

COBEM2019-0883 - DEGRADATION OF ARAMID FILAMENTS BY HYDROLYSIS

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Abstract: *Aramid fibers are among the fibers used for offshore mooring and operation system, thus being continuously exposed to a marine environment. This paper presents data regarding a study about the accelerated degradation of aramid yarns by hydrolysis in salt water, at a temperature of 80 °C. Three different aramids were tested by their Yarn Breaking Loads throughout a 147 days period with regular tests, in accordance with the technical standard ASTM D 885-03: Standard Test Methods for Tire Cords, Tire Cord Fabrics, and Industrial Filament Yarns Made from Manufactured Organic-Base Fibers, and showed different hydrolysis resistance. Two proved to be hydrolysis resistant, as stated by the manufacturers, showing no signs of degradation and one showed a clear decrease in its Yarn Breaking Load, but still complying with the technical standard ISO 17920: Fibers ropes for offshore stationkeeping- Aramid.*

Keywords: *aramid fibers, accelerated degradation, heated sea water, hydrolysis, mooring.*

1. INTRODUCTION

According to Sperling (1932) and Canevarolo Jr. (2002) polymers are long-chain molecules formed by subunits bonded by covalent bonds. Also having secondary attraction forces between these long-chain molecules. One of the polymeric fibers that can be used in marine applications, such as offshore mooring, is the aramid, whose name comes from “aromatic polyamide”, a macromolecule composed of several aromatic rings (Fig. 1).

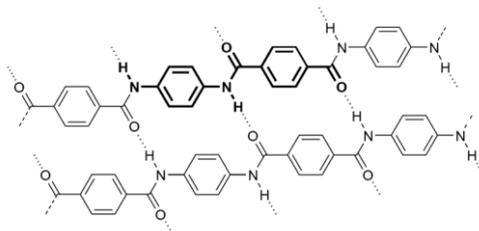


Figure 1. Structure of an aramid

Covalent bonds are significantly weaker than ionic bonds, they are subject to break more easily. One of the many ways to break a covalent chemical bond is through hydrolysis. As stated by Greenwood (1995) hydrolysis is a chemical reaction in which the water reacts with the material to break the polymeric chain, reducing the molecular weight and the tensile strength. When in an alkaline environment the process will occur with the ion OH^- , forming a different compound. This type of hydrolysis, in which the outer portion of the material is the part exposed to the environment, is referred as external hydrolysis.

Taking into consideration that the majority of researches on the effects of hydrolysis on aramids are conducted focusing in the use of spectrometry to determine the evolution of the chemical reactions, the study of density (weight

loss) to measure the degradation as did Derombise et al., (2009), and x-ray scattering measurements as did Springer et al., (1998). Derombise et al., (2009) could not measure a significant degradation, but Springer et al., (1998) did, whilst studying different aramids. The experiment proposed herein was performed in order to measure the effects of hydrolysis quantifying the progressive drop of the Yarn Breaking Loads (YBL) values throughout a specified timeline, as per ISO 17920.

Two of the three types of aramid fibers evaluated herein were referred as hydrolysis resistant. All three of them were exposed to heated (80 °C) salt water, with a controlled pH. Submerging in water is the standard procedure, not only for Aramid but also for other polymers and textile fibers, and this method was used by Davies and Evrard, (2007), Springer et al., (1998), Derombise et al., (2009), Haghhighatkish and Youseff, (1992) Rahman and Alfaro, (2004) and Aquino et al., (2010). When exposed to a heated environment the multi-filaments degradation is accelerated, reducing the time of the experiments to only a few months. It was thought that temperature would cause a degradation by itself, but as proved in Duarte et al., (2019) its contribution is neglectable. Later on, the results can be applied to a mathematical equation to predict how many years it would take to reach the desired level of degradation in a 4 °C environment (sea bottom temperature), as in Duarte et al., (2019).

In order to achieve a full perspective of the degradation of aramid fibers this work carries out a in depth study of the hydrolysis effects on aramids' YBL (Yarn Break Load) throughout 147 days, with periodic withdrawals, far beyond the three weeks proposed in ISO 17920: Fibers ropes for offshore stationkeeping- Aramid.

2. MATERIALS AND METHODS

In this work three different aramid fibers were used for testing. Two of the them are claimed to be hydrolysis resistant (identified as Aramid 1 and Aramid 2) being the third one an ordinary multi-filament aramid (Aramid 3).

