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PHYSICAL CHARACTERIZATION OF DEGRADADED ULTRA-HIGH MOLECULAR WEIGHT POLYETHYLENE (UHMW-PE) AND NYLAMID

CARACTERIZACIÓN FÍSICA DEL POLIETILENO DE ULTRA ALTO PESO MOLECULAR (UHMW-PE) Y DEL NYLAMID DEGRADADOS

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Abstract

Ultra-high molecular weight polyethylene (UHMW-PE) is an advanced polymeric material with a wide range of applications. Also, Nylamid is a polymer that has very interesting mechanical properties to work as a substitute for many types of steels. However, the media to which they may be exposed can degrade or age them, affecting the characteristics of the materials.

The objective of this work was to analyze the effect of the degradation of UHMW-PE and "mechanic" nylamid on their physical and chemical properties when they are aged in degrading substances. The change in morphology and surface roughness was analyzed as part of their physical properties and the FTIR characteristics as part of their chemical properties. The degradation of the polymers was carried out by immersion in seawater, 1% nitric acid solution, and castor oil. The results showed that there is a significant influence of the degrading medium on the polymer properties. Changes were observed in surface roughness and in the appearance of oil remnants on the surfaces of the materials degraded in castor oil and a visually rougher surface with degradation in seawater. Finally, it was observed the appearance of signals in the FTIR spectrum indicating an aging effect by hydrolysis and oxidation.

Keywords: Degradation, FTIR, Nylamid, UHMW-PE.

Resumen

El polietileno de ultra alto peso molecular (UHMW-PE), es un material polimérico avanzado con una amplia gama de aplicaciones. Asimismo, el Nylamid es un polímero que posee propiedades mecánicas muy interesantes para trabajar como sustituto de muchos tipos de aceros. Sin embargo, los medios a los que pueden estar expuestos pueden degradarlos o envejecerlos afectando las características de los materiales.

El objetivo de este trabajo fue analizar el efecto de la degradación del UHMW-PE y del nylamid "mecanico" en sus propiedades físicas y químicas cuando son envejecidos en sustancias degradantes. Se analizó el cambio en la morfología y rugosidad superficial como parte de sus propiedades físicas y sus características por FTIR como parte de sus propiedades químicas. La degradación de los polímeros se llevó a cabo mediante la inmersión en agua de mar, solución de ácido nítrico al 1%, y aceite de ricino. Los resultados mostraron que hay una influencia significativa del medio degradante sobre las propiedades del polímero. Se observaron cambios a nivel rugosidad superficial y en la aparición de remanentes de aceite en las superficies de los materiales al estar en contacto con el aceite de ricino, y una superficie visualmente más rugosa con la degradación en agua de mar. Finalmente, se observó la aparición de señales en el espectro de FTIR que indican un envejecimiento por hidrolisis y oxidación.

Palabras clave: *Degradación, FTIR, Nylamid, UHMW-PE.*

1. Introduction

Polyethylene is a partially crystalline polymer whose properties are strongly influenced by the relative amounts of the amorphous and crystalline phases [Coutinho, 2003]. Ultra-high molecular weight polyethylene (UHMW-PE) is an advanced material with densely packed and connected blocks of crystalline areas. It has an ultra-high specific modulus and outstanding impact resistance, properties of interest for advanced aerospace, military, automotive and biomedical applications [Silverstein, 1993]. Among the polymeric materials are polyamides, which are characterized by good mechanical and thermal properties. As a result, they are widely used commercially, and whose interest is determined by their properties. Due to their formation of hydrogen bridge bonds, they have high function points and high mechanical strength. Another of their great virtues is their ability to be biodegradable or biocompatible materials, which has generated great interest in the field of medicine [Billmeyer, 2004]. Therefore, it is of interest to predict the behavior of these polymeric materials due to their increasing use in different industries and in the academic sector. In order to more accurately predict the behavior of these materials, it is necessary to subject them to environments where they may have a practical application. In this way, it is determined which physical and chemical factors could affect the premature wear of the material and its possible failure. Degradation of polymers may be due to one or more environmental factors, such as exposure to light or heat and contact with other chemicals (acids, alkalis and some salts), among others. For this reason, an acidic substance (nitric acid) was chosen to analyze the behavior of the materials under very aggressive conditions, as well as vegetable oils that have been analyzed for possible use as a substitute for mineral oils. These materials are also present in subsea applications, so it is interesting to analyze this type of degradation. Degradation affects the various mechanical, physical and chemical characteristics and properties of polymers. The degree of degradation of a polymer can be observed to a greater or lesser extent, when: the capacity to withstand mechanical loads is reduced and deformations at the macromolecular level can be seen, observing how the surface topography is altered. Thus, the physical properties have been modified. And when there is a change in the structure or chemical composition it can be said that chemical degradation has occurred [Halim, 2014].

