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Thermogravimetric Characterization of A Three-Layered Composite Reinforced With Glass Fiber and Applied In Oil Pipelines

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ABSTRACT
The oil & gas industry has to constantly face equipment corrosion challenges due to the chemical characteristic of the oil, gas and contaminants in the reservoirs. In 2010, a three-layered composite was developed, reinforced with glass fiber, for the terrestrial production pipelines as an alternative to Grade B API 5L steel, which was commonly used and more susceptible to corrosion. In this work, samples of pipes made of this composite were collected from two oil wells, which have been operating with this material for a few years. The internal and outer layers (in contact with fluid and soil, respectively) of the well samples were analyzed by thermogravimetry (TGA) and derivative thermogravimetry (DTG) and compared with a new control sample in order to evaluate if there was any undesirable event or degradation of the layers and to know the temperature limits of this new material. The results revealed that there was no significant change in the well samples (when compared to the control sample), because the same events occurred at similar temperatures. The material was also observed to be able to work at its specified development temperature, since the events occurred above 200°C.
KEYWORDS*: thermal analysis, thermogravimetry, composite, petroleum piping.*

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I. INTRODUCTION

The oil exploration industry is hindered significantly by the corrosive process due to the complex characteristics and composition of the fluids in oil reservoirs. Mature terrestrial fields (old fields with declining production) have the characteristic of possessing enough water and other corrosive agents along with the oil, such as O_2, CO_2, H_2S and sulfate-reducing bacteria, which tend to attack the steel piping from the inside, in addition to the soil and atmosphere, which also tend to cause external corrosion in this type of equipment.

For some years already, composite materials have been consolidated as an alternative to be used in corrosive environments, replacing metal alloys because they combine more properties of more than one material **[1].** Their structural characteristics promote attractive property combinations, such as low density, high specific resistance, high modulus of elasticity, and high chemical resistance, which enable the manufacture of parts with complex geometries and high resistance to corrosion and degradation in various industrial environments **[2].**

Glassfiber reinforced polymer matrix composites (GFRP) are the most common in this category. The main advantages of these composites are their low cost, good tensile strength, good chemical resistance and excellent insulating properties. The disadvantages are their relatively low modulus of elasticity, high density (of the commercial fibers), sensitivity to abrasion during handling (which often reduces tensile strength), relatively low fatigue strength and high hardness (which causes excessive wear in molds and cutting tools) **[3].**

In general, several factors are of influence on the mechanical behavior of composites. These factors include the manufacturing process used, the manner in which the loads are applied, the developed damage mechanism, the presence of adverse humidity and temperature conditions, the respective volume fractions, the properties of the interface, the presence of voids, in addition to the properties of the constituent elements **[4].**

Thermal analysis involves techniques that evaluate the physical or chemical properties of a sample as a function of controlled temperature and time. Polymers and composites are materials that are susceptible and sensitive to temperature variations, and their properties can alter drastically and harm their applications. Thermal analysis techniques are therefore very commonly applied in the study of these types of materials **[5].**

In this work, samples of pipes made of this composite were collected from two oil wells, which have been operating with this material for a few years. The internal and outer layers (in contact with fluid and soil, respectively) of the well samples were analyzed by thermogravimetry (TGA) and derivative thermogravimetry

(DTG) and compared with a new control sample in order to evaluate if there was any undesirable or degradation event and to know the temperature limits of this new material. This study may assist in the prevention of future failures of this new material due to harmful changes in its properties, avoiding future problems with operational, personal and environmental accidents.

II. EXPERIMENTAL DESIGN

Materials

In 2010, a three-layered composite (Figure 1) was developed for terrestrial oil production pipelines as an alternative to Grade B API 5L steel, which was commonly used and more susceptible to corrosion and failures. This composite was produced through the filament winding process, which is characterized by high dimensional control and mechanical strength **[6]**.

