

FULL-SCALE FIELD STUDY OF THE PERFORMANCE OF POLYAMIDE 12 ONSHORE OIL PIPELINES

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ABSTRACT

Oil and gas industries are frequently exposed to corrosion challenges in their equipment given the harsh composition of the fluids they usually are exposed to. In order to mitigate such problems, non-metallic materials have been used as a corrosion-resistant alternative to steel. This work aims to experimentally evaluate the use of an unplasticized PA12 (PA-U12) as an alternative to the API 5L steel grade commonly used in onshore oil pipelines, yet more susceptible to corrosion. Test specimens were machined from pipelines operating in onshore fields, and their properties were evaluated. Mechanical properties of PA-U12 were largely preserved even after 8000h of exposure to produced water (pH~7) with hydrocarbon fractions at temperatures ranging from 40 to 80 °C. Analysis of Variance (ANOVA) confirmed that both temperature and position within sample thickness (innermost and outermost surfaces) are statistically significant input factors, however with a limited range of changes and no interaction effect between temperature and position within the thickness. Overall, no significant changes have been observed in mechanical properties that would compromise pipe performance based on the limits established by ISO 23936-1 and API RP17B for small-scale analysis. Therefore, it is possible to conclude that PA12 maintained satisfactory stability for this application in a moderately aggressive environment, compliance with the required mechanical performance defined in widely used international reference documents and criteria.

KEYWORDS: onshore pipelines; polyamide 12 (PA12); PA-U12; mechanical performance.

I. INTRODUCTION

Transporting oil over long distances between collection points, refineries, terminals, and distribution centers has been historically and effectively done worldwide using pipelines. Oil pipelines consist of ducts that operate transporting oil with or without other fluids such as water or gas, which are then referred to as multiphase pipelines and are historically made of steel. Depending on the characteristics of the reservoirs, the oil production supply chain may be exposed to significant corrosion challenges in its equipment, mainly in steel pipelines, given that their base material (carbon steel) is pronouncedly susceptible to corrosion. Such a process of material degradation affects practically all sectors of society and it is estimated that the current cost of corrosion in the United States is about US\$ 276 billion or 3% of Gross National Product (GDP) [1].

Polymeric materials have for decades represented a well-established and consistently corrosion-resistant alternative to conventional metals for use in harsh environments. They have even been used to replace some metallic alloy components due to their excellent chemical resistance to oil and various

contaminants commonly found in reservoirs. One of the main limitations of their use in engineering applications, however, is their mechanical properties when compared to metallic solutions. Although this drawback has historically been addressed not only as the industry advances technologically with emerging high-performance polymers but also with the increasingly common adoption of polymer-based glass/carbon-fiber composite solutions. These new high-performance polymers present structural characteristics that combine attractive properties such as low density, increased mechanical strength and modulus of elasticity (Young's Modulus) and outstanding fatigue and chemical resistance. In addition, their manufacturing processes enable the production of parts with complex geometries, especially with the emergence of advantages brought by 3D printing, offering unique products with higher resistance to corrosion and overall degradation even in the most complex industrial environments [2].

A great example of a high-performance polymer is polyamide, a synthetic thermoplastic known for its impressive physical and chemical properties. Given its outstanding performance, it has historically stood out as one of the most versatile materials for a wide range of industrial and commodity applications. The first known one dates back to the beginning of the 20th century, in the form of fibers for the production of socks, receiving then the still popular name of nylon [3].

Long chain polyamides are polyamides based on at least one monomer having a long alkane segment with 10 or more methylene groups (e.g.: PA11, PA12, PA6.10, PA10.10). Unplasticized long chain polyamides (i.e., polyamide-12 or PA-U12, and polyamide-11 or PA-U11) have been extensively studied and qualified as pressure piping materials for use in natural gas distribution networks at pressures traditionally served only by steel [4]. PA-U12 has been shown to be highly resistant to softening and loss of strength when exposed to liquid hydrocarbons. For these reasons piping system engineers are including PA-U12 as a design option instead of steel in on-shore oil and gas gathering networks and other industrial piping applications [5].