Among the applications of UHMW-PE in the medical field, research has shown that it can be a substitute for cartilage in joint arthroplasty, also showing its affectation to wear with synovial fluids [Hussain, 2019]. From the mechanical point of view, other researchers have concluded higher wear when the material has been degraded according to ASTM F2003-00 [Petrica, 2015]. As for nylamid, its characteristics make it a suitable material for gears, pulleys, seals, bearings, cams, among other applications where good tribological properties are required. They are lightweight and reduce production costs. [B. Sarita, 2019]. Studies have shown that the wear resistance of a polymer is mainly related to its mechanical and morphological properties, such as crystallinity, and that the wear resistance of a polymer is mainly related to its mechanical and morphological properties [Sperling, 2008]. Research has shown that an increase in crystallinity in polymers such as UHMW-PE leads to an increase in yield strength and modulus of elasticity [Bergstrom, 2003].

Based on the above, the objective of this work is to analyze the influence of the degradation of ultra-high molecular weight polyethylene (UHMW-PE) and mechanical nylamid on their physical and chemical properties. The degradation of the polymers was carried out in batches for one and two weeks by immersing them in three degrading media: seawater, 1% nitric acid solution, and castor oil. The latter was used as a substitute for mineral lubricants. To determine the physical and chemical changes due to degradation, a Fourier transform infrared spectroscopy (FTIR) analysis, surface roughness tests, and a surface topography analysis was performed.

2. Methodology

Materials

The study materials for this work were ultra-high molecular weight polyethylene (UHMW-PE) and mechanical nylamid which were purchased commercially from a local supplier. The castor oil used as the degradation medium was purchased commercially and did not require any additional preparation for use. Seawater was prepared by homogeneously mixing deionized water (Fermont® from Monterrey, Mexico) and sea salts (Sigma-Aldrich S9883) at a concentration of 40 g/L. The 1 % nitric acid was prepared in the same way using a 100 ml solution with 4.173 ml of nitric acid and the rest of distilled water.

Preparation of UHMW-PE and nylamid samples

Samples of UHMW-PE and nylamid were obtained in the form of 5 mm thick discs from a cylindrical bar of 1-inch diameter. The cross faces of the samples were polished with abrasive paper to perform the analyses with the same surface quality, reaching a roughness of 0.1 µm at Ra. The following sizes of silicon carbide abrasive paper were used to achieve the final finish: 80, 120, 180, 300, 600, 1000, 1500, and 2000. After polishing, the samples were cleaned in an ultrasonic bath with distilled water and finally dried in an oven at 50 °C for 24 hours.

Chemical characterization of the materials.

The materials were characterized and analyzed for degradation by Fourier transform infrared spectroscopy (FTIR). The analysis was carried out on a Spectrum 100 spectrometer (Perkin Elmer) equipped with a LiTa03 detector and a KBr beam splitter, and coupled to a ZnSe attenuated total reflectance (ATR) infrared sensor. Samples were scanned in the 600-4000 cm-1 range with a resolution of 4.0 cm-1 in transmittance.

