

Study of the Effect of Accelerated Aging by Sea Water on the Mechanical and Chemical Properties of High Density Polyethylene Bottles

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Abstract

The increase of plastic waste in the marine environment has several ecological, human and marine biota problems. In this paper, an accelerated artificial ageing study in seawater was performed, after immersion of samples extracted from high density polyethylene bottles for several ageing times and under two different temperatures. The degradation of the mechanical properties of HDPE at different ageing conditions was studied using static tensile and compression tests. The absorption of seawater by the samples is analyzed by a gravimetric procedure, and Fourier transform infrared spectrometry (FTIR). A further surface analysis of the samples during accelerated ageing was shown by scanning electron microscope SEM. The results obtained show that the high density polyethylene loses its ductility and changes from ductile to brittle failure. Fourier Transform Infrared Spectrometry (FTIR) analysis shows an increase in crystallinity over the ageing period.

Introduction

Plastic polymer pollution has been recognized as a serious problem in the world's oceans, the accidental disposal of plastic waste during transport through the oceans can cause the release of plastics into the sea directly or indirectly. Plastic waste in the oceans reaches 400 Million tons per year [1], these plastics have a persistence characteristic due to their easy transport by wind and water current, which introduces a slow degradation [2–3]. Until now due to irresponsible behaviour much of the waste thrown into the environment [4], Eriksen found that between 4.8 to 12.7 million metric tons of plastic waste is thrown into the oceans [5]. Ocean pollution remains a threat as ocean basins act as economic and ecological systems for human well-being [6].

Plastic pollutants are distributed in 3 scales according to their size variation, micro-plastics, miso-plastics and macro-plastics. Micro-plastics or secondary micro-plastics are obtained by the fragmentation of macro-plastic waste such as bottles, aged plastic bags [7], undergo processes such as photo-degradation due to sunlight, degradation by water salinity which modifies the plastic state, mechanical degradation, hydrolysis which allows the release of toxic chemicals, and bad consequences on human beings, people who ingest these micro-plastics can suffer physically by internal blockage or abrasion [8]. Macroscopic waste has serious impacts such as death of species by strangulation, blockage of boat propellers [9], and the possibility of increased microbial attack due to the reduction in molecular weight and oxidation of functional groups in polymer chains [10–11]. Plastics are in high demand in Africa and the European Union [12–13]. In Africa, plastic waste is being channeled into water bodies such as the Atlantic and Mediterranean oceans due to poor waste management, which combines with increased toxicity in food webs and the marine environment due to the ageing of plastic particles [14]. The most consumable plastics in the world are polyethylene terephthalate PET, high density polyethylene HDPE, poly (vinyl chloride) PVC, low density polyethylene LDPE, polypropylene PP and polystyrene PS. HDPE, PET and PP are commonly used as packaging materials because of their mechanical and odorless characteristics, low cost and durability [15–16].

HDPE accounts for 79% of plastic waste collected from the marine environment [17], about 730 million tonnes of HDPE in the form of packaging and plastic were generated in 2015, but the amount recycled is only 5.5% [18]. The specific surface area of HDPE degrades in the marine environment by between 0 and 11 μm , such that the half-life of HDPE bottles is 58 years and pipes 1200 years using SSDR [19]. HDPE micro-plastics remain vertical at the water surface due to the high density of HDPE [20–23], e.g. HDPE particles were picked up by the gills and transferred to the digestive and lysosome system after three hours of exposure, triggering an inflammatory immune response [24].

The management of HDPE macro- and micro-plastic waste requires the control of the life span of this polymer as well as the control of their end of life. In this context, we cite the work of Nulson and all [25] which applied cyclic loadings on samples taken from HDPE cables artificially aged in sea water, Jennifer and all [26] also was done an estimate of the duration of exposure of HDPE and PP particles in the oceans.

The accelerated artificial ageing in seawater for HDPE bottles were however not treated in [25–26]. The purpose of this work is the development of the accelerated artificial ageing in seawater for HDPE bottles and samples extracted from these HDPE bottles. In the first part, the experimental aging methodology is described, as well as the procedure followed for tensile and compression tests, followed by an analysis of the crystallinity content using Fourier Transform Infrared Spectrometry (FTIR), and a study of the aged surfaces by Scanning Electron Microscopy (SEM).

Experimental Procedure

1.1 Accelerated ageing methodology

Before determining the mechanical characteristics of HDPE, two series of accelerated artificial ageing in the marine environment were developed in the laboratory of the Higher Institute of Maritime Studies ISEM [27], the ageing procedure is described as follows:

Firstly, unaged HDPE bottles are cut into parallelepipedic test pieces of dimensions (100x20x1.10) (Fig. 1).

The sea water is taken directly from SIDI Rahal and filtered before use. For each ageing time 3 samples and 3 bottles were used.

The first series of ageing tests was carried out at a temperature of $23\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$ and a humidity between 15% and 20%, this temperature being the temperature of the surface of the oceans, in which the HDPE samples were immersed in glass molds filled with seawater from SIDI Rahal and the bottles were filled with the same seawater as shown in Fig. 2 (Fig. 2.a). The samples and bottles were not irradiated, they were isolated in a dark area.

The second series of tests was carried out in a MEMMERT type oven with a temperature of $80\text{ C}^{\circ}\pm 1\text{C}^{\circ}$, this temperature is lower than the melting temperature of HDPE. A glass mold filled with seawater and the bottles were placed in the oven (Fig. 2.b and Fig. 2.c), which maintained a temperature control to fix the ageing in marine environment only under the effect of seawater and temperature increase.

Ageing tests at 23C° and 80C° in the marine environment were carried out for 9, 18, 27, 36 and 72 days according to ASTM D543[28] with one sample every 9 days.

