

# 17º Congresso Brasileiro de Polímeros 29 de Outubro a 02 de Novembro de 2023 Joinville - SC





Associação Brasileira de Polímeros

Copyright © 2023 para os autores

Revisão textual e gramatical: Resposanbilidade dos respectivos autores.

Todos os direitos reservados 2023 A reprodução não autorizada desta publicação, no todo ou em parte, constitui violação de direitos autorais (Lei 9.610/98).

#### Dados Internacionais de Catalogação na Publicação (CIP) (Câmara Brasileira do Livro, SP, Brasil)

Congresso Brasileiro de Polímeros (17. : 29 out. - 2 nov. 2023 : Joinville, SC) Anais do 17° Congresso Brasileiro de Polímeros [livro eletrônico] / organização Associação Brasileira de Polímeros. -- Joinville, SC : Aptor Software, 2023. PDF Vários colaboradores. ISBN 978-85-63273-55-0 1. Polímeros 2. Polímeros e polimerização 3. Química - Congressos I. Título. 24-188263

#### Índices para catálogo sistemático:

Química : Congressos 540
 Eliane de Freitas Leite - Bibliotecária - CRB 8/8415



## EVALUATION OF MECHANICAL BEHAVIOR OF OFFSHORE MOORING POLYESTER FIBERS BY HYDROLYSIS PROCESS

Ignácio Melito<sup>1</sup>, Daniel Magalhães da Cruz<sup>2,\*</sup>, Aleones José da Cruz Júnior<sup>3</sup>, Ivan Napoleão Bastos<sup>4</sup>, Ana Lúcia Nazareth da Silva<sup>5</sup>, Jakson Manfredini Vassoler<sup>2</sup>, Fernanda Mazuco Clain<sup>1</sup> and Carlos Eduardo Marcos Guilherme<sup>1</sup>

 1 – School of Engineering (EE), Federal University of Rio Grande (FURG), Rio Grande, RS, Brazil
 2 – Department of Mechanical Engineering (DEMEC), Federal University of Rio Grande do Sul (UFRGS), Porto Alegre, RS, Brazil

 \* Corresponding author: <u>daniel.cruz@ufrgs.br</u>
 3 – Federal Institute of Education, Science and Technology of Goiano, Trindade, GO, Brazil
 4 – Polytechnic Institute (IPRJ), Rio de Janeiro State University (UERJ), Nova Friburgo, RJ, Brazil

 5 – Institute of Macromolecules Professora Eloisa Mano (IMA), Federal University of Rio de Janeiro (UFRJ), Rio de Janeiro, RJ, Brazil

#### Abstract

High-performance polymeric fibers have been used in the recent decades for offshore mooring, such as polyester (PET), which is used due to its low cost, high strength, ease of processing, and recyclability. The application in the offshore branch promove a series of studies with the PET fibers, whether analytical, experimental, or numerical studies, and with different load, exposure and environmental conditions. This work experimentally studies the breaking behavior of different polyester fibers that go through a hydrolysis process at different temperatures. Methodology applied is hydrolysis with sea water in an appropriate tank, followed by rupture tests for varied withdrawal. As a result, it is evident that the hydrolysis process decreases the strength performance of all PETs. For some temperature groups, it shows a gradual decrease in strength with increasing hydrolysis time. As future study, more data should be collected to capture behavior and represent it by mathematical models.

Keywords: Mechanical characterization, Synthetic yarns, Hydrolysis reaction, Sea water, Tensile test.

## Introduction

In recent decades, the offshore sector has advanced into deeper waters, even replacing traditional systems in steel ropes and catenaries, and adopting an approach with ropes made of high tenacity polymeric materials [1].

The challenges in the offshore area led to the development of the use of polymeric synthetic fibers in anchoring systems. From the point of view of materials, there is a wide variety of options for synthetic polymeric fibers to be used: polyester, polyethylene, high modulus polyethylene (HMPE), aramid, polyamide, polyethylene, liquid crystal polymer (LCP), among others. In the present work, attention was given to polyester, polyethylene terephthalate (PET) [2].

Considering mooring ropes, the structures operate in severe environments: sea water, bioencrustation, wind action, wave and tidal movements, which can lead to significant changes in their mechanical properties. This context is an incentive for several research activities related to offshore branch, whether in samples of ropes, sub-ropes or multifilaments, or even in numerical or experimental analytical approaches [3-6].

One of the main aging phenomena that occurs in some polymers in service in the oil field is hydrolysis [7], in which the polymer chains are broken when in contact with water, resulting in a

rapid decrease in molecular weight and subsequent deterioration of some properties, such as mechanical properties, especially tensile strength [8-11].