Degradation process

Samples of UHMW-PE and nylamid were immersed in closed glass bottles containing 75 ml of the degrading substances. The residence times in the degradation media were 1 week for 3 samples of each material in 3 different degradation media and similarly 3 other samples of the materials for 2 weeks. The temperature was kept controlled in a conditioned room at a temperature of 25 °C with an approximate humidity of 30%. At the end of the degradation time, the samples were removed, washed with distilled water without rubbing and dried in an oven at 50 °C for 24 hours.

Evaluation of degradation

To measure the level of degradation, physical and chemical tests were performed. The physical tests consisted of the evaluation of the surfaces by optical microscopy analysis and the change in surface roughness. The chemical tests consisted of detecting changes in signal intensity in the infrared spectrum of the UHMW-PE and mechanical nylamid.

Surface topography analysis

A review of the surface topography of UHMW-PE was performed to analyze the changes at the microscopic level and to observe if there was an effect due to degradation. Images were taken with an Axio Imager.A1 m optical microscope (Zeiss) using a dark filter at 500x. Also, the change in surface roughness of the degraded samples was analyzed using an SJ-400 contact profilometer (Mitutoyo).

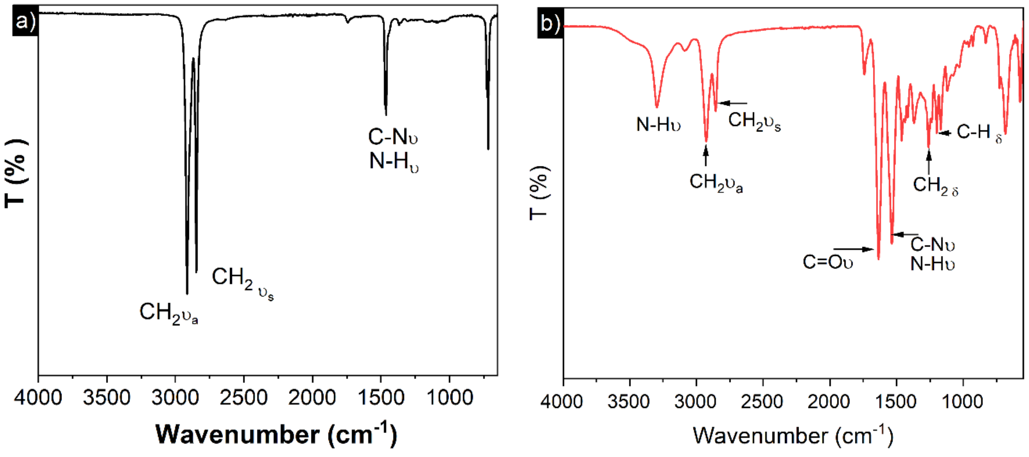
Chemical analysis by FTIR

To analyze the chemical changes in the UHMW-PE, the degraded samples were analyzed by ATR-FTIR with the equipment and conditions described above. The spectra were compared with the spectrum of the non-degraded material in transmittance to determine the signs of degradation by analyzing the full spectrum with emphasis on the hydroxyl and carbonyl groups as a result of oxidative reactions.

