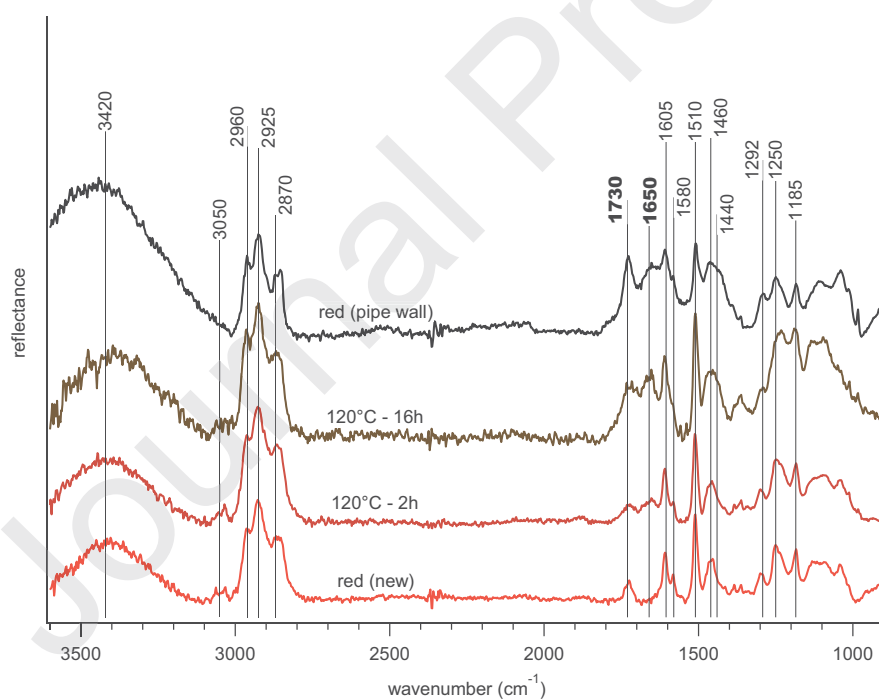

Figure 11. FT-IR spectra of new red coating (bottom curve), red coatings aged at 120°C for 2h (dark red curve) and for 16h (brown curve) and red coating detached from the pipe wall (black curve).
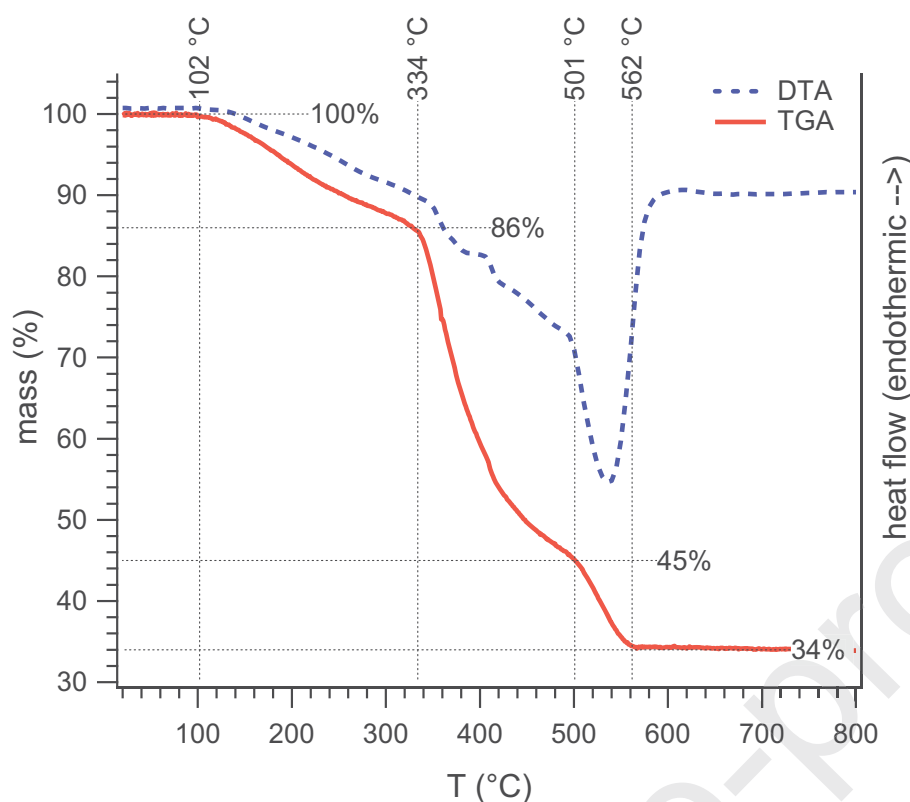
Figure 12. TGA and DTA curves of coating produced in laboratory.

3.3. DSC-TGA measurements

DSC measurements on the coating detached from the pipe wall and on fresh prepared coating did not show any exothermic peaks in the 20°C-200°C range, pointing out a complete cross-linking [11,12]. The fresh coating showed a glass transition temperature around 165°C, in line with previously reported data for similar compounds [13]. We performed simultaneous thermal analysis (TGA and DTA curves) on the fresh coating, to study mass change and heat evolution as a function of temperature. TGA and DTA are reported in Figure 12. Coating starts losing mass above 100 °C; a first degradation step (102-334°C) correspond to a loss of 14% original sample mass; a second, faster degradation step (335-501°C) – residual mass 45%; and the final step concluding around 560°C. Residual inorganic mass is about 33% of the original sample mass. The starting temperature of the first degradation step (102°C) complies with the starting of the thermo-oxidative degradation detected after aging simulation in oven. DTA show evolution of heat between 110°C and 600°C, with two exothermic feature between 102-300°C, 330-500°C, and one exothermic peaks around 540°C, corresponding to the mass decreasing steps seen in TGA.

4. Conclusions

An investigation has been performed in order to evaluate the degradation of some coating flakes, detached from the inner wall of a heat exchanger, by means of optical microscopy,

infrared spectroscopy (FT-IR) and thermal analysis (DSC, STA). The following conclusions derive from these analyses:

- optical microscopy shows some surface sediments, pores and many cracks spread all over sample surface;

- FT-IR spectroscopy reveals two peaks at 1730 cm^{-1} and 1650 cm^{-1} for detached coating samples: the former is related to carbonyl stretch and usually associated with generic thermo-oxidative degradation of polymers, while the latter is related to an "amide-I" vibration;

- the absence of exothermic peaks in DSC traces points out that paints were completely cured;

- FT-IR spectroscopy performed after thermal aging tests demonstrates how the degradation of both red and green resins can be simulated using an oven. Thermo-oxidation starts at 100-120°C, and increases both for temperature and exposure time;

- TGA shows that epoxy coating starts losing weight above 100 °C.

Considering the temporary stop/malfunction in the water cooling supply reported by end-user, experimental findings leads to the conclusion that coatings were exposed to vapor (120-130 °C) for several hours, without the cooling effect of the conveyed fluid. This situation has most likely led to pipe wall overheating (over 100-120°C), causing a thermo-oxidative degradation of the coating. This degradation led to an embrittlement and change in the coating surface chemistry, negatively affecting its adhesion properties [14] and causing a subsequent detachment from the pipe, with the thermal stress resulting from the overheating being a concurrent cause. In normal operative condition, conveyed seawater has been able to avoid this overheating problem.

5. References

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