The objective of this work is to evaluate samples of polyester multifilament supplied by three different manufacturers, in terms of performance at break by hydrolysis process in different temperatures, 60°C, 65°C and 70°C, during around 100 days of exposure.

## Experimental

## Materials

Three polyester fibers from different manufacturers were used, and all these fibers are used specifically for making cores for offshore mooring ropes. The names of the manufactures cannot be disclosed, so they are called polyester A, B and C. Polyester A and Polyester B has a linear density indication of 2200 dtex, and Polyester C has a linear density of 3300 dtex.

#### Hydrolysis test

The hydrolysis process is carried out on the polyester samples in a temperature- and levelcontrolled tank. It is noteworthy, through the specific application of the fibers for the offshore sector, that the hydrolysis was carried out with water collected from the sea, this is not saline water reproduced in the laboratory, but authentically seawater.

The hydrolysis test was performed with different temperatures: 60°C, 65°C and 70°C. For the three polyesters, the withdrawal times were slightly different, but the total time of hydrolysis test is close to 100 days. The hydrolysis tank is shown in Fig 1, and withdrawal times for each polyester are given in Table 1.



Figure 1 – Hydrolysis tank.

Table 1 – Hydrolysis	withdrawal	times	for	each
temperature condition.				

For 60°C	For 65°C	For 70°C
0	0	0
14	19	19
28	33	26
42	47	33
56	61	40
70	82	47
84	96	54
98		61
		68
		82
		89
		103

Note: Withdrawal times are not exactly the same because of technical difficulties, related to the operation of the tank and also to sample quantities.

## Yarn Breaking Load

After the immersion time (hydrolysis), 20 samples for each group were broken in a rupture test, to acquire the Yarn Breaking Load (YBL), following the ISO 2062 [12] procedure. The specimens were twisted at a rate of 60 turns per meter for homogenization before the rupture, and then the test followed with recording of force and elongation in the Instron 3365 test equipment where the extension rate was set at  $250 \pm 5$  mm/min. The length of the samples is  $1000 \pm 2$  mm for clamping the samples in the grips of the equipment, the useful test length being 500 mm.

Rupture test procedure is performed in standard atmosphere described in ISO139 [13].

### **Results and Discussion**

As a first result to be considered, the YBL test was performed on samples without exposure hydrolysis condition. The results are presented in Table 2.

Polyester A			Polyester B			Polyester C		
Linear density [dtex]	Breaking strenght [N]	Strain [%]	Linear density [dtex]	Breaking strenght [N]	Strain [%]	Linear density [dtex]	Breaking strenght [N]	Strain [%]
2200	173.77	15.58	2200	174.44	16.40	3300	261.15	13.58

 Table 2 – Reference data for fibers (without hydrolysis).

Tables 3, 4 and 5 show the rupture results for the polyester samples analyzed in the hydrolysis process.

Table 3 – YBL results for hydrolysis at 60°C.

	PET A		PET B		PET C	
days	Force [N]	Dimensionless [%]	Force [N]	Dimensionless [%]	Force [N]	Dimensionless [%]
0	173,77	100,00	174,44	100,00	261,15	100,00
14	165,53	95,26	172,70	99,00	256,73	98,31
28	159,83	91,98	169,32	97,07	248,30	95,08
42	156,72	90,19	167,19	95,85	241,93	92,64
56	160,63	92,44	165,54	94,90	248,45	95,14
70	158,50	91,21	165,63	94,95	244,32	93,56
84	157,39	90,58	169,53	97,18	242,27	92,77
98	159,11	91,56	164,43	94,26	242,48	92,85

## **Table 4** – YBL results for hydrolysis at 65°C.

	PET A		PET B		PET C	
days	Force [N]	Dimensionless [%]	Force [N]	Dimensionless [%]	Force [N]	Dimensionless [%]
0	173,77	100,00	174,44	100,00	261,15	100,00
19	166,58	95,86	173,60	99,52	257,41	98,57
33	162,27	93,38	163,98	94,01	254,88	97,60
47	154,80	89,08	158,84	91,06	250,86	96,06
61	152,03	87,49	155,86	89,35	251,03	96,13
82	147,44	84,85	151,24	86,70	246,57	94,42
96	146,45	84,28	147,00	84,27	239,17	91,58

Table 5 – YBL results for hydrolysis at 70°C.