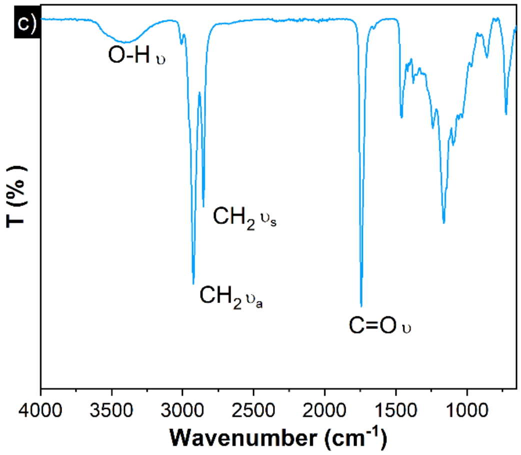
3. Results and discussions

Chemical characterization of the materials

Figure 1 shows the transmittance infrared spectrum of the undegraded UHMW-PE (Figure 1a) and nylamid M (Figure 1b). The stretching signals of the asymmetric and symmetric N-H and CH_2 functional groups can be observed, corresponding to the peaks between 3299-2750 cm^{-1} which are characteristic of this type of polyamides. The peaks corresponding to the N-H deformation and C-N stretching bonds, which occur approximately between 1650-1500 cm^{-1}, are the bonds that form the amides in the polyamide structures [Hernández, 2020]. On the other hand, figure 1c shows the infrared spectrum of castor vegetable oil. Two long peaks can be observed between 3000 and 2800 cm^{-1}, which are related to the asymmetric and symmetric CH_2 stretching bonds. The long peak at wave number 1750 cm^{-1} corresponds to the signal of the carbonyl group C=O [Stuart, 2004]. Signals smaller than 600 to 1500 cm^{-1} belong to the vegetable oil fingerprint [Stuart, 2004]. The small broad peak around 3430 cm^{-1}, uniquely present in castor oil, corresponds to stretching vibrations of the O-H group which is the unique feature of this oil.



a) UHMW-PE *b) Nylamid*



c) Castor oil

Figure 1 ATR-FTIR spectrum.

The spectra of seawater and nitric acid are not presented because only the water molecule appears as an important link. Surface topography analysis

Figures 2 and 4 show the optical micrographs of the surfaces of undegraded UHMW-PE and nylamid. While figures 3 and 5 exhibit the optical micrographs of the 2-weeks-degraded surfaces of UHMW-PE and nylamid, respectively. Figure 3a belongs to the degradation in seawater and clearly shows a rougher surface compared to the undegraded sample. As for the nitric acid degradation (Figure 3b) of UHMW-PE, a slightly higher roughness is also observed, but to a lesser extent than with seawater. Whereas, with castor oil, a completely different surface is observed, due to the fact that remnants of the oil were impregnated on its surface even though they were previously washed and dried. This is also observed on the surface of the nylamid degraded with castor oil (Figure 5c), with areas of lower and higher accumulation of these remnants. Finally, it is observed in the degraded samples of nylamid with seawater and nitric acid (Figures 5a and 5b respectively), only a slight change with a rougher surface than in the undegraded sample.

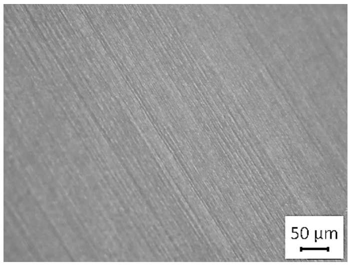
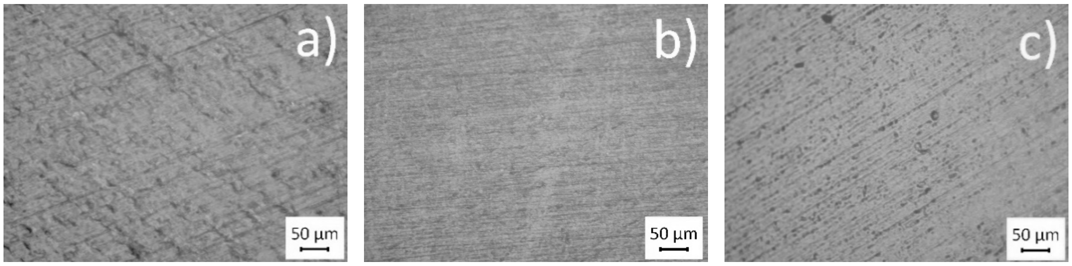


Figure 2 Optical micrograph of the UHMW-PE surface without degradation at 200X.



a) Seawater *b) Nitric acid 1%* *c) Castor oil*

Figure 3 Optical micrographs at 200X of degraded UHMW-PE surfaces.

