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Failure analysis of a GFRP pipe for oil transport

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ABSTRACT

The study was conducted on a pipe sample of GFRP. There was widespread damage in the internal structure of the tube. The flow area was blocked due to landslides helical fibers. The matrix was an epoxy–anhydride system (Diglycidyl Ether of Bisphenol A). There was an advanced state of diffusive processes that reduced the glass transition temperature (T_g) of the material to critical levels. The material showed a major irreversible hydrolytic attack. The mechanical behavior would indicate a considerable degree of structural compromise. The sample showed an advanced state of degradation, with clear signals of processes activated at temperatures close to T_g and catalyzed by the diffusion of low molecular weight organic species. The irreversible chemical degradation process especially attacked the fiber–matrix interface reducing the mechanical performance.

1. Introduction

The use of GFRP pipes is growing sharply in the oil industry, by replacing the traditional steel pipes in the processes of transport and more recently the extraction of petroleum. Composite pipes are a low cost alternative for reducing corrosion problems arising when using steel pipes, especially in regions with mature reservoirs where large quantities of water are injected in the wells in order to obtain the oil (which in some cases represent less than 15% of the total extracted fluid). But even when GFRP pipes do not suffer corrosion, they do degrade in contact with solvents and water [1,2]. This process can be dramatically accelerated when the temperature in increased [3]. Previous results have clearly shown the influence of diffusion process in FRP piping degradation [4]. Several publications have studied the effect of water in the degradation process of epoxy/glass composites. Imielińska and Guillaumat [5] studied the impact behavior of glass–aramid fiber/epoxy laminates after water immersion aging. They found that the aging process affected microstructural integrity, causing numerous internal defects and a reduction in the impact resistance and compression strength after impact. Also Buehler and Seferis [6] found a decrease of the mechanical properties of epoxy/glass composites (mode I and mode II Mode I interlaminar fracture toughness) upon water absorption. In Addition, the effects of hygrothermal degradation can be worsened by sorption and desorption cycles. Jacquemin and Vautrin [7] studied the effect of cyclic hygrothermal degradation in thick composites pipes. They found a strong stress concentration (and therefore fatigue) within a narrow region near to the surfaces where holds the periodic moisture concentration.

The operation temperature is another important variable that determines the degradation resistance of the composite pipes. Over the market, low and high temperature products can be found. Usually low temperature products are recommended for operate up to 65 °C, meanwhile high temperature products are expected to operate at 93 °C maximum. In both cases the difference between the matrix glass transition temperature (T_g) and the operating temperature (Top) is between 40 and 50 °C, which assure to be operating far enough of the glass transition in order to avoid network mobility consequences.

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However, many times according weather and operating conditions the fluid temperature can easily increase getting up to 75–80 °C, especially when electrical submersible pumps are used. In case of low temperature FRP piping working above 65 °C the difference between the T_g and Top decreases up to 25 °C. This condition increases network mobility not only decreasing mechanical properties but also increasing diffusion process. A catalytic degrading process takes place. The speed of diffusion increased, the low molecular weight species intake also increases and the T_g decreases [3]. The lower the T_g, the closer it will be to Top (o the smaller (T_g–Top)). The continuous decreasing in T_g makes it reach values really close to Top which induce erosion effects produced by fluid shear forces acting on the pipe inner wall. The situation is fairly influenced by the fluid composition. Among low molecular weight organic species, aromatics diffuse faster and reach high absorption values reducing drastically T_g [8]. On the other hand when water is the main component diffusion is slower but in epoxy–anhydride systems, hydrolytic degradation takes place.

In this work the damage level in a 8″ GFRP pipe is evaluated and the degradation mechanisms present in the component are analyzed in order to find its failure causes.

2. Materials and methods

2.1. Operation conditions and geometrical characteristics

Information about the operation conditions of the pipe was gathered from the field and supplied by the manufacturer. A dimensional analysis using standard calipers and micrometers was performed in order to obtain the main geometrical parameters of the tube.

