25th ABCM International Congress of Mechanical Engineering
October 20-25, 2019, Uberlândia, MG, Brazil

COB-2019-0913
ANALYSIS OF THE EFFECT OF HYDROLYSIS IN THE MECHANICAL RESISTANCE OF POLYAMIDE APPLIED TO OFFSHORE PLATFORM CABLES

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Abstract. *Offshore platforms and other marine structures have long been anchored with steel cables, however, synthetic fiber cables have recently become a very advantageous alternative for the oil and gas industry. The smaller mass and smaller submerged area required, with equivalent mechanical resistance, presented decisive characteristics of the synthetic compounds in front of the steel. Throughout this recent update of offshore anchorage, studies on the mechanical performance of synthetic materials under real conditions become increasingly important to understand the behavior of this new alternative. The objective of this work is to investigate the influence of the hydrolysis phenomenon on the mechanical strength of polyamide fibers. Two specific temperatures (70 ° C and 80 ° C) were defined for the immersion of filaments in salt water. After the immersion periods, the rupture stress results were obtained. It was observed during the study that a new variable denominated here like "rest time" directly influences the value of the rupture tension increasing it proportionally to the time immersed. This fact can change ways of making fiber and open up a new field of study.*

Keywords: *Offshore anchoring, synthetic fibers, polyamide filaments, hydrolysis, tensile test*.

1. INTRODUCTION

Oil has become fundamentally and actively present in the life of society as a source of energy. The commodity has become so important that it is currently the most exploited natural resource (Bico, 2013). Despite its importance and relatively technologically supported, the oil and gas industry still has to overcome many frontiers in the field of oil exploration. According to Morais (2013), there are three specificities that result in a high degree of technical difficulties in the exploration and production of oil, one of them, is intrinsically linked with the development of alternatives to conventional anchorage. For him, the great distances between the platforms and the wells on the ocean floor are grounds for numerous barriers to the development of the sector.

From the point of view of anchorage systems, these distances are a real challenge. At these depths, it becomes difficult to use conventional systems composed of steel cables (Bico, 2013). The use of catenary steel chains greatly increases the vertical load supported by the platform, increasing, the risk of breaking the chains and the cost of them, as a require increased diameters to support their own weight (Duarte, 2017). Compared to cables of synthetic fibers such as the polyamide cable, it is clear that there is an alternative to steel.

Polyamide, in turn, is a thermoplastic polymer composed of amide monomers connected by peptide bonds. Low creep, high abrasion resistance, good fatigue strength and high barrier properties are direct results of this type of bonding between chains (Dorna, 2016). When synthesized for anchoring cables, it exhibits tensile strength very similar to steel, lower mass and lower submerged area required. Thus, when submerged in salt water, the polyamide undergoes the process called hydrolysis that according to Piske (2002), is a break or change in the molecular chain of carbonic materials (polymers) caused by water at a certain temperature.

Once the material and its characteristics are known, it is important to research the literature about studies with polyamide 6 and to complement existing data. Greenwood in 1993, published results of his study on the effects of hydrolysis by thermal acceleration on polyester fibers at temperatures of 80 ° C and 95 ° C (this work uses values of 70 ° and 80 ° C). At the time, the author did a rupture analysis for each yarn and used the Arhenius model to calculate the equivalent time of aging.

Years later, Sudaia (2015), presented a submersion aging study, with thermal acceleration hydrolysis in polyamide, PET and LCP fibers. However, due to experimental failures, only strong results were obtained for the polyester.

Finally, the most recent survey is from Duarte (2017), which characterized the behavior of PET, Liquid Crystal Polymer (LCP) and Aramid fibers. In his study he also used the Arhenius model to calculate the aging time by submersion.

Notably, the construction of new contents and studies in the area contributes to the advancement of polymers research, characterizing the importance of this present work.

2. MATERIAL AND TEST METHODS

2.1 Experimental procedure

Before testing the material on the influence of salt water, it is necessary to have data of the polyamide still virgin. For this, a rupture test, a microscopic analysis of the material and the specifications according to the manufacturer are carried out. With the data in hand, it is possible to begin the immersion process.