Additionally, a mechanical characteristic of PA-U12 is its tenacity, exhibiting large deformation under stress prior to failure (superplastic behaviour). Despite having lower water absorption, PA12 is subject to aging caused by hydrolysis in the presence of water particularly at elevated temperatures, non-neutral pH values, and over sufficient exposure time, something quite common in the oil and gas industry due to the characteristics of due to the typical flows of oil reservoirs, presenting not only water but also gases like, but not limited to, CO₂ [6].

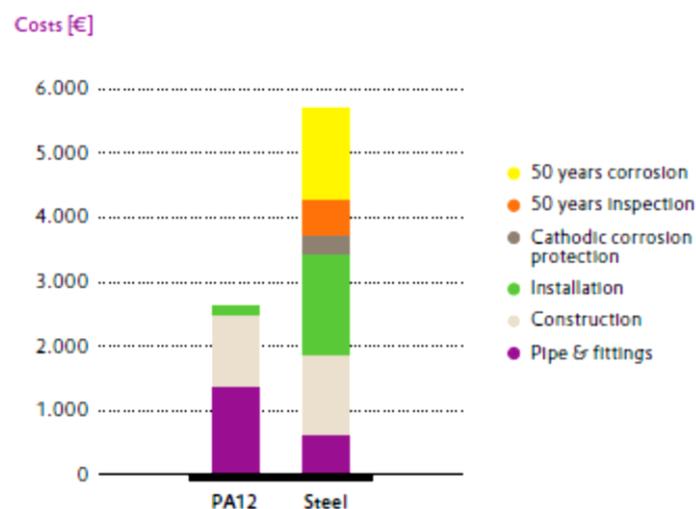


Figure 1 – Cost difference between steel and polyamide 12 pipelines [7].

This work aims to perform an integrity analysis of onshore PA-U12 pipes operating in mature oil fields with over 40 years of production. For this unprecedented application, PA12 has the potential to provide significant benefits to the oil industry, including long-term cost reductions exceeding 50% when compared with steel (Figure 1). In addition, the use of PA12 contributes to mitigate corrosion-related degradation mechanisms that may otherwise result in personal, operational, and environmental damage in the event of failures in conventional steel pipelines used in oil production.

II. METHODOLOGY

2.1. Field installation

Short-length samples of pipes made of unplasticized polyamide 12 (PA-U12) were connected and buried with three carbon steel pipelines from existing oil wells (Figure 2). The 4" (OD) PA12 pipes were 10 mm thick and 1 meter long between weld joints. A pristine control sample (identified as CS) was saved for comparison purposes.

The existing carbon steel pipelines operated with highly corrosive fluid (with contaminants like O₂, CO₂, H₂S and sulphate-reducing bacteria) and temperatures of 40 °C, 60 °C and 80 °C (Table 1). As these were mature wells, the percentage of water was quite high, reaching over 90% with pH of 7, which was relevant to the test and to verify whether PA12 had undergone significant hydrolysis-induced aging after one year. A recently published paper showed no detectable PA12 degradation in this type of environment after one year of exposure [8]. The maximum pressure of the wells was 7.9 kgf/cm², aligned with other industrial PA12 applications in treated gas distribution pipelines with pressures of up to 18 kgf/cm² in Ceará (Brazil). A minimum time of one year of operation (above 8000 h) was targeted for retrieval and analysis. This period is well above that suggested, for instance, by API Technical Report 17TR6 which proposes three months or ISO 4433 which proposes for exposure of thermoplastics to chemicals for up to 112 days [9,10]. Finally, this period is also longer than the one proposed by ISO 23936-1 for non-metallic materials in contact with media related to oil and gas production, which is typically up to three months as they intend to short-term aging, not long-term aging, as aimed by this work [11].