The material has an internal layer made of a glass fiber reinforced epoxy polymeric matrix, an intermediate layer of a glass fiber and silica reinforced polyester matrix and an outer layer coated with high density polyurethane. The material was specified for 3-inch pipes, a maximum operating pressure of up to 5.17 MPa (750 psi) and a design temperature of 95°C **[6].**

The innermost epoxy layer with glass fiber is the most important layer of the material, since this is the layer that is in first contact with the pressure, temperature and characteristics of the fluid that flows through the pipeline and therefore needs to have the best properties. The intermediate polyester and silica layer is meant to improve the rigidity of the composite without the need to increase the thickness of the internal layer, saving on the final cost of the material **[6].** The outer layer of high-density polyurethane, on the other hand, is meant to serve as an insulating, mechanical and corrosive protection against agents present in the soil or atmosphere **[7]**.

Samples of these types of composite pipelines were taken from two oil wells in distinct fields that have been operating with this material for eight years, and a sample was also taken from a control pipe that was never used. Table 1 identifies the samples and the year they entered into operation.

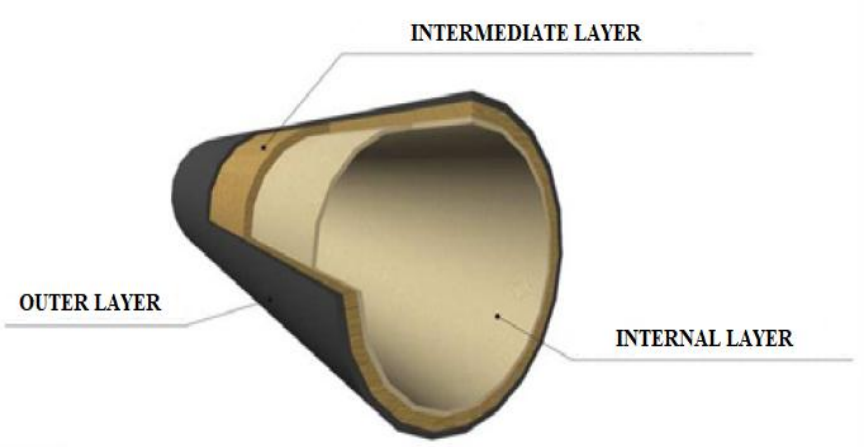

Figure 1. Three-layered polymeric composite **[6]**.

Table 1. Samples of composite production lines.

Sample Identification	Year of Operation
Control	-
RP-0147	2012
PL-0288	2012

III. METHODOLOGY

Three samples were taken from the pipes for thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG). The analyses were performed on TA Instruments' SDT Q600 equipment with a platinum reference sample, where approximately 10 mg of the samples were heated from room temperature to 600ºC in a synthetic air atmosphere at a heating rate of 10 ºC/min. Only the internal and outer layers of each composite sample were analyzed because these are in direct contact with the fluid or the soil.

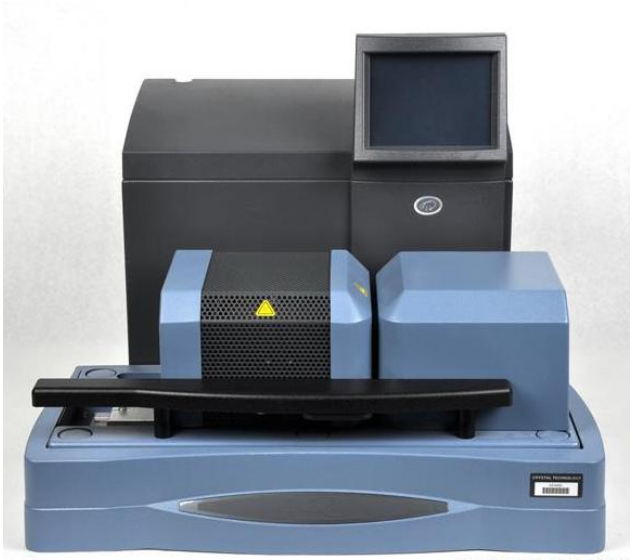

Figure 2. TA Instruments' Q600 equipment **[7]**.