To achieve aging by hydrolysis in synthetic fibers such as polyamide, some difficulties are found. Some mechanisms that meet all the specifications for the realization of the aging of synthetic fibers are not yet in the market. Another problem is that there are not enough technical standards to obtain the data sought. Thus, the Stress Analysis Laboratory uses two reactors to perform such tests based on the methodology of Greenwood (1993). If it is necessary to find more information about the equipment used, Duarte (2019) explains in its study some other characteristics. In these reactors, polyamide filaments are immersed for the initially times of 1,2,3 and 4 weeks. Temperatures were set at 80 ° C and 70 ° C, only varying the exposure period for the same defined salinity and ph medium.

Figure 1- Reactor for aging by hydrolysis in the Stress Analysis Laboratory
Available from: Nícolas Vannucchi Nadalin.

Paoli (2008) characterized the seawater as slightly alkaline with pH between 7.5 and 8.4 and salinity of 35 grams of salts for each liter of water, its highest concentration being sodium chloride. In this study, these parameters were followed for the environment in which these reactors provide.

The test specimens are twisted in metal studs with hooks at both ends. This arrangement avoids any contact with other bodies that may affect the performance of the tests. Therefore, the material is only exposed to the salt water.

After the immersion period, the filaments are removed and dried for periods previously set under ambient temperature. Now submitted to the other rupture test a curve can be obtained comparative to the tests performed with virgin material. In this way, it is possible to analyze the degree of influence of the molecular breaking process on the tensile strength of the fiber as a whole and to identify if the rest and drying period influences the results.

2.2 Yarn Break Load

The initial rupture test with virgin materials provides the YBL which becomes the reference value. The procedure followed the specifications of the ASTM D2256 standard of the American Society for Testingand Materials. 48 tests were performed, resulting in table 1. The mean value in the study becomes the most relevant.

Table 1- Experimental results of polyamide tensile test on virgin specimens
Available from: Stress Analysis Laboratory

	Maximum Load [N]	Strain [%]
Maximum	214.45	21.41
Minimum	188.15	14.91
Mean	207.37	18.75
Standard Deviation	5.30	1.27

*Polyamide 6, 500 mm (22°C).

2.3 Hydrolysis process

Hydrolysis (hydro-lysis) consists of the reaction of a water molecule with a certain chemical group, with breakage of the connection and addition of oxygen and hydroxyl to each of the remaining groups. It can be cause by enzymes (hydrolases) or by ordinary chemical process. The hydrolysis reaction is accelerate in acidic or basic medium. (Paoli, 2008). The increase in temperature and time of exposure also influence the acceleration and intensity of molecular breakdown.

In the Polyamide, the reaction of breaking of its molecules is represent by the following reaction (Fig 2).

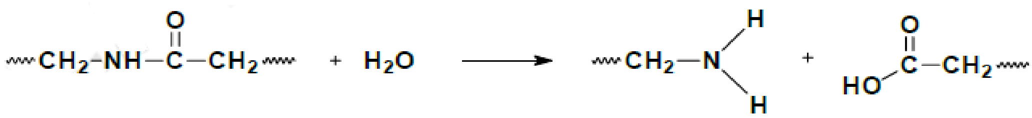

Figure 2- Polyamide hydrolysis reaction
Available from: Paoli, (2008)

Greenwood (1993) describes the hydrolysis as a chemical process in which water reacts with the material generating cleavages in the chain thereof. In the case of PA6 exclusively, used in this study, the break occurs in the amide group, causing decrease of the molecular weight and the tensile strength of the material, latter, being the object of study of this work.

3. RESULTS AND DISCUSSION

3.1 Graphics and Results

The polyamide fiber was immerse in brine at temperatures of 70 ° C and 80 ° C, separated into sets of filaments within the reactors. The properties of water as pH and sanity were monitored during the different periods and remained practically constant.

During the first procedure, immersing the filaments in salt water at a temperature of 70 ° C and testing them in breaking methods gave the following results.