1.2 Tensile and Compression Test Methodology

The monitoring of the mechanical characteristics and properties of HDPE during accelerated ageing by tensile tests is a classical method very useful for determining the effects of degradation of samples of this material in sea water.

Tensile tests were carried out in accordance with ISO 1798[29], using the MTS Criterion Series 40 Universal Machine with a load capacity of 5KN as shown in Fig. 3 (Fig. 3).

The specimens aged at 23C° and 80C° were conditioned to dry at 50% (± 5) humidity before testing, and three measurements for each ageing time and temperature were taken.

Three unaged specimens were tested to characterize the behavior of the material.

The important compression test to identify the compressive strength of bottles. Compression tests are performed on HDPE bottles obtained by the extrusion process. The HDPE bottles also undergo two series of ageing by sea water at 23C° and 80C° for 9, 18, 27, 36 and 72 days. At the end of the ageing process, the bottles were emptied and dried, after which they were placed between two compression plates (Fig. 4) according to the ASTM D2659 [30] standard with the same MTS machine used in traction, for each ageing time and each temperature we carried out three compression tests.

1.3 Gravimetric monitoring

After each sampling, the immersed test tubes and bottles are removed and dried, weighed at room temperature and 50% humidity on a RADWAG type balance with an accuracy of 0.0001 mg (Fig. 5). In order to carry out these measurements, three samples and three bottles for the test conditions are measured.

The percentage of seawater absorption in the samples and HDPE bottles at 23C° and 80C° are shown in the results section.

1.4 FTIR and SEM

The effect of artificial ageing accelerated by seawater at 23C° and 80C° at different ageing times was observed using a scanning electron microscope type SH 4000M (Fig. 7), after drying the samples are

metallized by carbon and are conducted in the SEM.

The calculation of the crystallinity rate as a function of ageing time was done using SHIMADZU-IRRAFINITY FOURIER transform infrared spectrometry (Fig. 6).

The HDPE samples observed by SEM, and subjected to FTIR were tested under the same conditions as described in the section "Tensile test methodology".

Results And Discussion

1.1 Measurement of seawater absorption rate

As described in section 1.3, the gravimetric monitoring consists in calculating the percentage of seawater absorption by the samples and HDPE bottles, this mass percentage is calculated by the following relation (Eq. 1).

$$M_P (\%) = \frac{M_{ap,v} - M_{av,v}}{M_{av,v}} \cdot 100 \quad (1)$$

Where M_p is the percentage change in mass, $M_{ap,v}$ the calculated mass after ageing and $M_{av,v}$ the mass of the samples without ageing.

The following Fig. 8 (Fig. 8) and Fig. 8 (Fig. 9) show the results obtained at 23 C° and 80 C° of accelerated artificial ageing.

The figures of the sorption curves at 23C° and 80C° follow the same evolution (Fig. 8–9), this evolution can be divided into 3 stages:

First stage: it is characterized by a linear relationship between the absorption rate (M_p) of the seawater for both temperatures has been observed intermediate stage: it is characterized by a peak plateau at 15 H1/2 decrease. The detection of the equilibrium of the absorption rate is a bit complex in our case since a weak stabilization of the MP is found.

The last stage: it is characterized by the increase of the absorption rate after 30 H1/2 until reaching 33% at 80C° and 17% at 23C° in the case of aged samples, 10% at 23C° and 17% at 80C° in the case of aged HDPE bottles.

As a result, we can see the dependence of the temperature used on the increase in the absorption of seawater by the HDPE bottles and samples during immersion. As can be seen in the curve for 80C° and 23C°, the absorption at 23C° is lower than at 80C°. These results are justified by the phenomenon of hydrolysis due to the scission of the molecular chains of HDPE at high temperature.

1.2 Measurement of Crystallinity

The spectra of HDPE samples obtained for accelerated artificial ageing in the marine environment at 9 days and 72 days for the two test temperatures are compared with the spectra obtained for virgin HDPE samples (Fig. 10).

As expected, the spectra and peaks of the HDPE samples are changed during accelerated aging. Peaks generated describe several phenomena such as hydrolysis for aging at 80C° in 9 days and 72 days, the hydrolysis peaks have a remarkable value of 3606cm⁻¹ with a significant amplitude at 72 days. The formation of alkenes and carbonaceous double bonds for the 1663 cm⁻¹ bands, these results are in agreement with the study of [1].

On the other hand, for aging at 23C°, we can notice the generation of CH₂-scissoring bonds and CH₃ bonds after 9 days of aging, other bonds generated at 72 days such as -C(CH₃) of the RCH₂ = CH₂ out of bending type.

This change in the morphology and chemical properties of HDPE is described by the crystallinity ratio of this material, the calculation of the crystallinity ratio X_c (Fig. 11) is based on the 1462cm⁻¹ and 1472cm⁻¹ bands according to the following relation:

$$X_c (\%) = 100 - \left(\frac{\frac{1 - \frac{I_a}{I_b}}{1.233}}{1 + \frac{I_a}{I_b}} \cdot 100 \right) \quad (2)$$

- I_a et I_b are the sub-areas of the peaks determined from the 1463cm⁻¹ and 1473cm⁻¹.bands.
- 1.233 is the relationship of the band intensities of I_a and I_b for fully crystalline HDPE.

Figure 11 shows the evolution of the crystallinity rate as a function of the accelerated ageing time, we can see the decrease of X_c of HDPE initially from 99% for the two temperatures studied until reaching a critical crystallinity rate of 97% at 36 days for the 23C° temperature, and 96.57% at 27 days of accelerated ageing at 80C° as it is shown in the small curve of figure 9. After these critical values the X_c increases again to a stabilization level below the pristine crystallinity level. These phenomena describe the processes of degradation of HDPE crystalline chains by salinity for the temperature 23C°, which increases the amorphous morphology of this material, and the formation of branching and hydrolysis in the case of the temperature 80C° which increases the mobility of the chains towards the amorphous phase.