IV. RESULTS AND DISCUSSION

Control Sample

Figure 3 shows the result of the thermogravimetric analysis of the internal layer of the control sample, where four events were identified. The first event, with a mass loss of 0.6233%, occurs between the temperatures of 50ºC and 225ºC, approximately, and is related to the exit of free water. The second and third events, between the temperatures ranges of 225ºC - 325ºC and 325ºC - 450ºC, probably correspond to the degradation of the resin at two different moments. The fourth event, in the temperature range from 450ºC to 600ºC, corresponds to the beginning of the degradation of the glass fibers that make up this layer. The peaks of the derivative curve show that the second, third and fourth events occur at maximum intensities approximately at the temperatures of 282ºC, 375ºC and 536ºC (the first event did not generate a peak because it has a very subtle curve).

Figure 4 shows the result of the thermogravimetric analysis of the outer layer, where we observe a significant loss of mass between the temperatures of 200ºC to 360ºC, resulting from the deterioration of the polyurethane, with maximum intensity occurring at the temperature of approximately 350ºC (derivative curve).

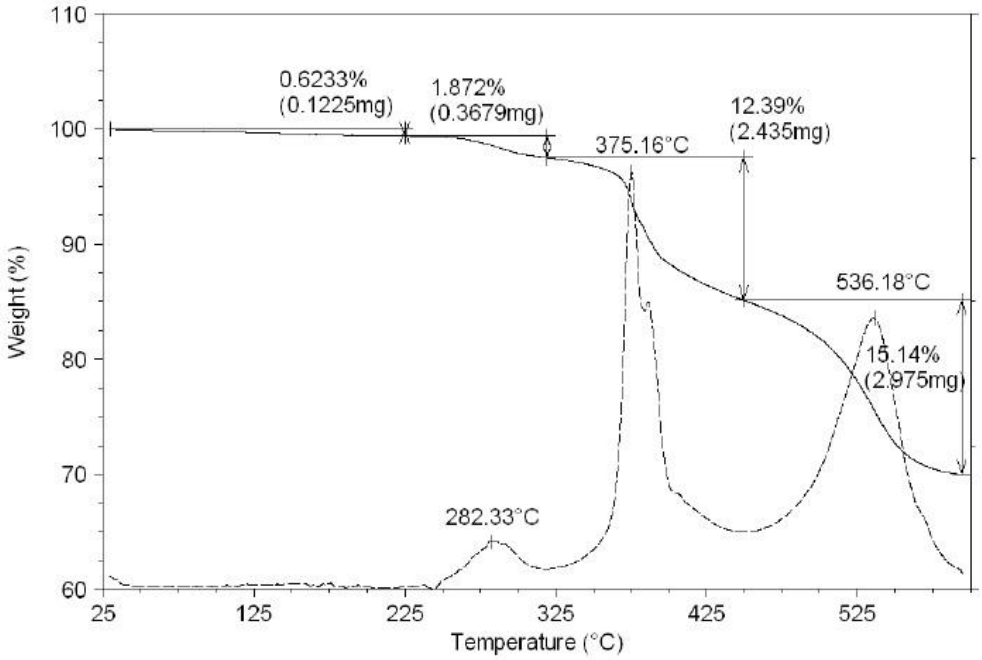

Figure 3. TGA and DTG graph of the internal layer of the control sample.