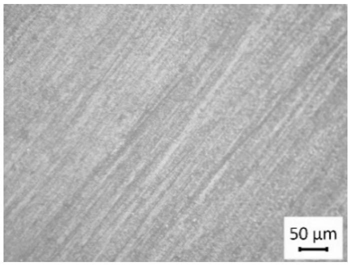
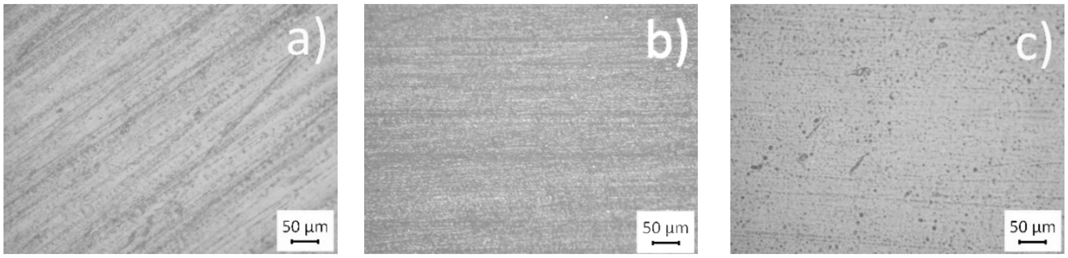


Figure 4 Optical micrograph of the nylamid surface without degradation at 200X.

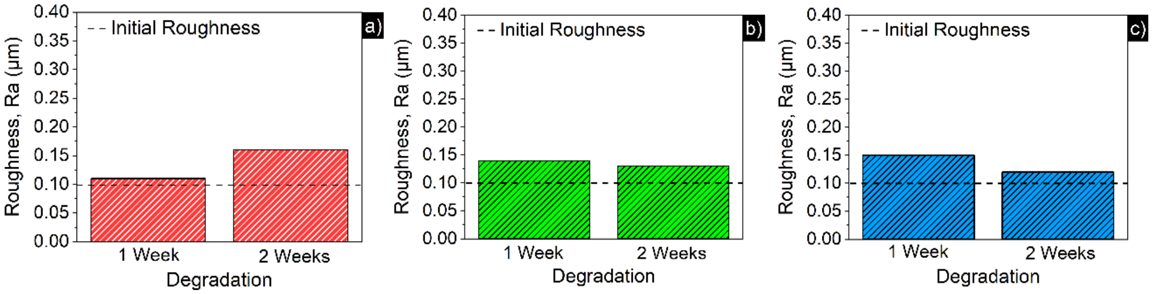


a) Seawater *b) Nitric acid 1%* *c) Castor oil*

Figure 5 200x optical micrographs of degraded nylamid surfaces.

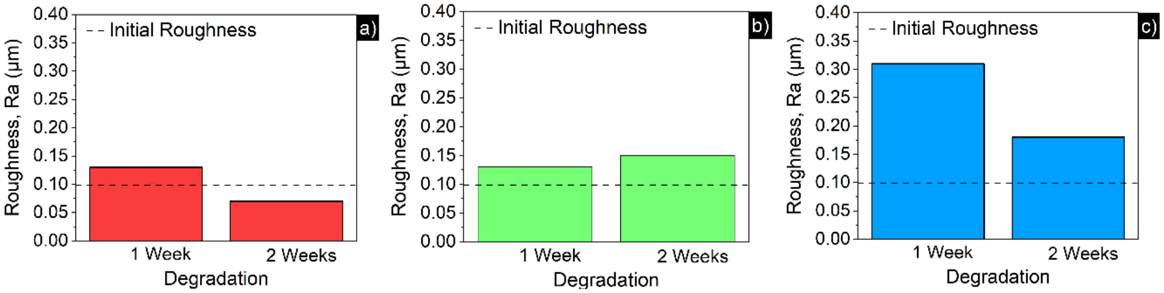
To quantify the surface damage of the UHMW-PE and nylamid samples caused by degradation, the surface roughness was evaluated. Figure 6 shows the roughness values (Ra) of the degraded UHMW-PE samples under different conditions. It can be observed that in the seawater (Figure 6) the roughness increased over the weeks up to 50%. While in nitric acid (Figure 6b) an increase in roughness is also observed, however, it does not show an upward trend with the passing of the weeks.