Table 2- Results for the temperature of 70°C
Available from: Stress Analysis Laboratory

Submerged Time (Day)	0	7	14	21	28
Mean Burst Load (N)	207,37	204,39	205,04	204,03	218,88
Standard Desviation (N)	5,30	3,85	3,28	3,74	4,17
Percentage of mean (%)	100	98,56	98,88	98,39	105,55

During this first test, the average burst load practically did not change over time. However, when the filament was exposed for longer times it was noticed an increase in the mean not expected.

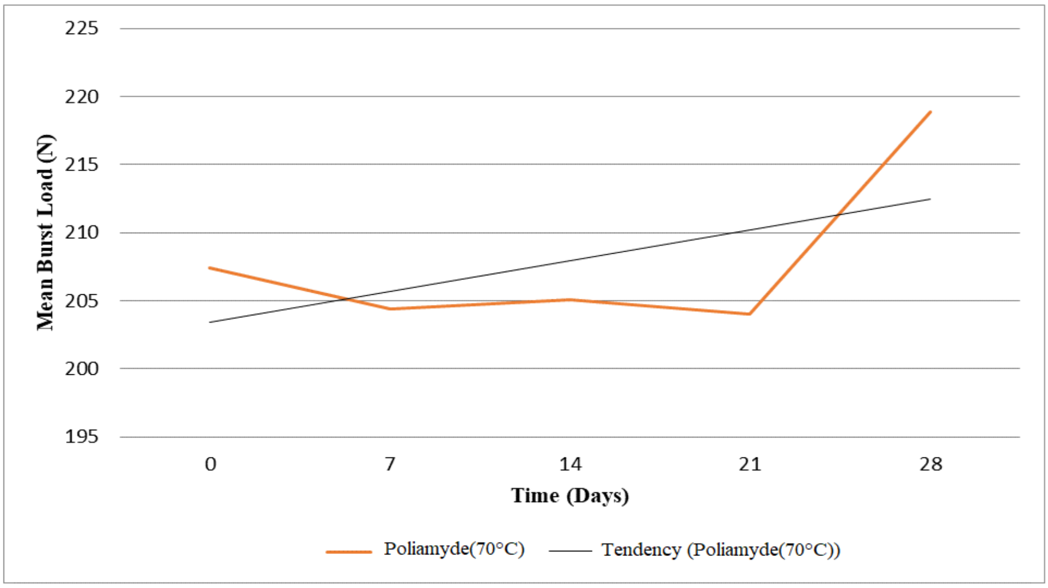

Figure 3- Breaking test for filaments immersed in salt water at 70°C
Available from: Stress Analysis Laboratory