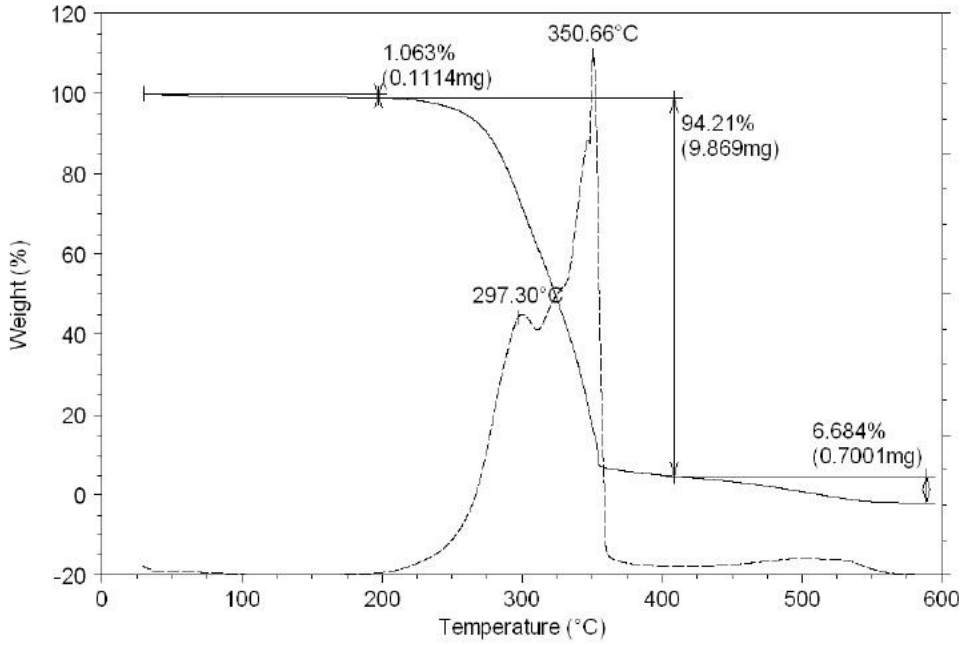

Figure 4. TGA and DTG graph of the outer layer of the control sample.

Sample RP-147

Figure 5 shows the result of the thermogravimetric analysis of the internal layer of the sample from well RP-0147, where four events were identified. The first event, with a mass loss of 0.5639%, occurs between the temperatures of 50ºC and 210ºC, approximately, and is related to the exit of free water. The second and third events, between the temperatures ranges of 210ºC - 325ºC and 325ºC - 450ºC, correspond to the start of the degradation of the resin at two different moments. The peaks of the derivative curve can be seen, where the events occur with greater intensity at temperatures around 288ºC, 374ºC and 529ºC (the first event also did not generate a peak because it has a very subtle curve).

Figure 6 shows the result of thermogravimetric analysis of the outer layer of the RP-0147 well sample, where we observe a significant loss of mass between the temperatures of approximately 220ºC and 360ºC, which is a result of the deterioration of the polyurethane, with the peak of the derivative indicating greater intensity of the event at the temperature of 349ºC.

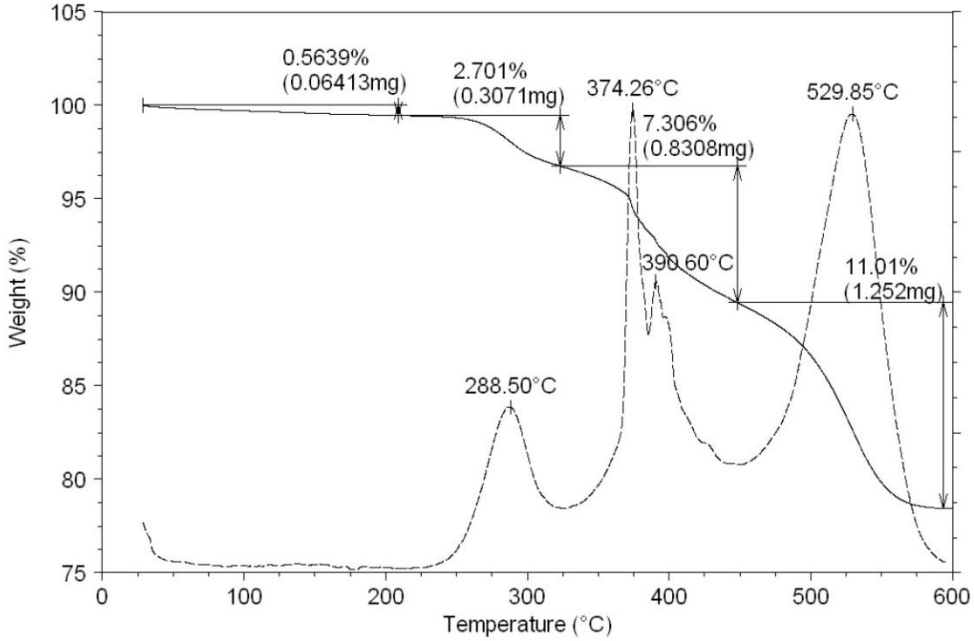

Figure 5. TGA and DTG graph of the internal layer of the RP-0147 sample.