On the other hand, for the samples degraded in castor oil, an increase in roughness of 50% is observed in the first week and then a slight decrease of 18% in the second week. On the nylamid side we can see the changes in roughness in figure 7. Where the degradation in seawater (Figure 7a) had an increase of 30% in the first week followed by a decrease of 30% in the second week. With nitric acid (Figure 7b) there is a tendency to increase the roughness over the weeks with an increase of 30 and 50%. While castor oil (Figure c) occurs something similar to UHMW-PE, where a strong increase is observed in the first week and then a smaller increase in the second week. In all cases, both in nylamid and UHMW-PE, a notable increase in roughness is observed (with the exception of the second week in nylamid seawater).



a) Seawater *b) Nitric acid 1%* *c) Castor oil*

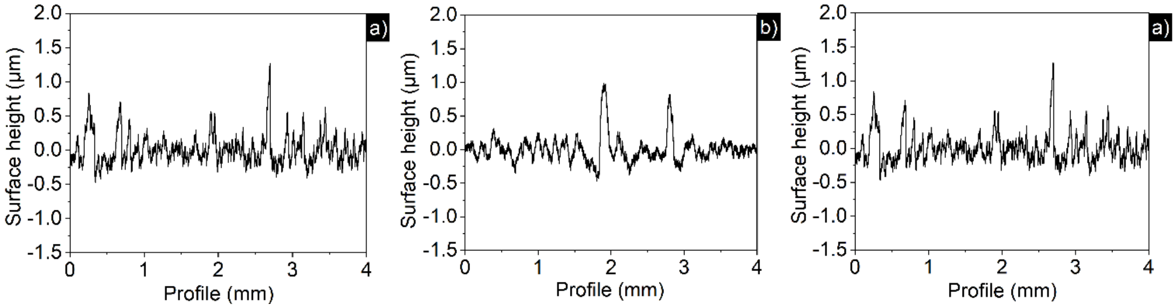
Figure 6 Roughness (Ra) plot of the degraded UHMW-PE surface.



a) Seawater *b) Nitric acid 1%* *c) Castor oil*

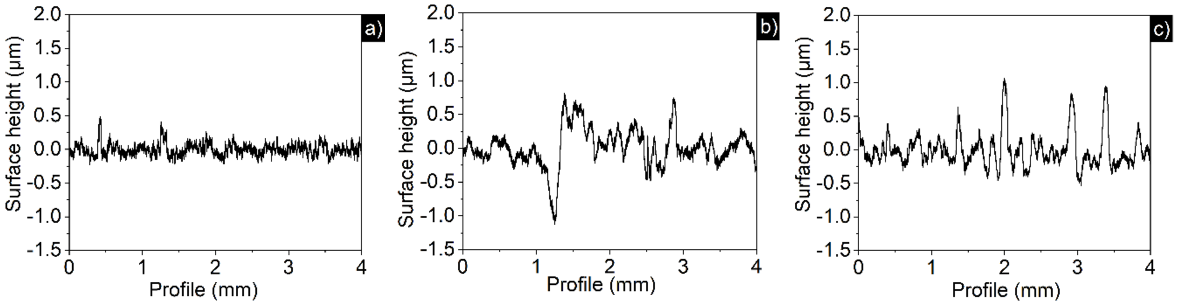
Figure 7 Roughness (Ra) plot of the degraded Nylamid surface.

Figures 8 and 9 show the roughness profiles of the degraded surfaces of UHMW-PE and nylamid. For each system of both materials an increase in roughness is observed. The roughness on the nylamid increased by 60% at 2 weeks degradation in seawater and an increase of 30 and 20% in nitric acid and castor oil respectively.



a) Seawater *b) Nitric acid 1%* *c) Castor oil*

Figure 8 Roughness profile UHMW-PE degraded two Weeks.



a) Seawater *b) Nitric acid 1%* *c) Castor oil*

Figure 9 Roughness profile nylamid degraded two Weeks.