1.3 Mechanical Properties

a. Tensile Test

To determine the ductile-to-brittle transition of HDPE, static tensile tests were carried out as described in section 1.2, the results of the tests at different temperatures and aging times are shown in the following figures.

Firstly, the unaged specimens all exhibited ductile behaviour followed by strain at a yield of 4%. A yield strength of 39.8MPa was measured. After ageing, the specimens did not show the same behaviour.

For both temperatures studied at 9 days of ageing (Fig. 12 and Fig. 13) the specimens failed in a ductile manner with a high yield strength. However, after 9 days, all specimens failed in the elastic part, i.e., once this brittle behaviour was identified, and for longer ageing times in seawater beyond 9 days, the tensile strength decreased from 43MPa (9 days) to 20MPa (72 days) for a temperature of 23C° (Fig. 12), and from 34MPa (9days) to 17MPa (72days) for the temperature of 80C° (Fig. 13) and a drop in the elastic stress also during the increase of the ageing time which describes the brittle ductile transition of the HDPE behaviour during ageing.

It can be seen that the degradation processes were accelerated when the ageing condition and the temperature increase condition are used simultaneously (Fig. 14), it can be seen that the increase of the hydrolysis rate with the increase of the temperature describes that the HDPE fracture is strongly affected by the degradation in seawater at 80C° more than 23C° which leads to a decrease of the

strain at break, the stress at break and the Modulus of elasticity.

b. Compressive Test

The compression results obtained during ageing in the marine environment are shown in the following figures.

It can be seen that the force increases with displacement until a maximum force is reached in compression (Fig. 15–16), which causes buckling of aged HDPE bottles, the occurrence of residual loads after buckling decreases the forces and increases the displacements.

The drop of the maximum compression force during compression from 22–63% for the temperature of 23C° (Fig. 15), and from 61–81% in the case of aging at 80C° (Fig. 16), it is noted that the drop of the maximum compression force is very important at 80C° compared to 23C° (Fig. 17).

1.4 SEM analysis

In this part we deal with the results obtained for the experimental procedure of the scanning electron microscope dedicated in section 1.4.

The evolution of the surface can indicate degradation processes which lead to the untwisting of the polymer caused by the increase of the temperature at 80C° and the increase of the ageing time (Fig. 18.g), this is not present in the case of 72 days at 23C° (Fig. 18.f) which represents cavities in the surfaces with smaller diameters than those obtained at 80C°. The unaged surface represents a less rigorous and less smooth surface compared to the samples aged at 23C° (Fig. 18.b-d-f) which confirms the dependence of the toughness mechanisms and the ductility of HDPE on the sea water absorption mechanisms. The generation of pores, cavities and scratches resulting from the weakening of HDPE bottles during ageing due to the high salinity and chemical composition of water molecules.

Conclusion

In this work, the problem of degradation of HDPE bottles in the marine environment by an artificial ageing process accelerated by two different temperatures was addressed.

The mechanical properties during ageing are studied using static tensile and compression tests, and it was found that simulated ageing and increasing temperature is a very important phenomenon for accelerating the degradation of HDPE in seawater.

The FTIR analysis allows to identify the hydrolysis phenomena that decreases the crystallinity rate of the aged samples during the increase of the accelerated aging time.

The results obtained from the SEM images allow to defend the effect of salinity and temperature increase on the degradation of the surfaces of the aged samples through the observation of micro-cavities with

different sizes.

Declarations

Funding

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Author Contribution

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Abdelilah Hachim 1-3

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Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Figures



Figure 1

Example of a bottle of high-density polyethylene used with its cutting.



Figure 2

Accelerated artificial ageing procedure in seawater: (a) ageing of samples at 23C°, (b) ageing of samples and bottles at 80C°, (c) ageing of bottles at 23C° in seawater.