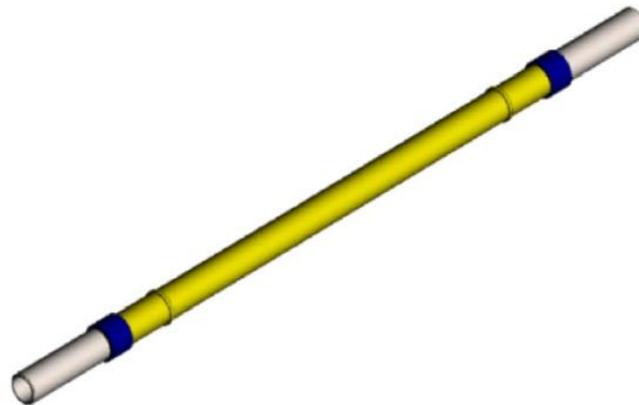


Figure 2 – PA12 pipe details with steel transitions [8].

Table 1 - Operating conditions of the samples.

Sample Identification	Pressure (kgf/cm ²)	Temperature (°C)
CS (Control Sample)	-	-
A40	6	40
A60	7.90	60
A80	7.90	80

The PA12 pipe samples have a polymer/steel transition, consisting of a connector in carbon steel API 5L Gr. B so that they could be connected to the original steel pipes. The pipes were buried 1 meter deep

to simulate the typical burial conditions of pipelines and ensure that solar radiation would not jeopardize the results. A hydrostatic test was performed on all sections containing the installed polymeric samples prior to exposure to ensure that PA12 would not fail under the maximum operating pressure of the steel piping. Figure 3 shows the installation of the onshore short length PA12 pipe samples between the steel pipelines in the field. Figure 4 illustrates the monitoring of well temperatures, carried out on a weekly basis, to ensure that the pipe temperatures remained within the expected range.

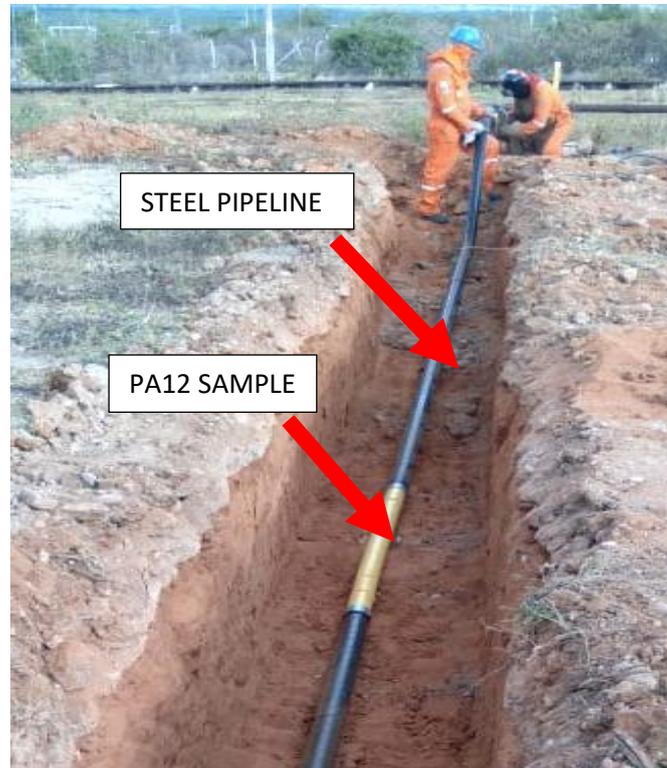


Figure 3 – Details of the PA12 sample in the field pipeline [8].



Figure 4 – Temperature monitoring in the well [8].

After the one-year exposure period, samples (pipe lengths) from all three temperatures (A40, A60 and A80) were retrieved so that they could be machined into small scale mechanical tests samples and evaluated in order to compare overall performance considering the original reference samples (control

samples - CS). It is important to mention that the results presented herein add to the results already published in [8].

2.2 Tensile test

The purpose of the tensile tests was to verify whether there had been any change in the mechanical properties of the material after the service time under the operating conditions described in the previous section.

5 tensile test specimens (ASTM D638 Type I) were machined, from both internal and external surfaces of each retrieved pipe sample (A40, A60 and A80) and for the Control Sample (CS).