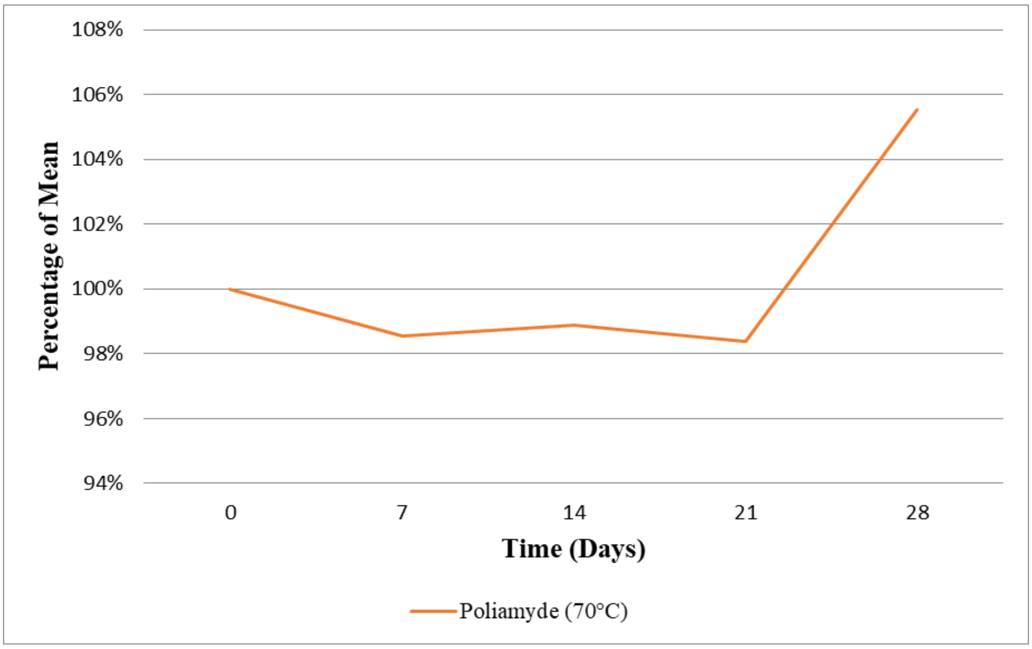

Figure 4- Percentage of mean at 70°C
Available from: Stress Analysis Laboratory

To investigate this anomaly in the hydrolysis process and to understand if the determinant variable would be the time, the tests were repeated at a temperature of 80 ° C with even longer times. Thus, according to the hydrolysis phenomenon discussed above, it was expected that the material presents even lower rupture mean and a constant decrease as a function of time. The results obtained were as follows:

Table 3- Results for the temperature of 80°C
Available from: Stress Analysis Laboratory

Submerged Time (Day)	0	14	28	42	56
Mean Burst Load (N)	207,37	210,96	207,08	211,43	202,86
Standard Desviation (N)	5,30	3,08	4,07	1,63	2,51
Percentage of mean(%)	100	101,73	99,86	101,96	97,82

During the trials it was noted that there were no significant variations in values. The following graphs demonstrate the results found:

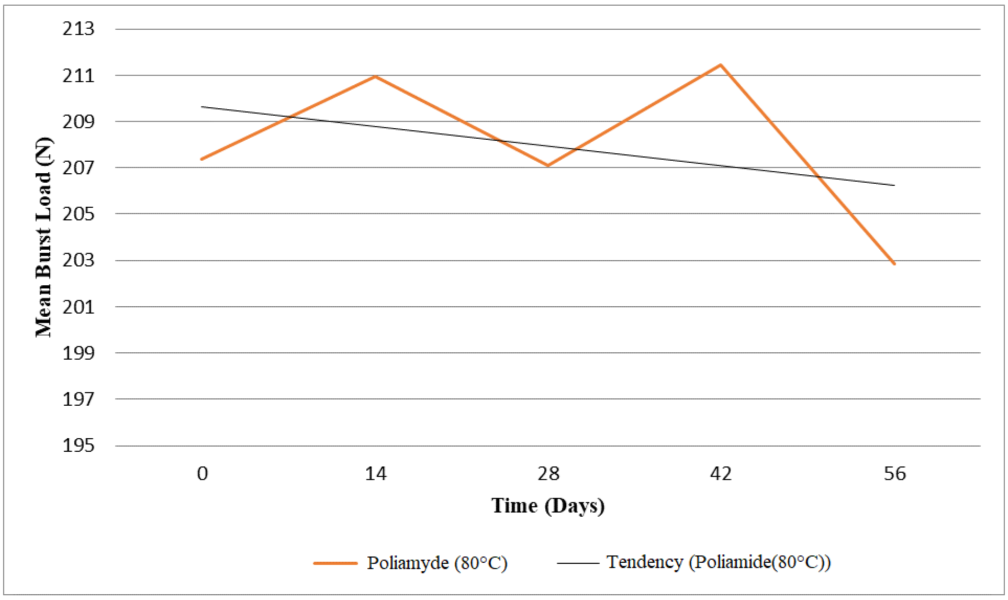

Figure 5- Breaking test for filaments immersed in salt water at 80°C
Available from: Stress Analysis Laboratory