Firstly, a mechanical characterization of unaged samples of the three aramid fibers was necessary. For such, tensile tests according to ASTM D 885-03 were performed to determinate their Yarn Breaking Loads (YBLs). The tests were made in an Instron 3365, with a load cell capacity of 5 kN. Equipped with a cord and yarn grip, with a capacity of 2 kN, a 500 mm length between clamps and a velocity of 250 mm/min. Before testing, the specimens were stretched on a table, secured with a bonded joint on both ends (Fig. 2) followed by 60 torsions per meter around its axis while applying a load of 1 N on the opposite direction. 30 specimens were tested for each determination of YBL, thus reducing the standard deviation.

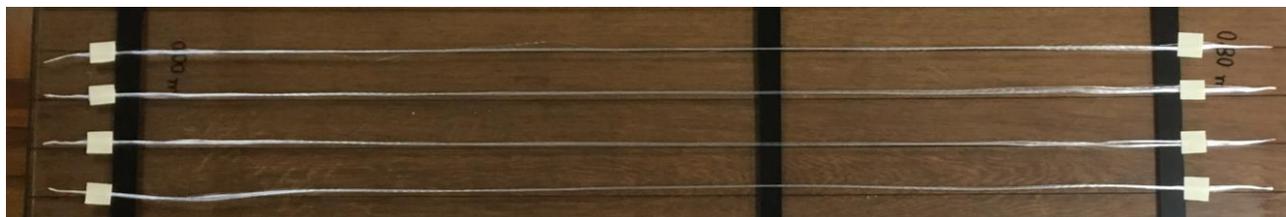


Figure 2. Specimens ready to be twisted.

Later on, the fibers' linear density was determinate according to the ISO 2060 using 1 m specimens and an OHAUS Adventurer scale, with a maximum capacity of 210 g.

The hydrolysis deterioration process was conducted in an apparatus to perform hydrolysis designed by the *POLICAB Stress Analysis Laboratory* team. The apparatus consists of a thermally isolated water tank able to seat several stainless-steel frames that hold the polymeric yarns. The tank is equipped with an auxiliary water heating system (temperature is used to accelerate the degradation, as per ISO 17920) that heats the water from room temperature to the experiment's desired temperature, maintaining it by means of a thermocouple system as stated in Corrêa and Stumpf, (2014).

Sea water was used to more closely emulate the marine environment, it was also adopted as one of the aging environments by Derombise et al., (2008). The same paper used de-ionized water with a specified concentration of NaCl, as did Derombise et al., (2009) and Springer et al., (1998).

To conduct the degradation first the filaments were placed on a frame all built in stainless steel with hooks at the upper and lower ends. All three materials were arranged in the frames with 30 specimens per material (assembling a set), properly spaced apart and slightly stretched, so the yarns would not stick to one another (Fig. 3). This process was repeated seven times, one for each withdrawal, totaling 210 specimens per material for all withdrawals.



Figure 3. Specimens arranged on the stainless-steel frame.

After all frames were submerged into a tank with heated salt water, on a temperature of 80 °C (ISO 17920) and a controlled pH of 8,27, in accordance with ASTM D 1141: Standard Practice for the Preparation of Substitute Ocean Water, Derombise et al., (2008) and Derombise et al., (2009) used pH of 9 to 11, way above what is stated at the technical standard. Every twenty-one days (period proposed in ISO 17920) one set (30 specimens per aramid) was withdrawn from the tank, followed by a drying period of 5 days. After the samples are completely dry, the 90 specimens (30 specimens per aramid) were tested in the tensile testing machine aforementioned.

The testing procedure was repeated seven times every twenty-one days until all specimens from all the seven withdrawals were properly tested.

3. RESULTS AND DISCUSSIONS

Table 1 presents the initial data regarding the mechanical characterization of the three aramids tested herein.

Table 1. Materials' Mechanical Characterization.

Material	Aramid 1	Aramid 2	Aramid 3
New filament YBL (N) ¹	371,97 ± 7,5	358,75 ± 9,7	712,03 ± 15,1
Linear density (dTex) ¹	1.684 ± 11	1.670 ± 6	3.600 ± 3

¹ Data acquired in STP conditions

These data shows that the initial YBL for the Aramid 3 (ordinary fiber) and its linear density are significantly higher than the other two (the so-called hydrolysis resistant). After seven sample sets were retrieved, totalizing 147 days of testing, the YBL results (Table 2) were plotted in a graph according to the percentage of the respective fiber initial YBL (unaged), shown in Figure 4.

Table 2. YBL variation throughout the degradation period.