	PET A		PET B		PET C	
days	Force [N]	Dimensionless [%]	Force [N]	Dimensionless [%]	Force [N]	Dimensionless [%]
0	173,77	100,00	174,44	100,00	261,15	100,00
19	162,66	93,61	170,78	97,90	245,05	93,83
26	165,85	95,44	173,55	99,49	248,73	95,24
33	164,02	94,39	171,08	98,07	247,06	94,60
40	161,98	93,22	167,32	95,92	248,64	95,21
47	165,59	95,29	171,28	98,19	246,60	94,43
54	162,58	93,56	166,41	95,40	247,94	94,94
61	161,18	92,76	171,71	98,44	246,63	94,44
68	160,69	92,48	166,85	95,65	244,56	93,65
82	163,28	93,96	167,94	96,28	244,01	93,43
89	160,65	92,45	170,28	97,62	249,62	95,58
103	164,90	94,90	166,36	95,37	244,02	93,44

Figures 2, 3 and 4 show the data presented in Tables 3, 4 and 5, graphically, for better evaluation.



Figure 2 – Dimensionless rupture versus hydrolysis time, 60°C.



Figure 3 – Dimensionless rupture versus hydrolysis time, 65°C.



Figure 4 – Dimensionless rupture versus hydrolysis time, 70°C.

As can be seen from the curves, the hydrolysis process reduces the tensile strength property for all polyesters and groups tested. It is also noted that for 70°C there is a more abrupt drop in the resistance values for the first withdrawal when compared to the other temperature groups, however in the continuation of the withdrawals, 70°C presents more stabilized values, while in 60°C and 65 °C there is a decreasing tendency as time in hydrolysis evolves. Thus, in the 60°C and 65°C groups, the drop by hydrolysis occurs gradually with longer hydrolysis times, giving a characteristic to the gradual decay curve within the range tested.

It is observed for PET A and PET B samples, at 60°C and 70°C temperatures, the curves showed a more stable behavior; while at 65°C, the property values drop, showing the lowest values of breaking strength. For PET C, a more homogeneous behavior can be observed in the whole hydrolysis conditions analyzed.

### Conclusions

The mechanical degradation caused by hydrolysis in polyester multifilaments is notorious. The performance related to materials from different manufactures was not a determining factor, no manufacturer stood out for its resistance to the hydrolysis process.

In addition, data grouping presents different behaviors for temperature groups and also hydrolysis times. The continuation of the study should be done considering longer hydrolysis times with regular withdrawals and other temperature groups, both higher and lower. Perhaps a more complete database will enable the use of mathematical modeling to describe phenomena such as Krigeage surfaces, Arrhenius equation, among other techniques.

#### References

- 1. C. J. M. Del Vecchio, Ph.D. Thesis, University of Reading, 1992.
- **2.** E. Chailleux; P. Davies, Mechanics of Time-Dependent Materials 2005, 9(2-3), 147-160. https://doi.org/10.1007/s11043-005-1082-0.
- **3.** M. Rudman; P. W. Cleary, Ocean Engineering 2016, 115(15), 168-181. https://doi.org/10.1016/j.oceaneng.2016.02.027.
- **4.** Z. Liu; Y. Lu; W. Wang; G. Qian, Applied Sciences 2019, 9(6), 1075. https://doi.org/10.3390/app9061075.
- 5. D. M. da Cruz; A. Penaquioni; L. B. Zangalli; M. B. Bastos; I. N. Bastos; A. L. N. da Silva, Applied Ocean Research 2023, 134, 103513. https://doi.org/10.1016/j.apor.2023.103513.
- 6. E. S. Belloni; F. M. Clain; C. E. M. Guilherme, Acta Polytechnica 2021, 61(3), 406-414. https://doi.org/10.14311/AP.2021.61.0406.
- 7. B. Jacques; M. Werth; I. Merdas; F. Thominette; J. Verdu, Polymer 2002, 43(24), 6439-6447. https://doi.org/10.1016/S0032-3861(02)00583-9.
- 8. P. D. Calvert, British Polymer Journal 1986, 18(4), 278-278. https://doi.org/10.1002/pi.4980180422.
- **9.** I. Melito; F. M. Clain; C. E. M. Guilherme; A. H. M. F. T. da Silva in Proceedings of 25<sup>th</sup> ABCM International Congress of Mechanical Engineering, Uberlândia, 2019, COBEM-0883.
- **10.** N. V. Nadalín; I. Melito; C. E. M. Guilherme; F. M. Clain in Proceedings of 25th ABCM International Congress of Mechanical Engineering, Uberlândia, 2019, COBEM-0913.
- **11.** J. P. Duarte; C. E. M. Guilherme; A. H. M. F. T. da Silva; A. C. Mendonça; F. T. Stumpf, Polymers and Polymer Composites 2019, 27(8), 518-524. https://doi.org/10.1177/0967391119851386.
- 12. International Organization for Standardization, ISO 2062, 2009, Geneva.
- 13. International Organization for Standardization, ISO 139, 2005, Geneva.