A strain rate of 1 mm/min was adopted up to 1% strain for the evaluation of the Young's Modulus. After this deformation value, the rate used was increased to 50 mm/min to define the other properties, at yield and at break [12]. The equipment used was an EMIC DL 2000 testing machine and the reference criterion was a minimum elongation at break of 50%, as suggested by API RP 17B and referenced in technical report API 17TR2. It is important to highlight that, according to ISO 23936-1, it is suggested that the variation in mechanical properties should be less than 50% relative to the reference material.



Figure 5 – Tensile test of PA12 pipe samples.

The mechanical results were statistically evaluated using Analysis of Variance (ANOVA) considering the following input factors and their respective levels:

- Input factor: exposure temperature at 4 levels (CS, A40, A60 and A80) where CS is considered at 23 °C (no exposure) for the purposes of the statistical analysis;
- Input factor: position within pipe thickness at 2 levels (innermost and outermost surfaces).

Null hypothesis of residual normality was evaluated using Shapiro-Wilk and Lilliefors's tests. Null hypothesis of homoscedasticity was evaluated using Cochran-Bartlett and Levene's tests. Finally, pairwise comparisons between conditions were evaluated using Fisher's LSD tests. All analyses were performed at a significance level of $\alpha = 0.05$.

2.3 Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) were performed using the three-point bending method on a TA Instruments Discovery 850 instrument to evaluate the glass transition temperature (T_g) of the samples,

comparing the results with those of the control sample. Test specimens from the control sample (CS) and from the internal and external surfaces of each field sample (A40, A60, and A80) were machined to approximate rectangular dimensions of 20 mm in length, 10 mm in width and 3 mm in thickness, with two runs per sample. The tests were performed with heating from -90 °C to 120 °C, at a heating rate of 1 °C/min, at a frequency of 1 Hz, and at an amplitude of 0.02%. The T_g was defined by the intersection between tangents at the decline of the storage modulus curve, according to ASTM E1640.

III. RESULTS AND DISCUSSIONS

3.1. Tensile tests

The tensile test properties are presented in Tables 2 and 3 for the innermost and outermost layers of each pipe samples, respectively. The nomenclature for each sample is presented in Table 1. Parametric static premises preliminary evaluation showed that, in general neither Null Hypothesis (H₀) of Residual Normality nor Null Hypothesis (H₀) of Homoscedasticity was rejected ($p > \alpha$) for the results presented herein.

Table 2 – Tensile tests results for the inner layer of each pipe sample.

	CS	A40	A60	A80
Young's Modulus (MPa)	731 ± 41	878 ± 20	743 ± 112	789 ± 33
Stress at Yield (MPa)	35.5 ± 0.3	38.7 ± 0.4	38.2 ± 0.5	39.5 ± 0.8
Strain at Yield (%)	14.2 ± 0.4	12.4 ± 0.2	13.1 ± 0.4	13.6 ± 0.7
Stress at Break (MPa)	48 ± 4	57 ± 5	55 ± 7	51 ± 5
Elongation at Break (%)	293 ± 53	380 ± 72	371 ± 83	389 ± 25

Table 3 – Tensile tests results for outer layer of each pipe sample.

	CS	A40	A60	A80
Young's Modulus (MPa)	680 ± 49	714 ± 7	665 ± 78	690 ± 63
Stress at Yield (MPa)	32.6 ± 0.4	35.6 ± 0.2	36.6 ± 0.6	36.5 ± 0.2
Strain at Yield (%)	14.6 ± 0.3	13 ± 0.3	13 ± 0.3	14.5 ± 0.2
Stress at Break (MPa)	53 ± 0.9	58 ± 1	56 ± 5	55 ± 2
Elongation at Break (%)	364 ± 5	408 ± 9	387 ± 49	402 ± 18

Before any further analysis is performed, it can be observed that, for all exposure conditions (A40, A60 and A80) and for all surfaces (internal x external), exposed sample properties are within the ±50% criteria proposed by ISO 23936-1. Additionally, all elongation at break values are 6 to 8 times higher than the minimum elongation at break criteria of 50% suggested by API RP17B mentioned in API17TR2 document [14].