2.2. Desorption

Desorption was performed by placing the samples in an oven at 80 °C. The weight loss versus time was recorded. Six samples were placed: 3 from zones of the pipe with no delamination, i.e. with no detachment of layers of fibers (6.9 mm nominal thickness) and 3 from a delaminated area (4.0 mm nominal thickness). The latter are more representative of the failed zone.

2.3. Differential scanning calorimetry (DSC)

DSC tests were performed in a differential scanning calorimeter DSC-50 Shimadzu. A first run was carried out from room temperature to 200 °C at a heating rate of 10 °C/min, followed by rapid cooling and a second run at the same heating rate and to the same temperature. The study was conducted on as-received samples. The evaluation was performed on at least two specimens (duplicate), on the outside and inside the duct.

2.4. Thermogravimetric analysis (TGA)

Thermogravimetric analysis were conducted in a Shimadzu TA-50 equipment at a heating rate of 10 °C/min under nitrogen atmosphere. Samples from the inner part of an undegraded pipe (unused, from the same brand and characteristic that the failed one) and from two different portions of the failed tube were taken for the experiments.

2.5. Determination of the content and angle of the fibers

Three rectangular samples of 1 × 2 in. were cut, weighed and placed in muffle 2 h at 250 °C and 3 h at 565 °C. Then weighed again and found the content fibers each. The winding angle was calculated from the analysis of images of different layers of fibers obtained after calcination. The samples were cut with the long side perpendicular to the tube generatrix, in order to get a reference for the angle measurements. Before taking the images some fibers were extracted from the layer to reveal the lamination angle with respect to the generatrix. The images were obtained in an optical microscope (Olympus SZH10) and analyzed with appropriate software, in different areas of the pipeline. Particular attention was paid on those areas where degradation was observed macroscopically.

2.6. Flexural properties

Mechanical behavior was studied in a universal testing machine ISTRON 4467 under three point bending geometry according to ASTM D-790/03. The obtained curves and the values of initial stress–strain curve slope and the maximum strength were recorded. In order to establish occurrence of reversible or irreversible degradation processes, as-received and after desorption (equilibrium weight) samples were evaluated. Due to the fact that the amount of useful samples is limited by the degradation state of the tube, statistical analysis of the results were conducted in order to determine the significance of the mean values. Paired sample student's t-test were applied to the flexural strength values, with a limit for considering significantly different two set of results of $p < 0.05$.

2.7. Scanning electron microscopy (SEM)

SEM images of the internal and external surface of the material were taken in a SEM JEOL JSM 6460 LV. The images representing the state of each surface were reported.

3. Results and discussion

From a first visual inspection, the received pipe was characterized by the degree of macroscopic observable degradation. The following considerations were stated:

- The general condition of the surface was acceptable. No damage was observed considered due to the interaction with the external environment, as can be seen in Fig. 1a and b. Fig. 1c shows a pictured obtained in field.
- The flow area was blocked due to displacement of successive layers (fiber/matrix) of the material (Fig. 1d).
- A significant portion of the thickness of the pipe wall has been lost due to detachment of the inner layers (Fig. 1e).
- After removing loose material proceeded to take samples for make the characterization of the remaining wall. Unless otherwise stated, is called inner surface of the product to one that was obtained after removing the loose material that can be seen in Fig. 1d and e.
- When cutting interlaminar cracks were not observed in any of the surfaces exposed.