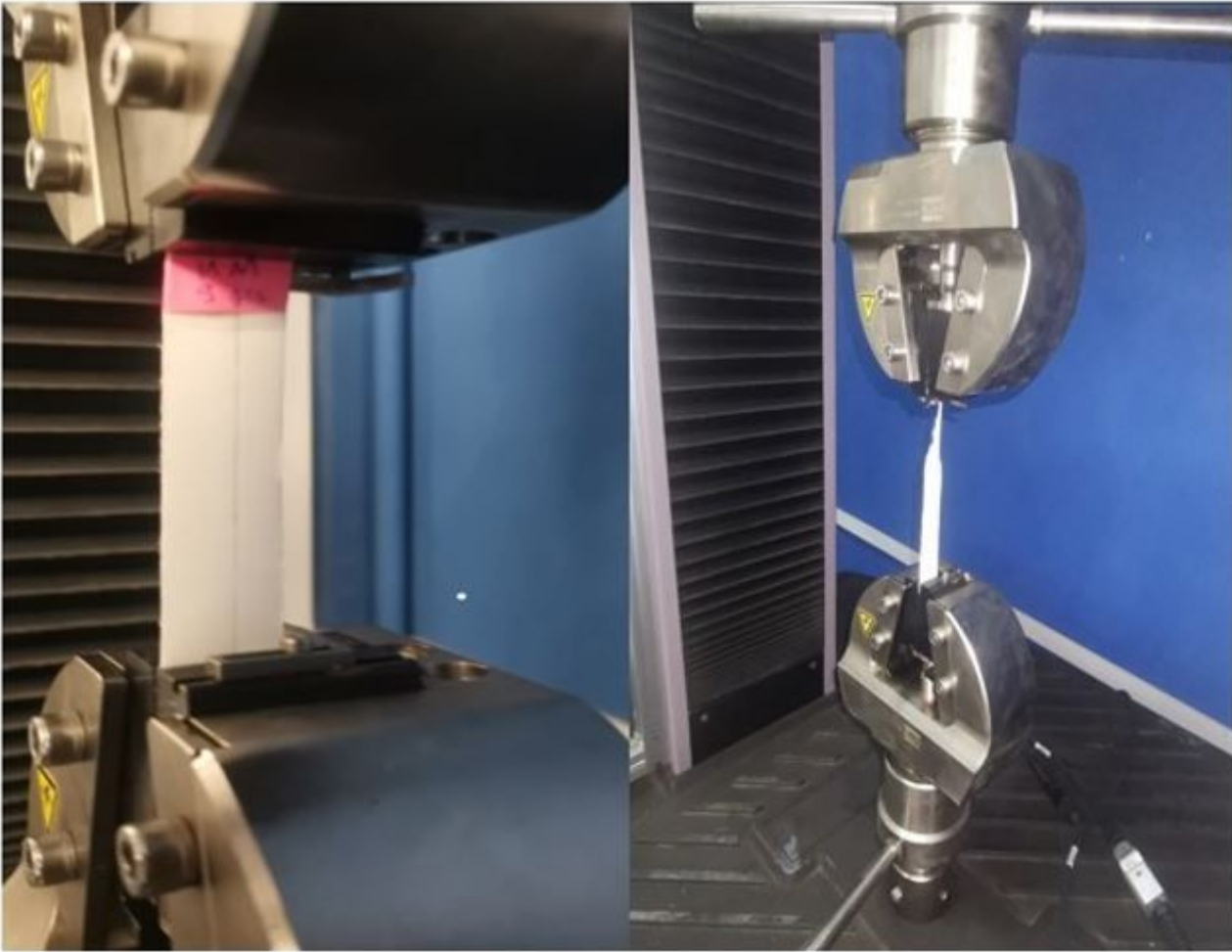


Figure 3

Example of an aged sample undergoing tensile testing by the MTS Machine.

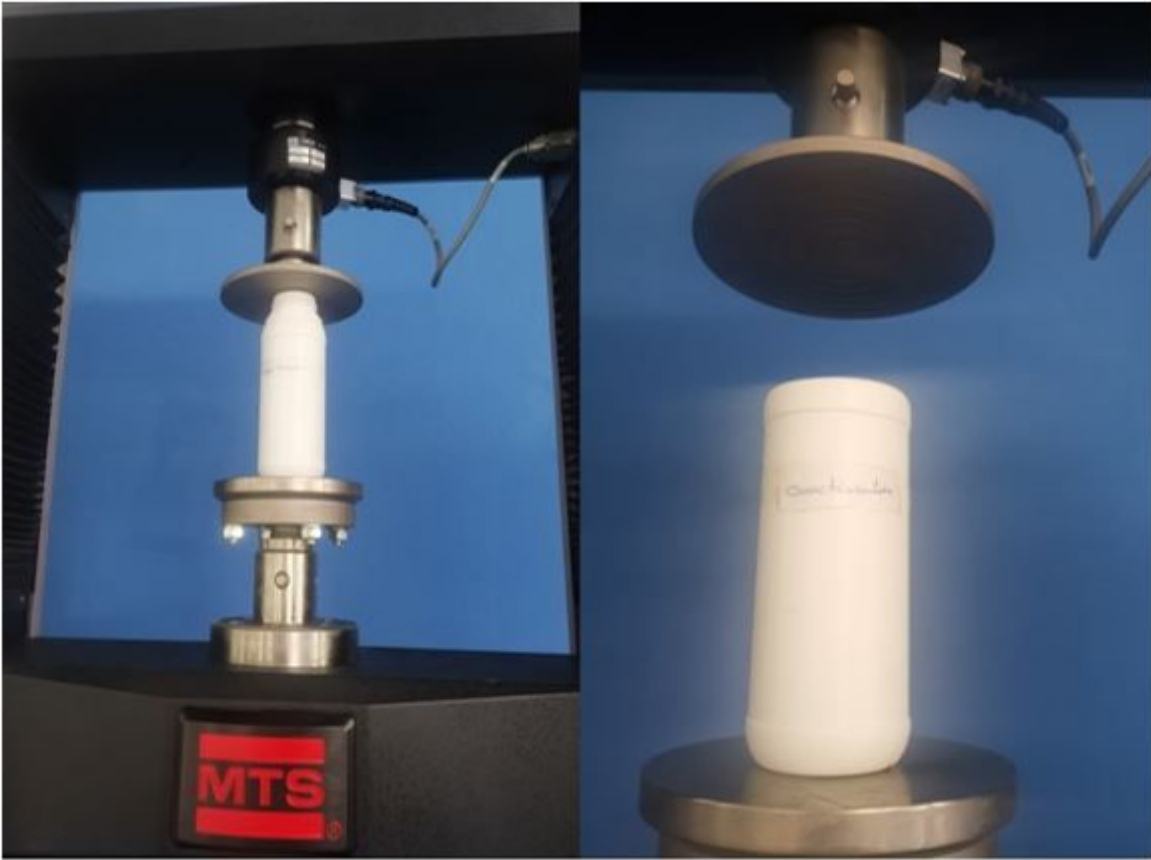


Figure 4

Example of an aged bottle undergoing compression testing by the MTS Machine.



Figure 5

ARADWAG device used for gravimetric measurements.