ANOVA Young Modulus showed that both exposure temperature ($p=0.00073$) and position of the sample within pipe thickness (internal x external surfaces - $p=0.000001$) were considered statistically significant ($p<0.05$). However, no statistically significant interaction effect ($p=0.12$) was observed between these two input factors. Figure 7 shows that, for all temperature exposures, there were no

statistical changes for the Young's Modulus considering the external surface compared to the original material, as expected. However, for internal surface, Young's Modulus for the sample A40 was statistically higher than the modulus plateau observed for the external-surface samples of A60 and A80. From previous work using the same exposure methodology [9], it was observed that for the innermost layer, the A40 Corrected Inherent Viscosity (CIV=1.64 dL/g) as well as crystallinity values by Differential Scanning Calorimetry (DSC, $\chi \sim 22.7\%$) did not differ significantly from these same results for the pristine material (CIV=1.69 dL/g and $\chi \sim 22.13\%$), which also applies for the A60 (CIV=1.64 dL/g and $\chi \sim 21.9\%$). Only for A80 (CIV=1.59 dL/g and $\chi \sim 23.1\%$) these values seemed a slightly higher than respective results for pristine material, leading to the conclusion that A40 Innermost Layer Young's Modulus was likely an outlier. Excluding the atypical behavior of A40, it can be observed that Young's Modulus values range from about 660 to 760 MPa (~ 100 MPa difference considering all groups), thus, as mentioned before, long-term exposure (8000 h) at temperatures from 40 to 80 °C at pH 7 water did not lead to significant changes in material Young's Modulus.

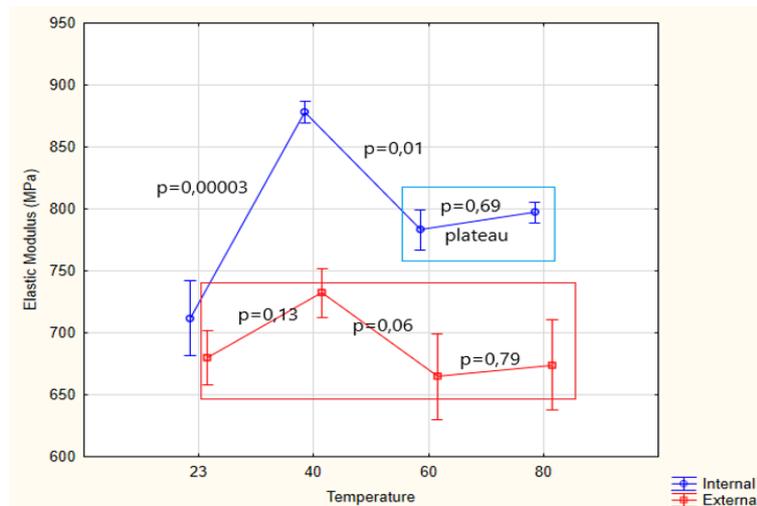


Figure 7 – ANOVA Young's Modulus evaluation with p-values for each pair of conditions according to Fisher-LSD test. Boxes representing property plateauing.

ANOVA Stress at Yield data showed that both exposure temperature ($p \rightarrow 0$) and position of the sample within pipe thickness in what regards internal versus external surfaces ($p \rightarrow 0$) were considered significant ($p < 0.05$), as well as their interaction effect ($p = 0.02$, which is close to the 0.05 threshold), but with an overall range of variation smaller than 10% (from about 32.5 to 39.5 MPa). Figure 8 shows that, for all temperature exposures, for both internal and external surfaces, there is a statistically significant increase in Stress at Yield compared to the original material, with some plateauing tendency between pairs of temperatures. As discussed above, from previous work based on this same sample exposure methodology [8] it is believed that this behavior was not caused by any significant hydrolysis-induced degradation process. This behavior may be aligned with a slight increase in stiffness associated with annealing effects [8], which can influence this property. Despite such increase, long-term exposure considering the methodology adopted herein did not lead to critical changes in material Stress at Yield.