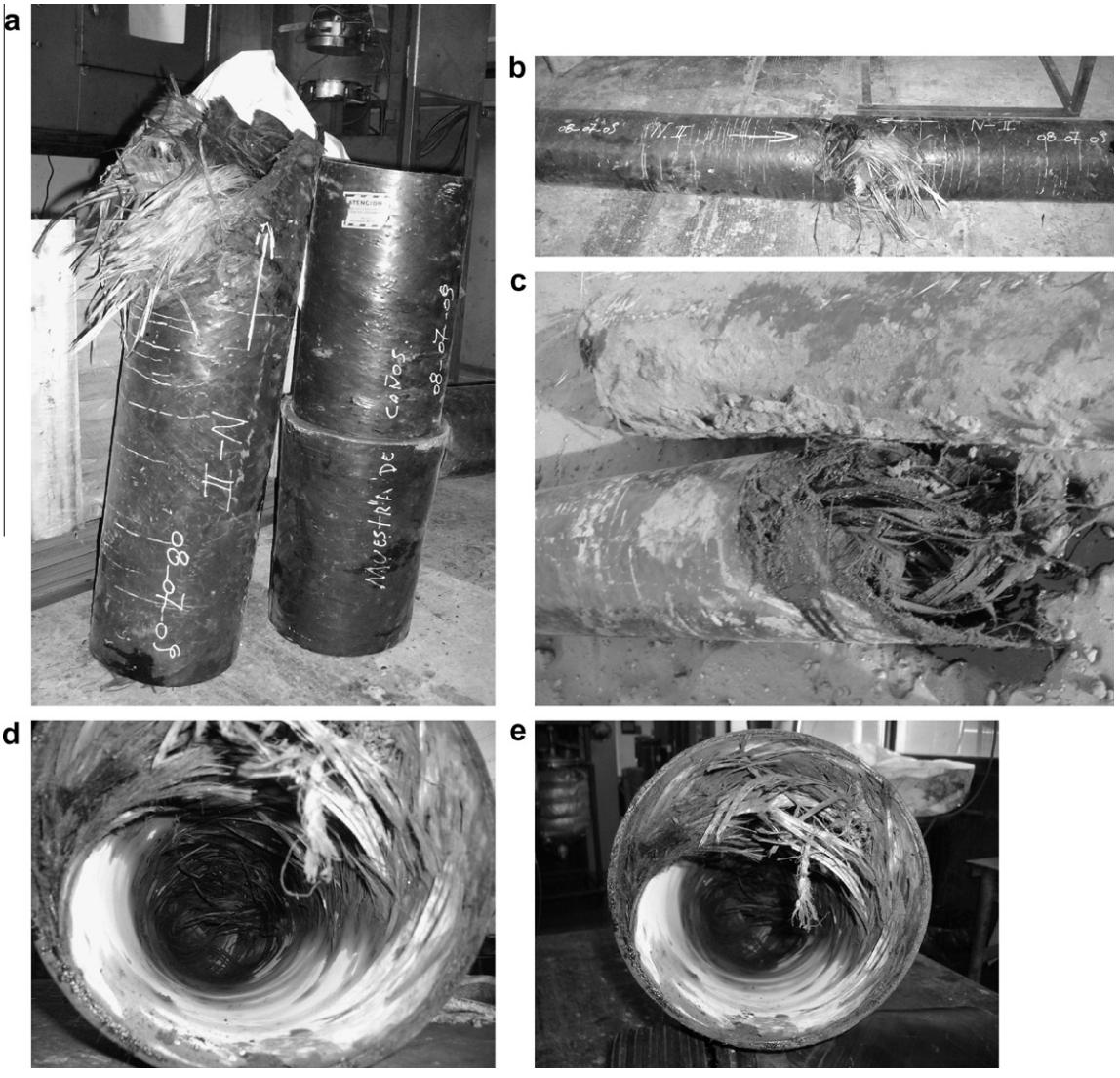

Fig. 1. Photograph of received pipe: (a) and (b) global view; (c) image obtained from field; (d) blocked flow area; (e) reduction in thickness due to detachment of fibers.

Table 1 presents the information gathered in field and from the pipe customer about the operation conditions and main geometrical characteristics. In order to check the actual dimensions of the tube, the thickness along the perimeter and the outside diameter were measured. The results are presented in Fig. 2, and summarized in Table 2. Fig. 2 shows that the thickness has high variations along the perimeter, in part attributable to the fabrication process but also due to loss of material caused by the degradation process. The reduction of the wall thickness is often the beginning of failure events, since it produces local stress concentration.

Fig. 3 presents the results of the desorption tests. It can be seen a clear different behavior between the samples from the delaminated area and the samples from the no delaminated zone. The equilibrium values obtained for the specimens of 6.9 mm in thickness are close to 1.2%. For samples of 4.0 mm nominal thickness values of 1.8% to 2.5% were reached. These values indicate very high content of low molecular weight species that spread in and plasticize the epoxy matrix composite, reducing the glass transition temperature and accelerating the relaxation processes that catalyze dissemination. Volatile contents above 0.75% can only be achieved at temperatures near T_g. It should be noted that according to our experience, and in agreement with other authors [2,3], at temperatures above 70 °C the hydrolytic degradation processes that affect

Table 1
Characteristic of received failure pipe.