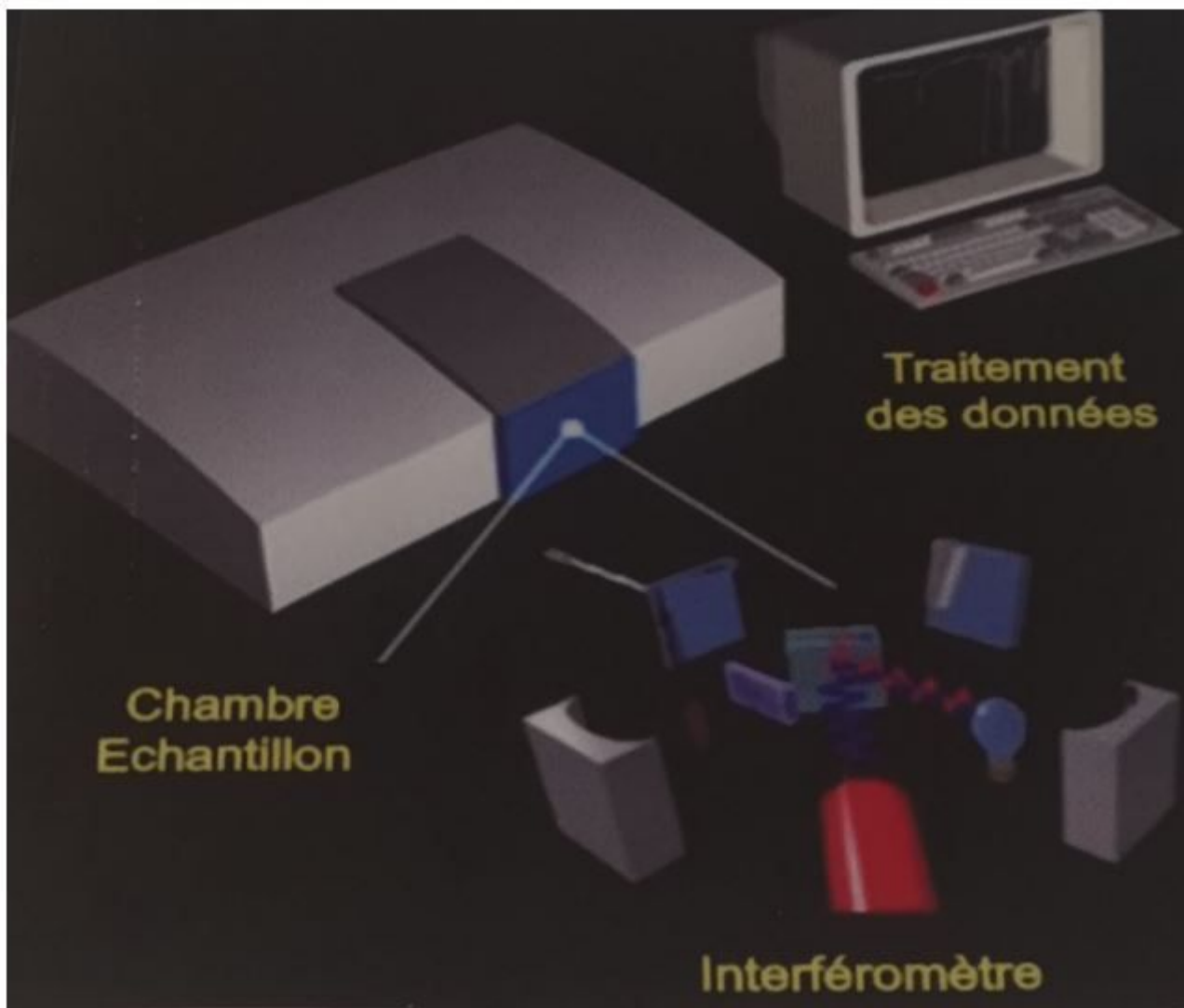


Figure 6

Principal of the SHIMADZU-IRRAFINITY FTIR apparatus.



Figure 7

SH 4000M apparatus for SEM.