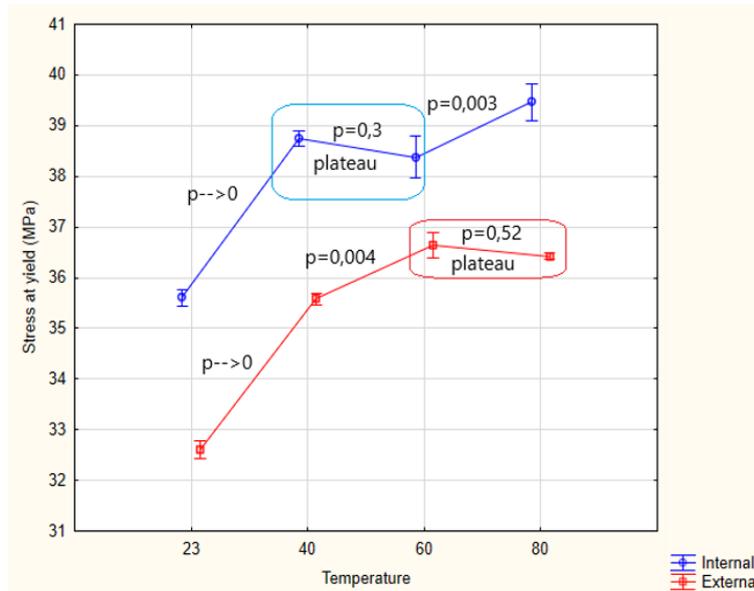


Figure 8 – ANOVA Stress at Yield evaluation. with p-values for each pair of conditions according to Fisher-LSD test. Boxes representing property plateauing.

ANOVA Strain at Yield data showed that both exposure temperature ($p \rightarrow 0$) and position of the sample within pipe thickness in what regards internal versus external surfaces ($p=0.0001$) were considered significant ($p < 0.05$). However, there was no significant interaction effect ($p=0.10$) between these two factors. Figure 9 shows that overall Strain at Yield values range between 12.2% and 14.6% and, based on previous work using the same exposure methodology [8], there is no evidence of critical hydrolysis-induced degradation process has occurred, keeping the Strain at Yield variability within the limits defined by ISO 23936-1.

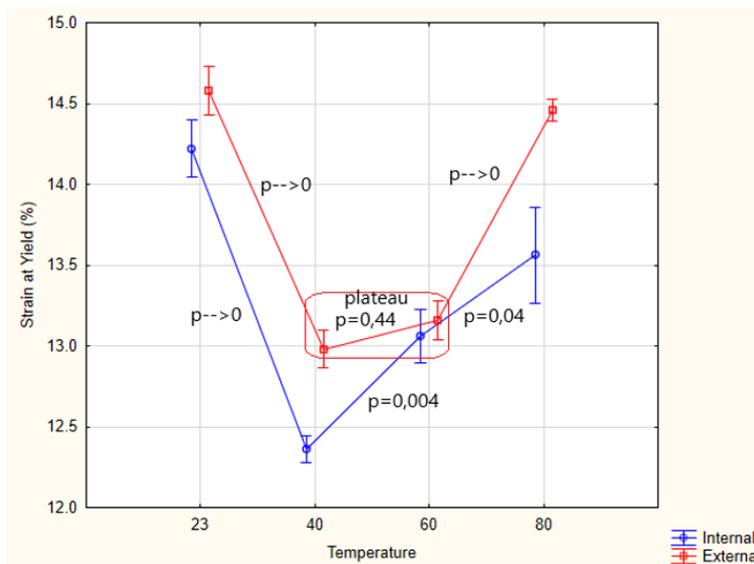


Figure 9 – ANOVA Strain at Yield evaluation with p-values for each pair of conditions according to Fisher-LSD test. Boxes representing property plateauing.

Properties at break were also evaluated using ANOVA. Stress at Break analysis showed that both exposure temperature ($p=0.00056$) and position of the sample in what regards internal versus external surfaces ($p=0.02$) were considered significant ($p < 0.05$). However, there was no significant interaction effect ($p=0.58$) between these two factors. Figure 10 shows that Stress at Break was statistically unaltered ($p \rightarrow 0.05$) or the external surfaces; for the internal surfaces, an increase compared to the original material was observed, with no significant differences among A40, A60, and A80. Overall

Stress at Break values range from 48 to 58 MPa considering all groups. Stress at Break variability remained within the $\pm 50\%$ variation defined by ISO 23936-1. These results indicate that no loss in overall mechanical performance occurred under the exposure conditions evaluated.