Outer diameter	229.5 mm (8.98″)
Nominal thickness (customer data)	6.99 mm
Chemical system	Epoxy–anhydride
Uptime	8 years
Operating temperature	50 °C
Distance from battery	3700 m
Flow rate	2400 m^3/day
Fluid composition	50% water/50% crude oil

Angle	thickness (mm)
16	5,62
49	6,66
81	5,96
114	6,06
147	5,68
180	6,70
212	6,76
229	6,34
245	6,08
261	6,10
278	6,58
294	7,14
310	6,98
327	7,06
343	6,72
360	5,84

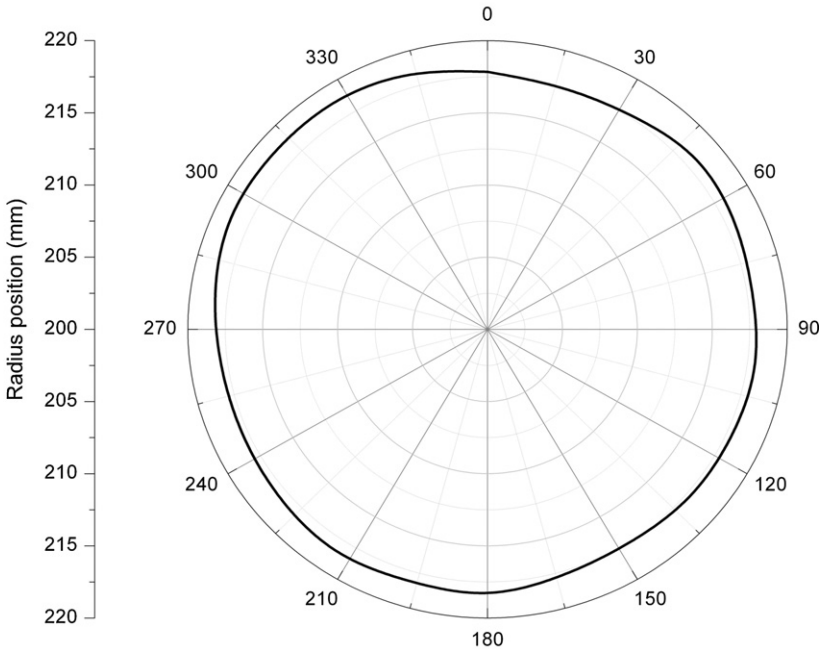

Fig. 2. Wall thickness at different points in of pipe perimeter.

Table 2
Dimensional analysis.

Section	Measurement
Outside diameter	229.5 mm (9.03″)
Average thickness (Fig. 2)	6.54[a] mm ± 0.8 mm

[a] Some sections swollen by solvent absorption with release of fibers have not been taken into account in the thickness average.

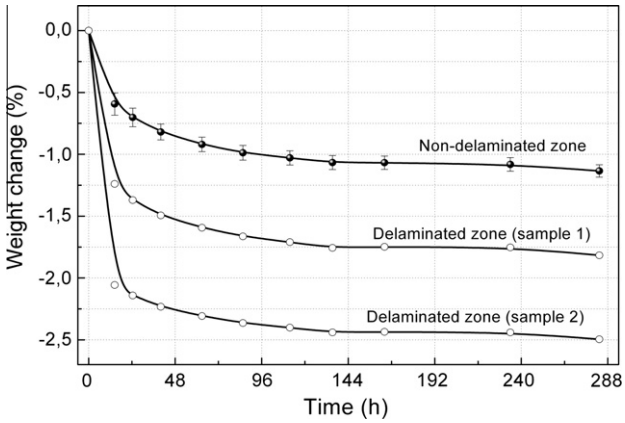

Fig. 3. Curves of weight variation as a function of time (desorption in an oven). The upper curve shows the average of 3 samples taken from the non-delaminated area. The two lower curves correspond to individual samples in the delaminated area (it is seen that the values are averages).