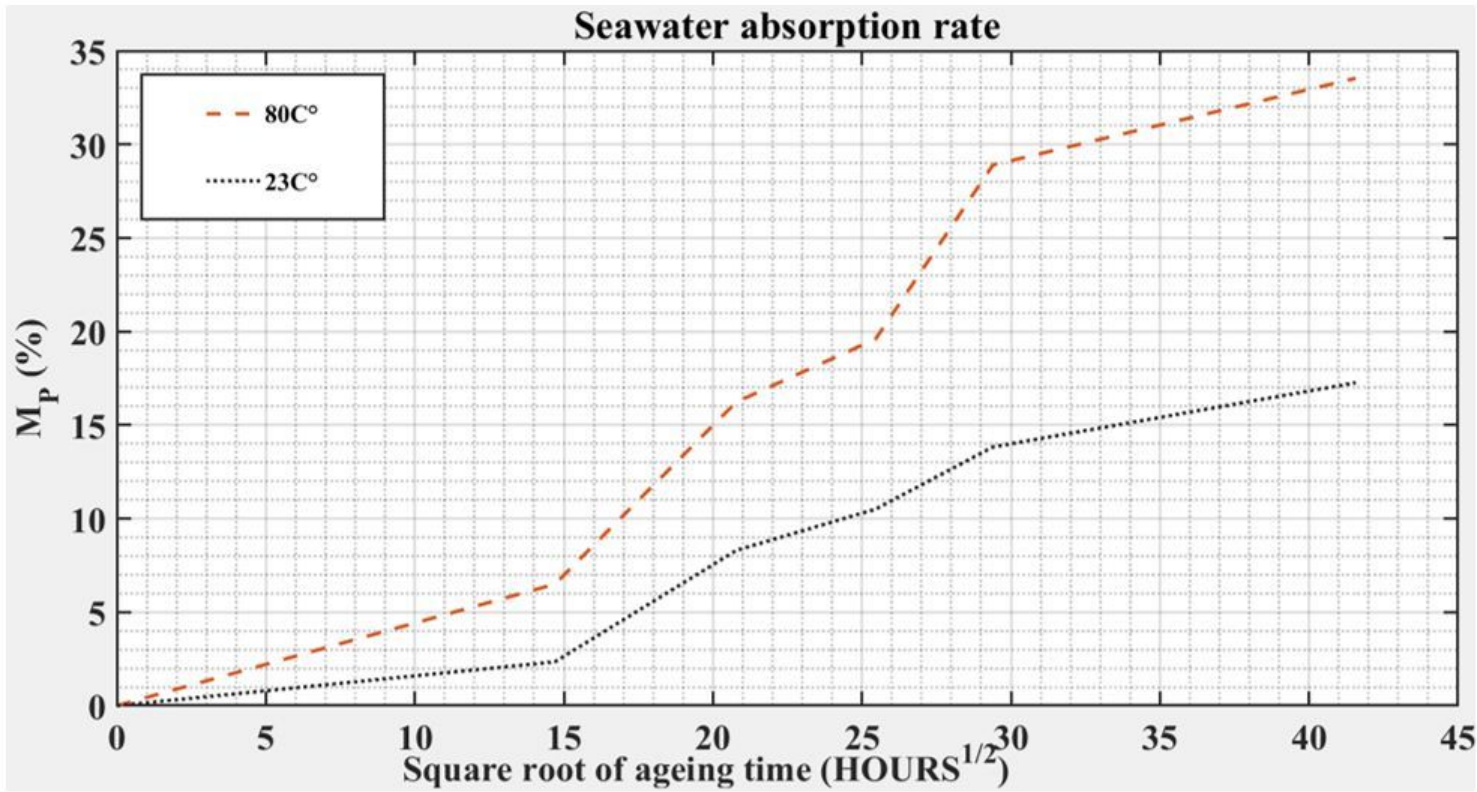


Figure 8

Rate of seawater absorption during ageing of HDPE samples at 23C° and 80C°.

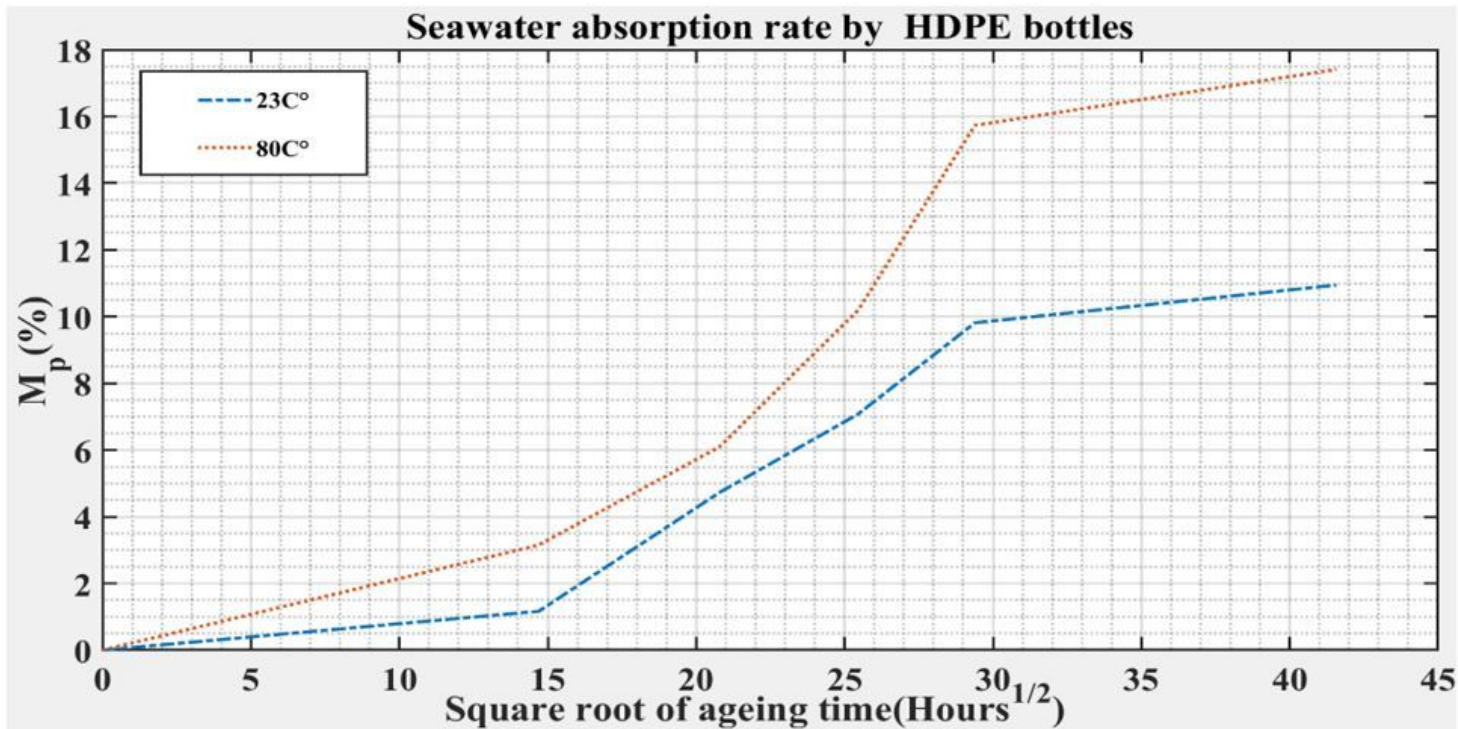


Figure 9

Rate of seawater absorption during ageing of HDPE bottles at 23C° and 80C°.