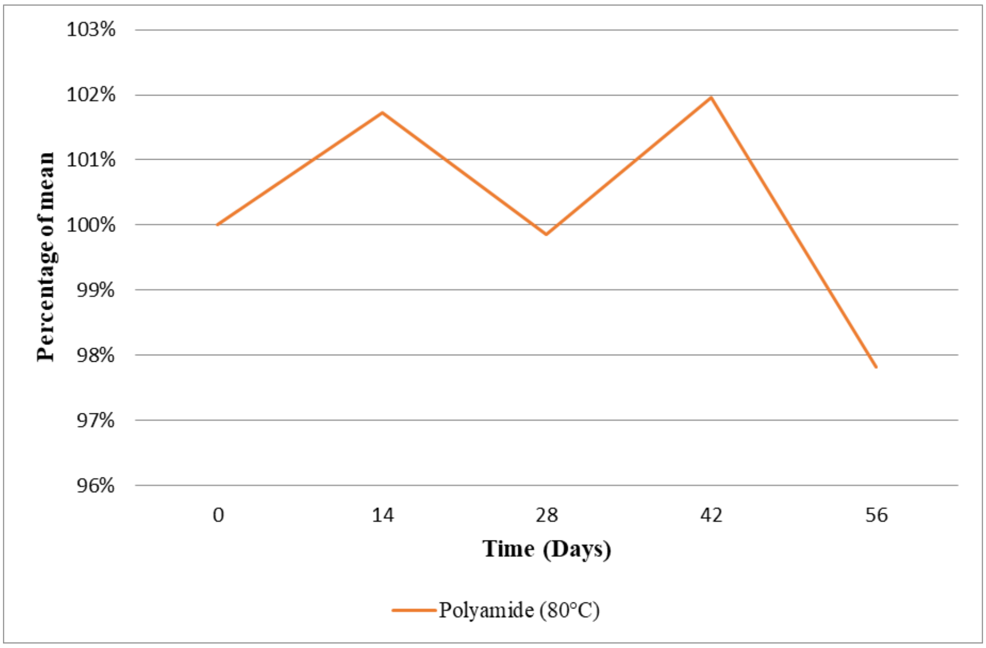

Figure 6- Percentage of mean at 80°C
Available from: Stress Analysis Laboratory

For all day categories (0,14,28,42 and 56), the filaments tested were all tested in the days following their withdrawal from salt water, to which they were submerged. However only half (48 filaments) were tested, leaving another 48 that were stored. The purpose of storing these filaments was to verify if a new variable could arise in the process.

3.2 New variable “Rest Time”

Stored over temperature and controlled humidity, the remaining filaments were placed on "rest" for 14 days. This time period was stipulated based on the two previous tests since the difference between the results obtained was a little more significant when submerged for 14 days compared to the first 7 days.

At first the material should behave in the same way as it was analyzed, since the hydrolysis process did not take place during the next 14 days. Even so, the data collection indicated a significant variation of the rupture stress after the rest process. The data were compiled in figures 7 and 8.