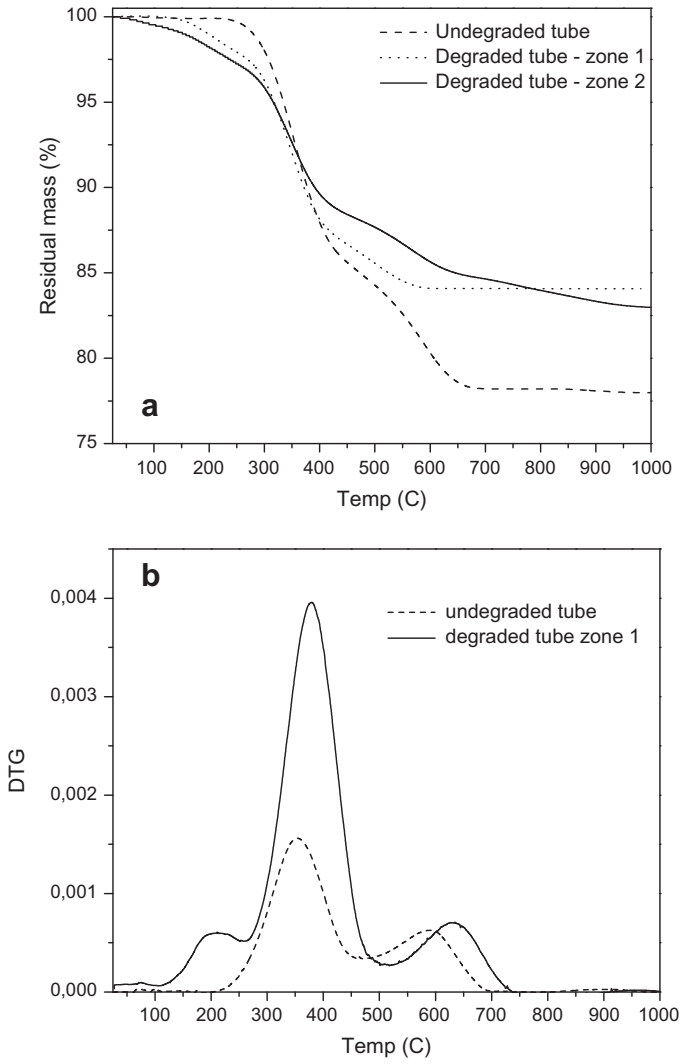

Fig. 4. (a) TGA curves for an undegraded epoxy–anhydride composite pipe and for different zones around the failure in the degraded pipe. (b) DTG curves for the same materials.

the matrix and fiber–matrix interface are accelerated considerably. The analysis of thick samples indicates that the diffusive processes extend throughout the thickness of material which could reduce significantly the mechanical behavior of the product. In order to have a better understanding of the kind of species that diffused in the polymer matrix, TGA studies were conducted. Fig. 4a shows the mass loss as a function of temperature for two zones near the failure in the used pipe and also for an unused pipe. The degradation of the epoxy–anhydride resin takes place in two steps, from 200 to 400 °C and from 500 to 700 °C. The main degradation peaks can be seen also in the DTGA curves (Fig. 4b). When comparing the undegraded and degraded pipes, a third peak arises in TGA analysis of the second one, which can be attributed to desorption of low molecular weight organic species. This process occurs from 100 to 200 °C and is different from the moisture evaporation that takes place below 100 °C.

Fig. 5 shows the thermograms obtained from the first, second and third run on the outside of the product (similar curves were obtained for the inside part of pipe). The curves obtained for samples from the outside pipeline exhibit the presence of an exothermic peak (Fig. 5) that could be an evidence of residual heat. The samples studied showed a low transition temperature, in the order of 50–60 °C, which could be attributed to the plasticizing effect produced by the diffusion of low