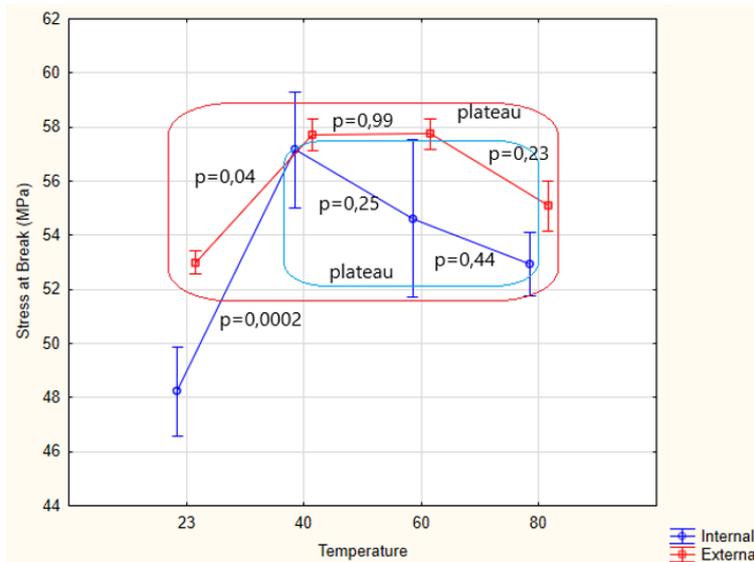


Figure 10 – ANOVA Stress at Break evaluation with p-values for each pair of conditions according to Fisher-LSD test. Boxes representing property plateauing.

Finally, as for ANOVA elongation at break data, only exposure temperature ($p=0.000002$) was statistically significant, showing that the sample position internal versus external surfaces ($p=0.051$) had no effect on the elongation at break and neither the interaction between these two factors ($p=0.061$). Figure 11 shows that elongation at break was statistically higher for the exposed materials, with overall no differences between position (internal versus external surfaces) and temperatures (A40, A60, A80) indicating that there was no loss in overall ductility after the exposure proposed herein, with results ranging from 300 to 410 far above the 50% absolute lower limit (defined by API RP17B) and all results remained within the $\pm 50\%$ variation defined by ISO 23936-1.

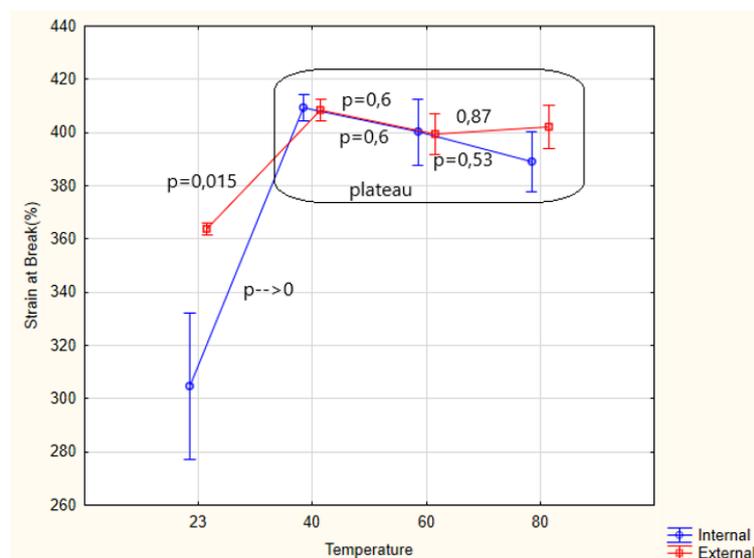


Figure 11 – ANOVA elongation at break evaluation with p-values for each pair of conditions according to Fisher-LSD test. Boxes representing property plateauing.