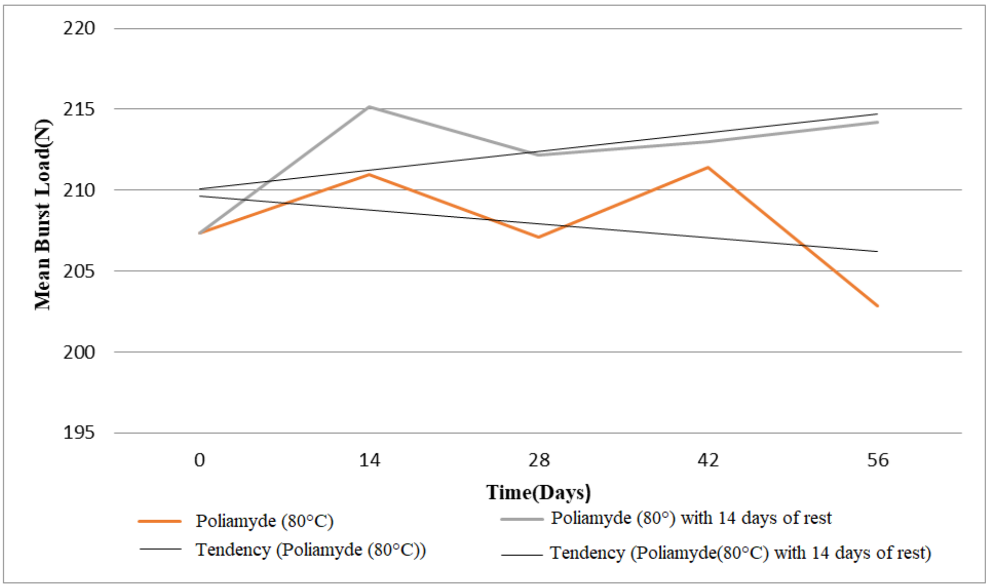

Figure 7- Comparision of rupture tests
Available from: Stress Analysis Laboratory

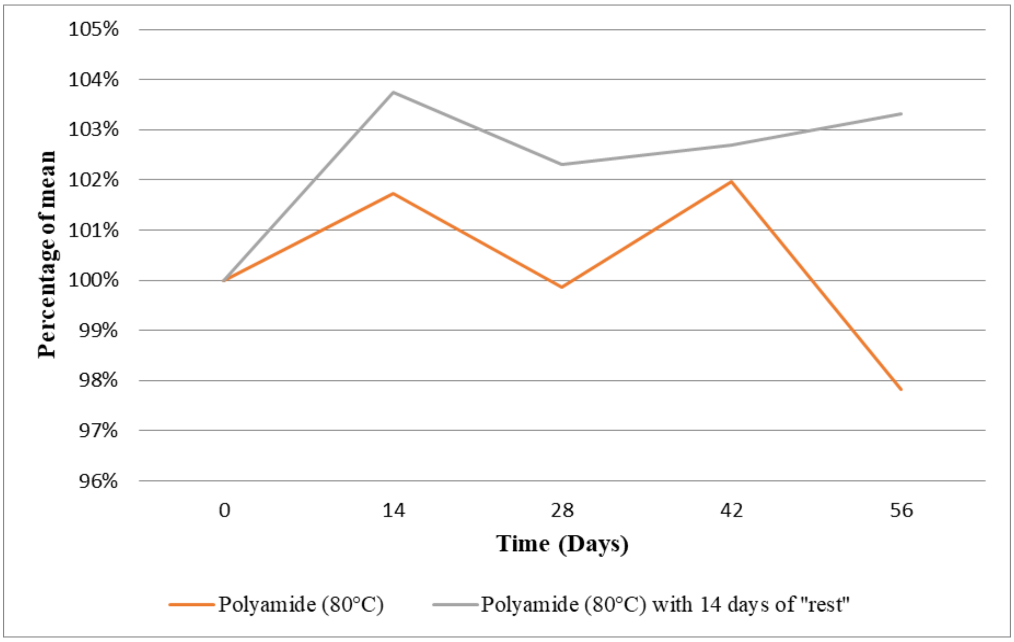

Figure 8 - Comparision of percentage of mean
Available from: Stress Analysis Laboratory

The data collection indicated that the "Rest Time" to the filaments, before the rupture test, increased its mean in relation to the filaments that were not submitted to the same procedure.

4. CONCLUSION

Knowing the importance of complementing current literature and research on synthetic materials, the present work brings new information about the study of Polyamide 6. The behavior of this fiber was analyzed and recorded at defined temperatures.

When exposed to 70 ° C and long periods of submersion, the fiber exhibits an anomalous behavior that can still be studied further down. However when exposed to the same temperature and smaller times, the fiber does not have significant variations of its resistance to rupture and follows the expected one.

By exposing Polyamide 6 at temperatures of 80 ° C the results showed the expected behavior. There was a decrease in its resistance and rupture stress, as a consequence of the hydrolysis process.

Finally, a new variable was identified which demonstrated that the "Rest Time" of the fiber of 14 days after its immersion in salt water at 80 ° C significantly increases its average rupture resistance. This phenomenon and result can still mean the creation of new procedures in the manufacture of Polyamide 6 cables and bring advances to the studies of synthetic materials.

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6. RESPONSIBILITY NOTICE

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