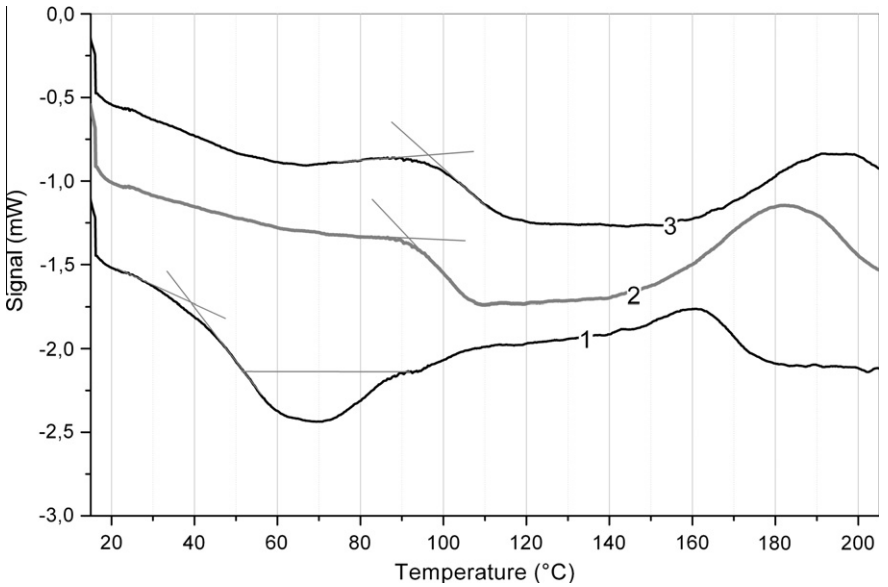

Fig. 5. Curve of signal (mW) as a function of temperature obtained by Differential Scanning Calorimetry (DSC) of the outside of the duct. Determination of glass transition temperature (T_g). The numbers (1, 2 and 3) indicate the run.

Table 3
Winding angles of received samples.

Layer from	Fiber angle β		Angle between layers
	Layer 1	Layer 2	
External third	55°37′	56°19′	68°04′
Internal third	56°06′	56°00′	70°53′

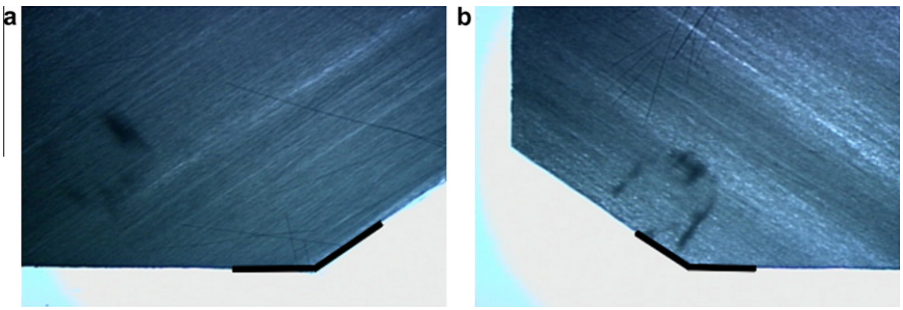

Fig. 6. (a) and (b) Micrographs showing the winding angle of two successive layers of fiber.

molecular weight compounds and/or to the hydrolytic degradation [9,10]. In general, both effects can be treated separately, as the former is reversible while the latter clearly is not.

Davies et al. [11] have studied long term behavior of epoxy–anhydride/glass composite tubes exposed to hygrothermal aging. They found that after 7 years of immersion in distilled water at 60 °C, the tubes showed a decrease in T_g from 124 °C to 86 °C. They have also found a dramatic fall in the expected lifetime if the temperature of immersion exceeds the 60 °C (less than 1 year at 80 °C). The lower values of T_g found in the failed tube suggests that the operation temperature could have been higher than the maximum operation temperature (65 °C). The composition of the transported fluid (50% water/50% oil) can worsen the operation condition by adding, to the hygrothermal degradation, the plasticizing action of the low molecular weight organic compounds [8].