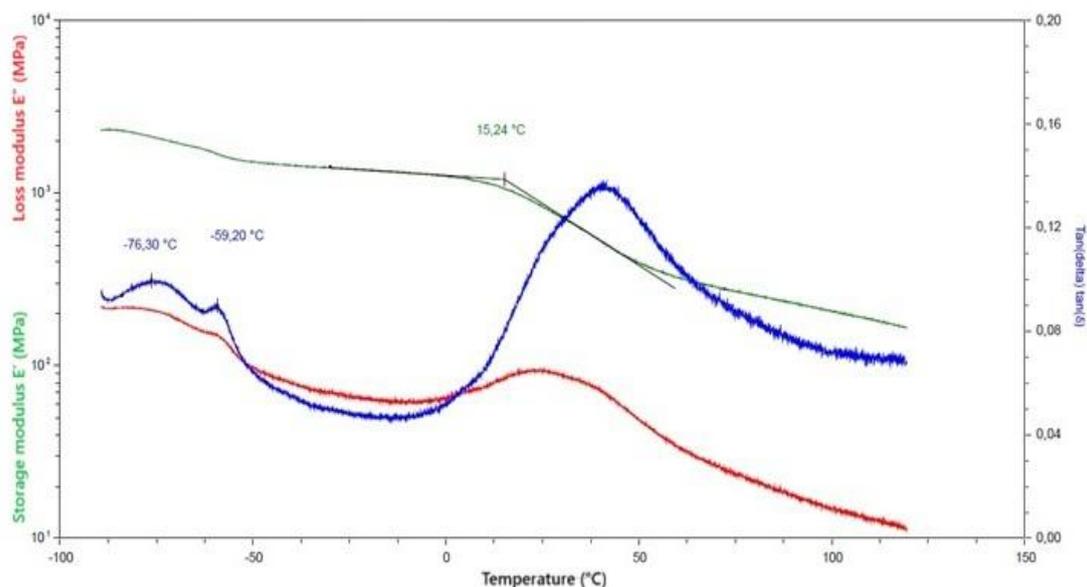
3.2 Dynamic mechanical analysis (DMA)

Table 4 shows the results of the dynamic-mechanical analysis.

Table 4 – Results of the glass transition temperature of the inner and outer layers.

Tg (°C)	CS	A40	A60	A80
Innermost Surface	16 ± 2	11.4 ± 0.2	16 ± 2	13.5 ± 0.9
Outermost Surface	17.3 ± 0.1	16 ± 1.6	11.2 ± 0.3	13 ± 1

By DMA results, the samples collected in the field tended to show Tg values equal to or lower than those of the control sample, which suggests that the operational conditions increased the mobility of the PA12 polymer chain. From previous work using the same exposure methodology [8], Thermogravimetric Analysis (TGA) indicated that only A60 and A80 exhibited an extractables content approximately 0.1–0.4% higher than that of the control samples. Hydrocarbon uptake and water absorption can plasticize polymers and lead to a decrease in Tg, particularly at elevated temperatures [8,13]. Despite this, considering the overall Tg range of 11–17 °C, no detrimental effects on the mechanical performance of the PA12 pipe were observed.

**Figure 11** –DMA curves (E' , E'' and $\text{Tan}\delta$) for inner surface of the the original material (Control Sample - CS).

IV. CONCLUSIONS

The results presented, together with previous findings [9] based on the same exposure methodology, indicate that the mechanical properties of an unplasticized PA12 (PA-U12) were largely preserved after 8,000 hours of exposure to hydrocarbons and produced water (pH 7), including hydrocarbon fractions, at temperatures ranging from 40 °C to 80 °C. No significant changes in polymer chain mobility, considering Tg values, were observed that could compromise the material's performance.

ANOVA confirmed that both temperature and position within the sample thickness were statistically significant factors, however with limited range of changes in this scenario of neutral pH condition which even makes more challenging to account for specific changes. Interestingly, ANOVA showed that, in most cases, there was no interaction effect between temperature and position within the thickness for the mechanical performance of the material. Overall, it have not been observed any significant changes in mechanical properties that would compromise the pipe performance based on the criteria established by ISO 23936-1 and API 17B.

Therefore, it can be concluded that PA-U12 maintained satisfactory stability for this application of moderately aggressive environment, ensuring compliance with internationally recognized mechanical-performance standards.

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