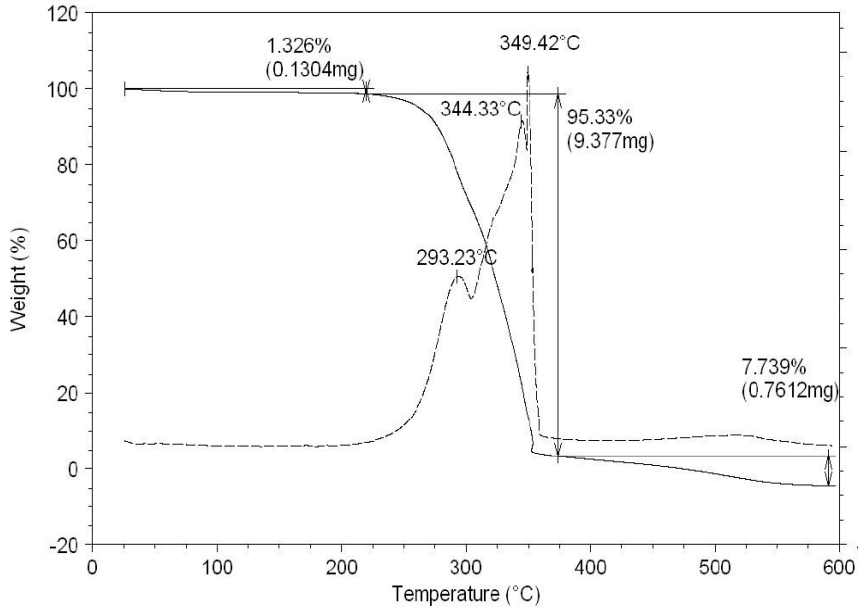

Figure 6. TGA and DTG graph of the external layer of the RP-0147 sample.

Sample PL-0288

Figure 7 shows the result of the thermogravimetric analysis of the internal layer of the sample from well PL-0288, where four events were identified. The first event, with a mass loss of 0.7481%, occurs between the temperatures of 50ºC and 225ºC, approximately, and is related to the exit of free water. The second and third events, between the temperatures ranges of around 225ºC - 325ºC and 325ºC - 460ºC, correspond to the start of the degradation of the resin at two different moments. The fourth event, in the temperature range from 460ºC to 600ºC, corresponds to the deterioration of the glass fibers that make up this layer. The peaks of the derivative TGA curve show that the second, third and fourth events occur at maximum intensities approximately at the temperatures of 286ºC, 376ºC and 541ºC (the first event did not generate a derivate peak because the TGA curve is very subtle).

Figure 8 shows the result of thermogravimetric analysis of the outer layer, where we observe a significant loss of mass between the temperatures of 200ºC and 360ºC, resulting of the deterioration of the polyurethane, which according to the peak of the derivative occurs at greater intensity at the temperature of approximately 350ºC.