From the burning of samples taken from the pipe, winding angles and fiber content were obtained. The average fiber content measured was 69.52%. Winding angles are listed in Table 3. Fig. 6 a and b show examples of the winding angles of two successive layers con the composite. The fiber content obtained is less than the nominal value of 75%. The reduction of the fiber volume fraction seems to be caused by variations in the manufacturing process, but is in the range of acceptable values for oil transport GFRP pipes. For his part, the winding angle showed no significant differences between delaminated and not delaminated areas. In both cases it remains close to the optimal value (±55°). This theoretical angle can be obtained by netting analysis, and it is based on the assumption that a simply pressurized structure is subjected to twice as much hoop stress as it is to axial stress, which is a design approach common in industry [12].

Mechanical properties obtained from flexural tests are summarized in Tables 4 and 5. The stress–displacement curves of the samples without desorption are shown in Fig. 7. It is difficult to establish a level of damage without the values obtained

Table 4
Results obtained in the flexural tests for samples before desorption (as received).

Id	Strength (MPa)	Modulus (GPa)
1	114.81	9.88
2	89.77	7.72
3	102.23	7.91
4	124.83	8.14
5	80.62	4.23
Mean value	102.4 ± 17.9	7.58 ± 2.1

Table 5
Results obtained in the flexural tests for samples after desorption.

Id	Strength (MPa)	Modulus (GPa)
1	71.73	11.61
2	67.15	6.22
3	80.81	5.53
4	118.91	8.14
5	121.80	5.13
Mean value	92.1 ± 26.3	6.5 ± 2.9

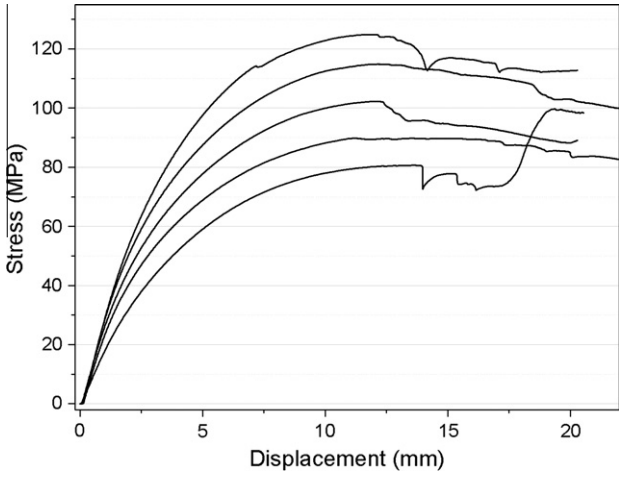

Fig. 7. Stress–displacement curves obtained in the flexural tests of samples without desorption.