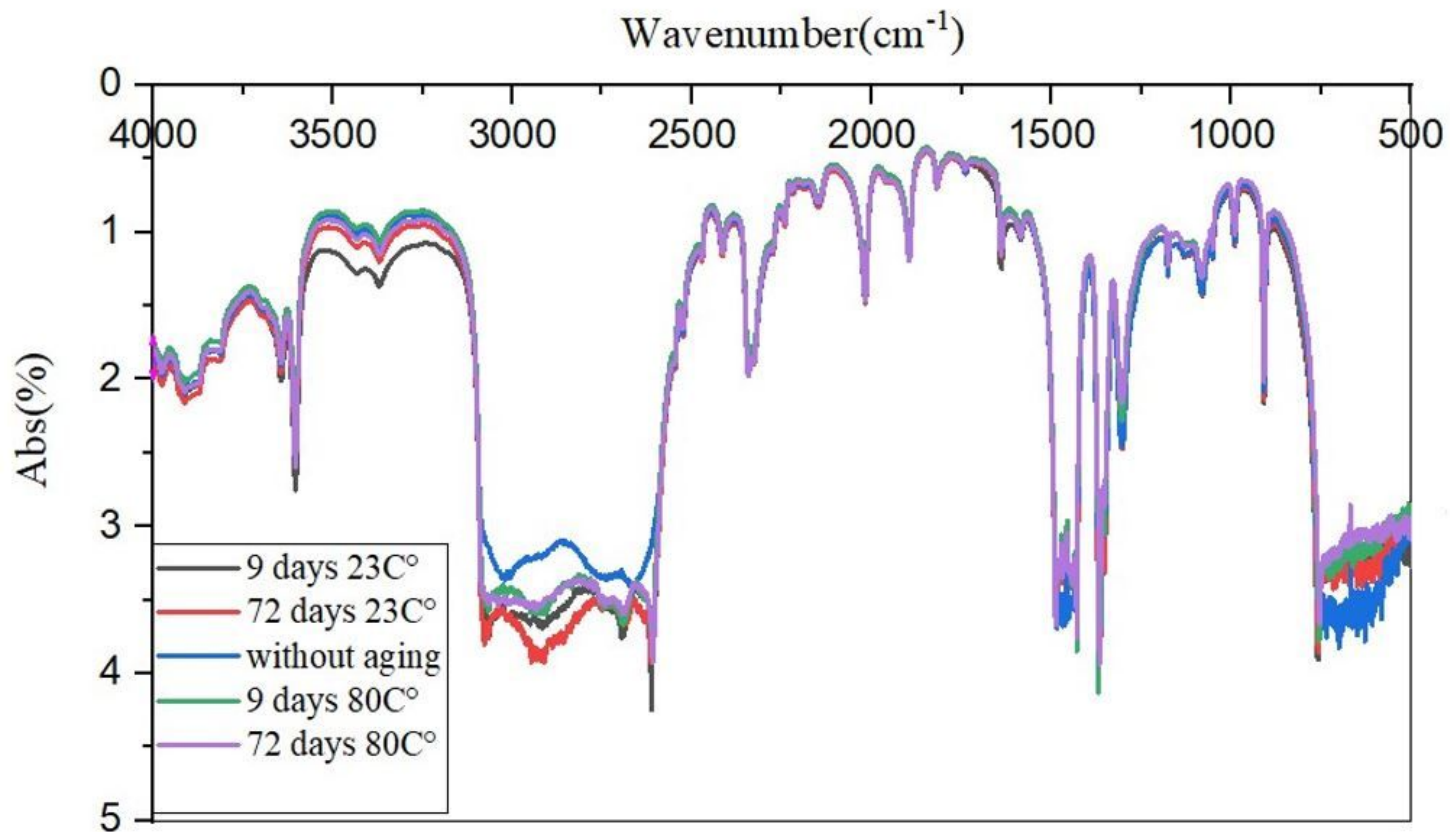


Figure 10

Results obtained by Fourier transform infrared spectrometry

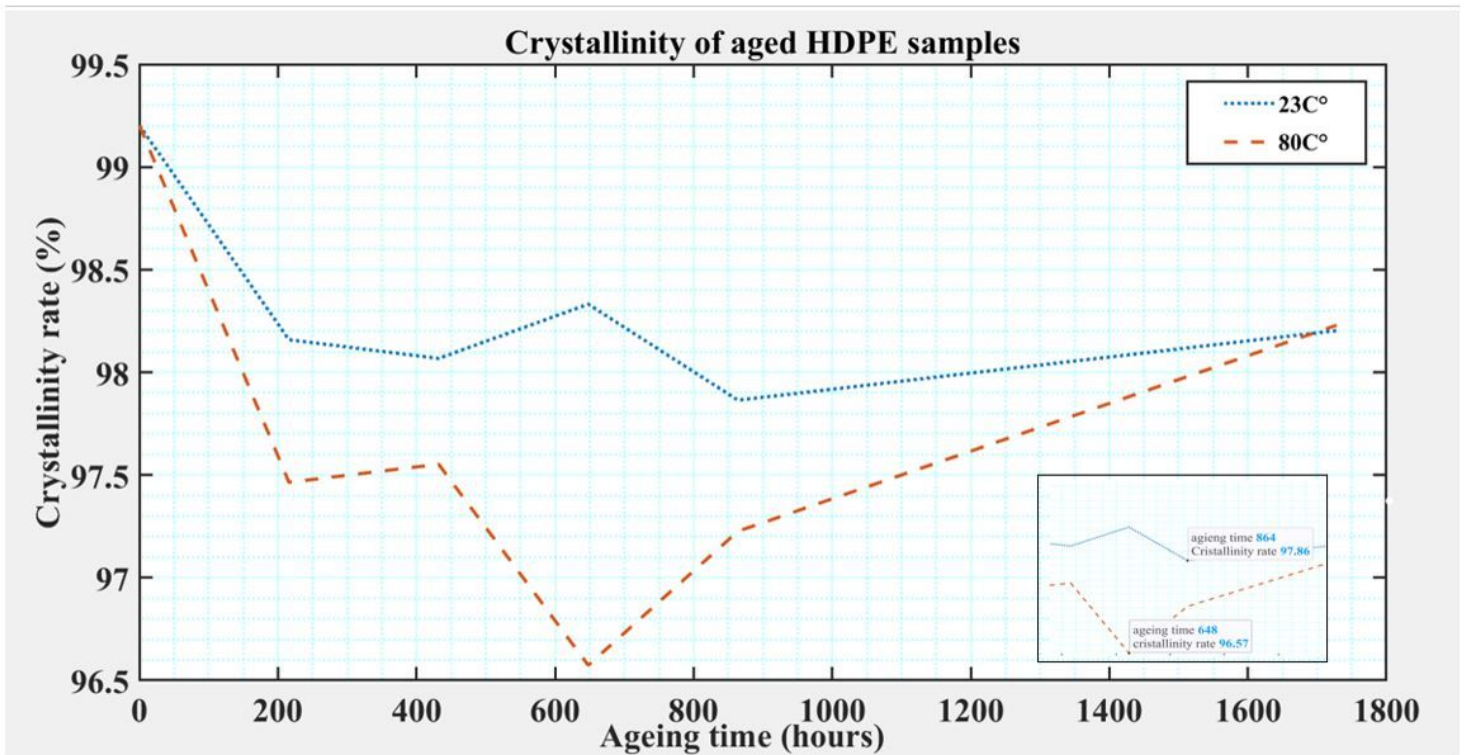


Figure 11