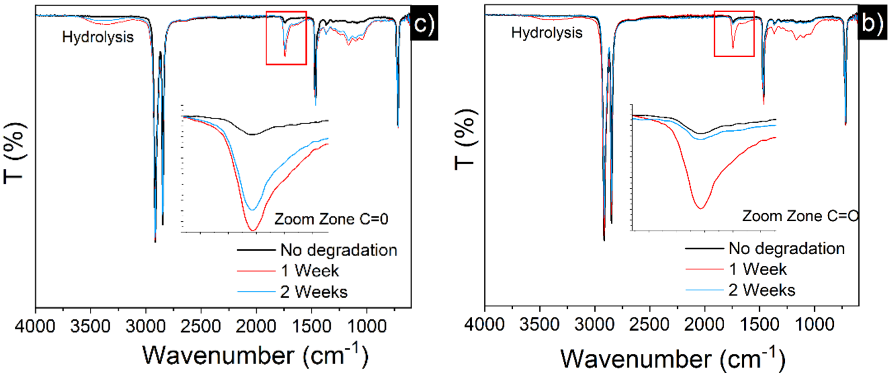
Similarly for the UHMW-PE, surface roughness increased by 50 and 80% for nitric acid and castor oil respectively. However, for the seawater system, a reduction in roughness of 30% was observed. In the roughness profiles shown, more pronounced peaks are observed with nylamid in the samples degraded with nitric acid and castor oil (Figures 9b and 9c), which generate a higher roughness than with seawater. For the UHMW-PE roughness profiles, some high peaks are observed that generate an increase in roughness especially in figures 9b and 9c. While in the degraded system in seawater we can see low, narrow and constant peaks, which show a greater regularity in the roughness of the surface of the sample. The sharp increase in roughness shown in week 1 with castor oil indicates that the oil performs a first phase of degradation with both materials, however, as it does not penetrate beyond the surface of the materials this degradation does not seem to affect as time passes but rather the opposite. Nitric acid and seawater cause a "swelling" of the surface of the polymers which causes an increase in roughness, although this swelling is less severe in nylamid over the weeks because nylamid has a better resistance to absorb moisture (in this case water from the degrading substances) than polyethylene.

FTIR degradation analysis

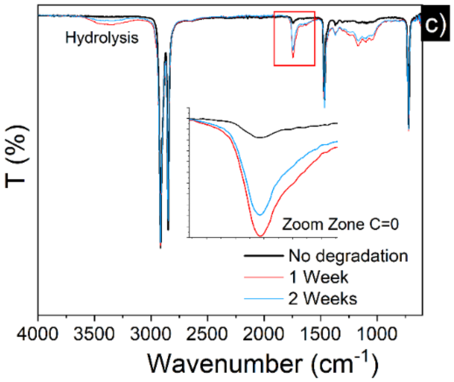
Figure 10 shows the FTIR spectra of the degraded UHMW-PE samples in the different media. For all samples, various signal changes are observed throughout the spectrum. The increase of a broad band around 3500 cm^{-1} indicating the presence of O-H bonds stands out. This may be due to the hydrolysis process, a dominant degradation mechanism in this type of polymer, which generates an increase in crystallinity [Dias, 2022].

Hydrolysis is observed in all degradation media and slightly more with castor oil. Likewise, changes in the CH. (3000 to 2750 cm^{-1}) and C.H (600 to 1700 cm^{-1}) signals were found indicating changes in the fingerprint region, which could be related to changes in the crystalline and amorphous phases [Stuart, 2004]. This increase in crystallinity is more noticeable in the two 2 weeks in the degradation with castor oil (figure 10c). On the other hand, in all cases, the appearance of a new peak located approximately at 1750 cm^{-1} was found, which represents the C=O bond.