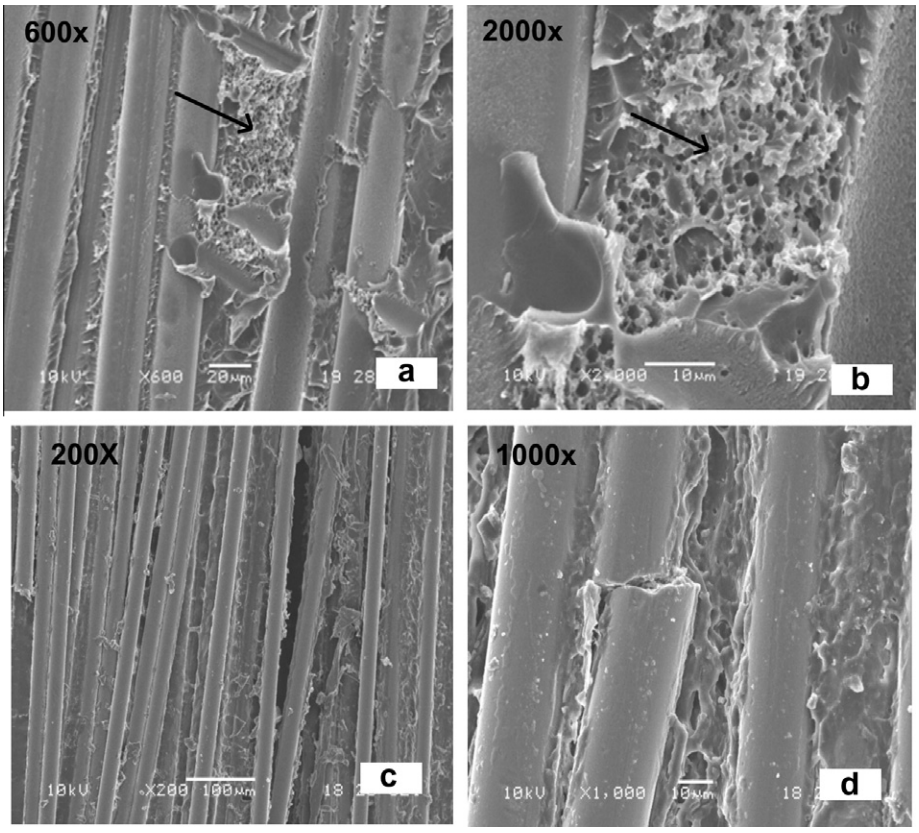

Fig. 8. SEM micrographs of the different layers of pipe: (a) and (b) fluid contact layer; (c) and (d) layer after layer fluid contact (closer to the outer surface).

on the evaluation of material at the beginning of its service life. A good approximation can be considering the deviation of the values registered for similar chemical systems. The obtained values of modulus (E = 7.58 GPa) are lower even in comparison with that expected for a product in extended service. Maximum strength values (102.4 MPa) also seem to indicate that the behavior at large deformation degrees has been worsened. The dispersion of results indicates a lack of homogeneity in the material. Some of the values obtained indicate the presence of highly degraded areas. The results obtained for desorpted samples evidence the combined effect of diffusive processes and chemical degradation. As it can be seen, after losing volatile components, the material did not recover their mechanical properties showing similar values than the original samples. This is confirmed by a statistical analysis (paired sample student's t-test) that reveals that there is no significant difference in the population means of the flexural strength for the as-received and desorpted samples (P = 0.51 which is beyond the limit of $p < 0.05$ for statistical significance).

Fig. 8 shows the images obtained by SEM. In all cases are images of the inner surface of the pipe, or layers near this. Fig. 8a and b are pictures obtained from a layer that was in direct contact with the transported fluid. They show signs attributable to hydrolytic degradation which comprises relatively widespread areas of the sample. Observed gaps in the matrix due to the removal of material and loss of fiber–matrix interface can also be observed. The presence of widespread areas of chemical degradation could significantly affect the mechanical behavior of the product (as is clearly demonstrated by the values obtained in the flexural tests). In Fig. 8c and d can be seen images of an inner layer (the following to the one in contact with the fluid). The damage that can be observed is minor, indicating that the degradation process starts inside the duct and progresses outward.

4. Conclusion

From the experimental studies, the following remarks can be done:

- The general condition of the outer surface of the pipe was acceptable.
- The flow area was blocked due to displacement of successive material layers whereas interlaminar cracks were not observed.
- The desorption results indicated an extremely high level of substance evaporation, more than 1.2–2.5% in some compromised areas.

- The electron microscopy images showed a concentration of defects relatively low, but a generalized irreversible hydrolytic attack.
- The mechanical behavior would indicate a considerable degree of compromised structural material especially for large deformations.
- The sample presents an advanced state of degradation, with clear signs of process activated at temperatures close to T_g and catalyzed by presence of organic species of low molecular weight.
- The irreversible chemical degradation processes have attacked especially the fiber–matrix interface by reducing the mechanical behavior at large deformations.

After conducting a physicochemical and mechanical characterization of a failed pipe it can be conclude that failure was a consequence of cumulative damage in the structure. This damage was not due to an external or sporadic factor but was mainly caused by the continuous hydrothermal degradation of transported fluid. The low T_g and high percentage of volatile solvents in the composites are signs that the working temperature have exceeded the limited temperature for epoxy–anhydride/glass pipes, that is 65 °C. When that happens, the diffusion of low molecular weight hydrolytic degradation of the matrix is activated, the matrix–fiber interface is degraded and the mechanical properties of the composite decrease. In our case of study, these phenomena were observed in the results of the flexural test, the SEM images and the presence of detached fibers inside the tube. The combination of lower mechanical properties due to the absorption of organic compounds and the decrease of the pipe thickness due to the lost of inner material, produce the final failure of the component.

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