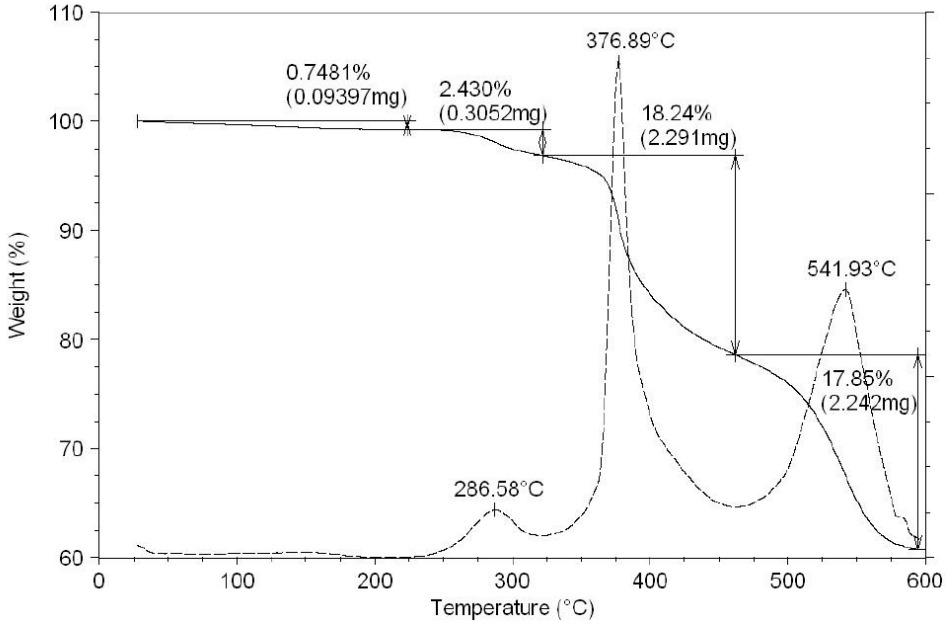

Figure 7. TGA and DTG graph of the internal layer of the PL-0288 sample.

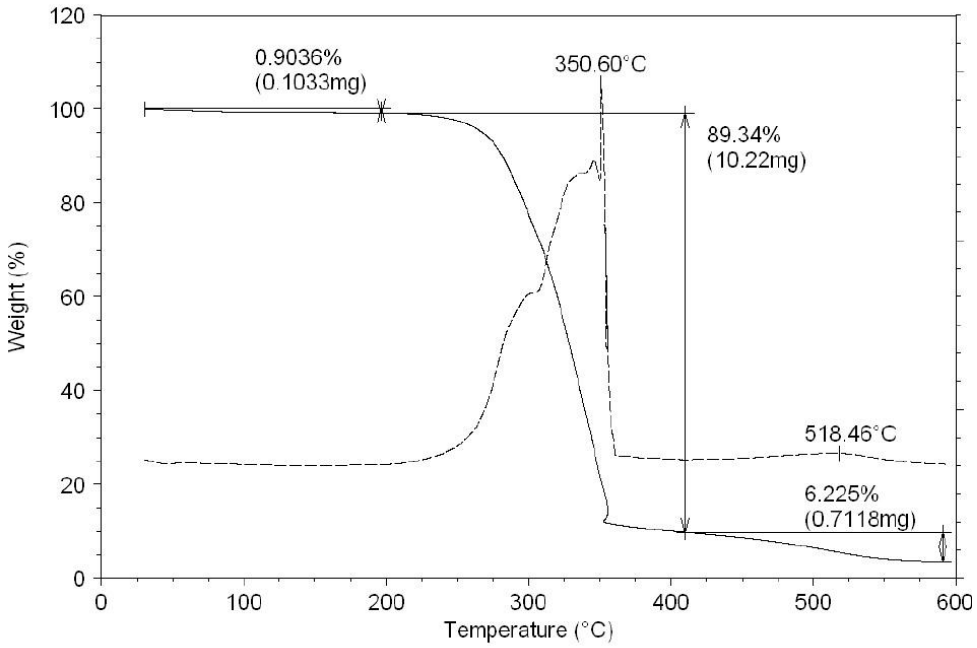

Figure 8. TGA and DTG graph of the external layer of the PL-0288 sample.

From the results of the thermal analyses of the individual layers it is possible to conclude that no significant discrepancies occurred and that the events occurred at similar temperatures and conditions as the control sample. It was also possible to see that the composite is suitable to be applied at the specified design temperature (95ºC), since all relevant degradation events occurred above 200ºC. An important detail is that the free water exit events from the internal layers were not detected in the DTG peaks because the TGA curves of these events were quite subtle (small mass loss).

The internal layer of well sample PL-0288 showed a slightly larger mass loss than the other samples, but the temperature ranges at which the events occur are very close. The outer layer of well sample RP-0147 had a slightly larger mass loss than the other samples, but with very similar temperature ranges for the events.

V. CONCLUSION

The individual thermogravimetric analysis of each layer (internal and outer) revealed that the degradation events occur at similar temperature ranges, from about 200ºC to 500ºC, well above the design limit temperature which is 95ºC; that is, the material is suitable for work up to this temperature. In addition, no discrepancies were observed in the mass losses during the events (when compared with the new control sample).

It is important to study the thermal properties of new materials in real-life situations in the field to understand their behavior and prevent failures that may cause personal, environmental and operational damage (especially in the petroleum industry, where temperature is an important process variable). These failures are often difficult to predict in the development stages of the material.

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