It can be observed that the increase of this signal is notoriously higher in the degradation with castor oil, followed by the degradation with nitric acid at 1% in the first week (Figure 10b) and to a lesser extent in the degradation with seawater (Figure 10a).



a) Seawater *b) Nitric acid 1%*



c) Castor oil

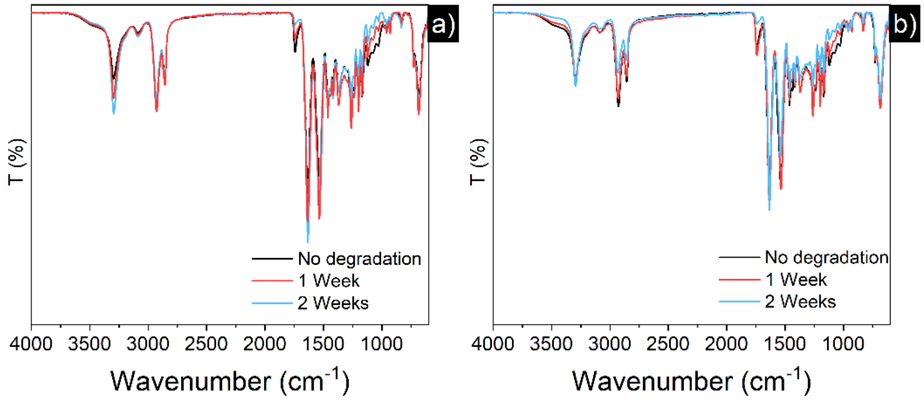
Figure 10 ATR-FTIR spectra of the degraded UHMW-PE.

While in figure 11 which shows the FTIR spectra of the degraded nylamid, changes in the C=O double bond located at the 1750 cm-1 wavenumber can also be observed. But they do not seem to represent oxidation. However, in the 3500-3250 cm^{-1} region, which belongs to the N-H bond, the greatest changes are observed within the whole spectrum, both in seawater and castor oil (Figures 11a and 11c). While with nitric acid (Figure 11b) the smallest changes were observed.

4. Conclusions

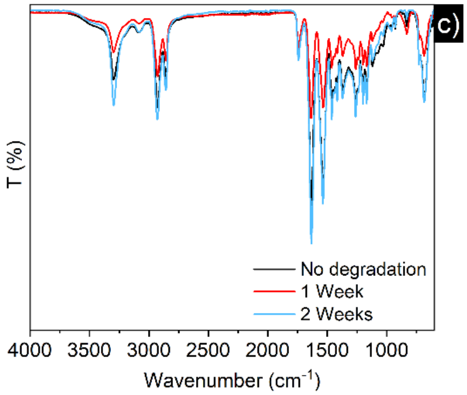
In this work, an analysis of the effect of some degrading media on the chemical and physical properties of UHMW-PE and "mechanical" nylamid was presented, which can be summarized as follows:

- In the samples degraded in castor oil for both systems an accumulation of oil remnants on the surface of the materials could be observed. While for the samples immersed in seawater, in both materials a rougher surface could be appreciated, especially in the UWHM-PE.



a) Seawate

b) Nitric acid 1%



c) Castor oil

Figure 11 ATR-FTIR spectra of the degraded Nylamid.

- R Roughness had a significant increase in all 3 systems for the UHMW-PE. In the seawater system, the increase was up to 70% in the second week. While in nitric acid the increase in roughness was similar in both weeks with 40% and 20% respectively. For castor oil, an increase of 50% was observed in the first week and then decreased to 20% above the initial roughness.
- In the three degradation systems used, a significant change in the roughness of Nylamid was observed. In seawater, the roughness increased by 30% in the first week and in the second week it decreased by 30% with respect to the initial

roughness, while in nitric acid, in both weeks the roughness was higher than the initial roughness with a tendency to increase in the second week up to 50%. Finally, for the castor oil system, an increase of up to 300% was observed in the first week followed by a decrease in the second week, but being 70% higher than the initial roughness.

- The FTIR study showed symptoms of degradation by hydrolysis and oxidation in the UHMW-PE in all the degraded samples and to a greater extent with castor oil. Similarly, for nylamid, an increase in the carbonyl group was observed.
- Finally, it can be concluded that all the degrading substances cause changes in the material, the most significant of which are: an increase in oxidation due to the increase in the C=O double bond together with an increase in roughness. Therefore, when in contact with these substances, both materials will have an evident degradation that could increase with the longer exposure time.

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