	0 days	21 days	42 days	63 days	84 days	105 days	126 days	147 days
Aramid 1	371,97 ± 7,5 N	371,80 ± 8,4 N	392,40 ± 9,4 N	384,90 ± 13,0 N	380,51 ± 10,4 N	394,12 ± 11,1 N	397,57 ± 8,2 N	403,48 ± 7,9 N
	(100,00%)	(99,96%)	(105,49%)	(103,48%)	(102,30%)	(105,95%)	(106,88%)	(108,47%)
Aramid 2	358,75 ± 9,7 N	354,59 ± 8,2 N	367,76 ± 7,6 N	358,26 ± 9,2 N	363,52 ± 6,0 N	378,88 ± 7,6 N	377,43 ± 5,9 N	392,63 ± 4,2 N
	(100,00%)	(98,84%)	(102,51%)	(99,87%)	(101,33%)	(105,61%)	(105,21%)	(109,44%)
Aramid 3	712,03 ± 15,1 N	637,5 ± 18,6 N	624,75 ± 37,7 N	600,75 ± 18,6 N	591,23 ± 18,5 N	585,65 ± 25,9 N	578,43 ± 18,0 N	569,50 ± 17,3 N
	(100,00%)	(89,53%)	(87,74%)	(84,37%)	(83,03%)	(82,25%)	(81,24%)	(79,98%)

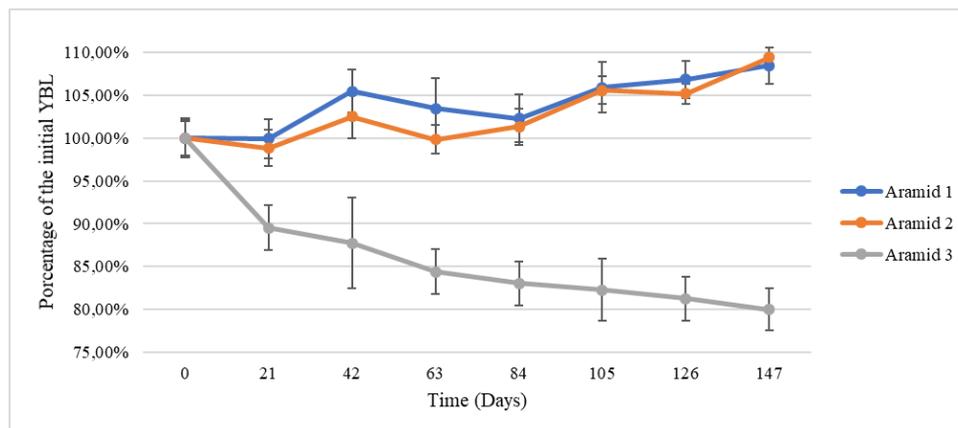


Figure 4. Results on percentage of the initial YBL.

According to ISO 17920, a material shall have a residual strength of, at least, 90% of its nominal YBL value (unaged) after an immersion period of three weeks in 80 °C seawater. In this case, it is clear that Aramid 1 and 2 easily comply with said requirement (99,96% and 98,84% > 90%), while Aramid 3 is at its limit YBL (89,53%~90%) regarding hydrolysis resistance.

Springer et al., (1998) pointed a slight degradation of aramids in a somewhat similar environment. This behavior can be seen in the Aramid 3 (ordinary Aramid) but in a more explicit way, where in 147 days reached 80% of its initial YBL.

Derombise et al., (2008) and Derombise et al., (2009) conducted studies on de-ionized water and sea water but did not see a meaningful degradation except in very specific situations, when bending the material over sheaves. Aramid 1 and Aramid 2 behaved the same way (both hydrolysis resistant), presenting no strength loss after 147 days in 80 °C sea water.

4. CONCLUSION

Complementing the literature on the subject of hydrolysis on polymeric materials this work comes as a study of the effects of this chemical reaction, based on ISO 17920, specifically for aramid yarns.

After analyzing the data, Aramid 1 and Aramid 2 seem to be temperature resistant, presenting no strength loss after 147 days (7 times longer than expected by ISO 17920) under 80 °C seawater. Aramid 3, on the other hand, presents a typical strength loss by hydrolysis degradation, reaching the limit of 90% residual strength proposed by ISO 17920 after 3 weeks in the 80 °C seawater, and reaching levels of 80% of its initial YBL by the end of the 147 days period.

The results presented here, show how important it is to properly consider the adequate polymer fiber, taking into account the application, as overall the degradation resistance, e.g. hydrolysis resistance, may differ from one polymer to another.

5. ACKNOWLEDGEMENTS

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