Crystallinity of HDPE samples aged in the marine environment at different temperatures.

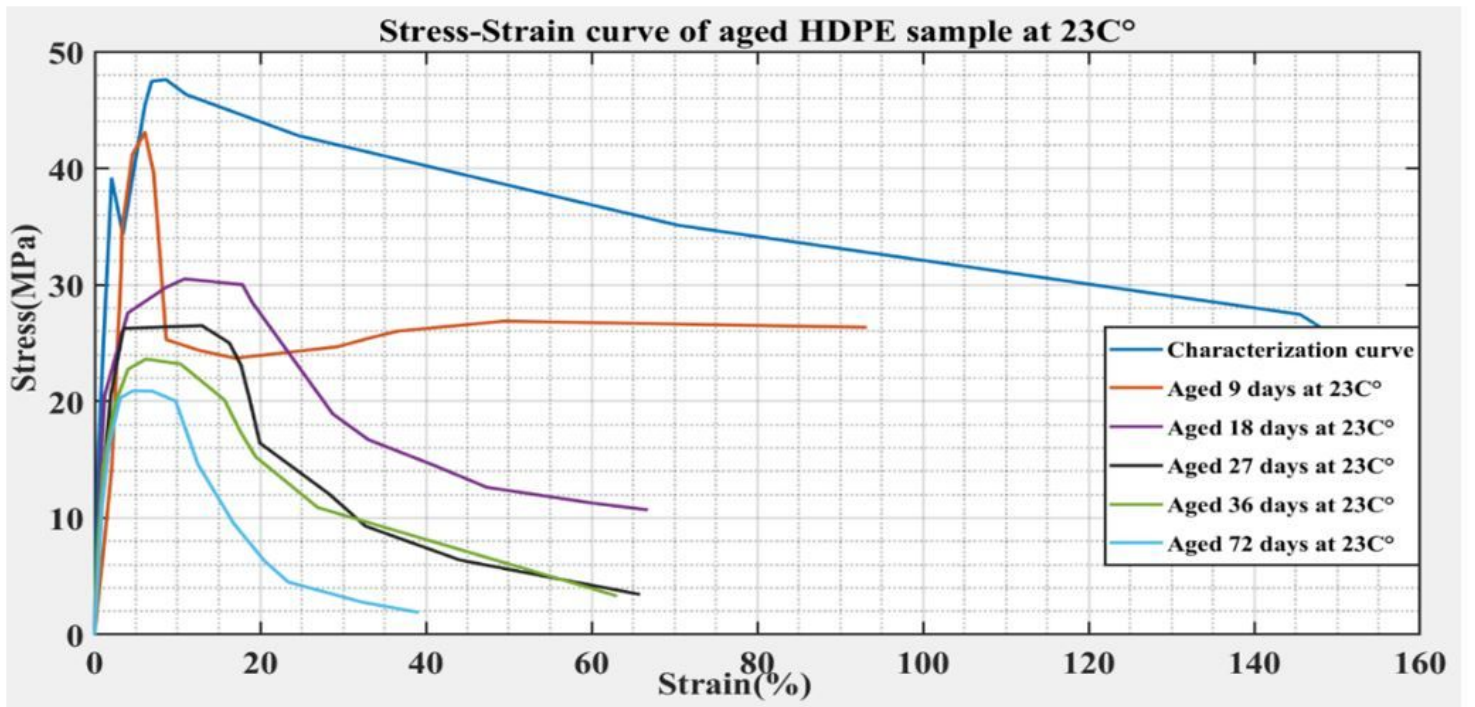


Figure 12

Stress-strain curve of HDPE samples aged in SEA water at 23°C.

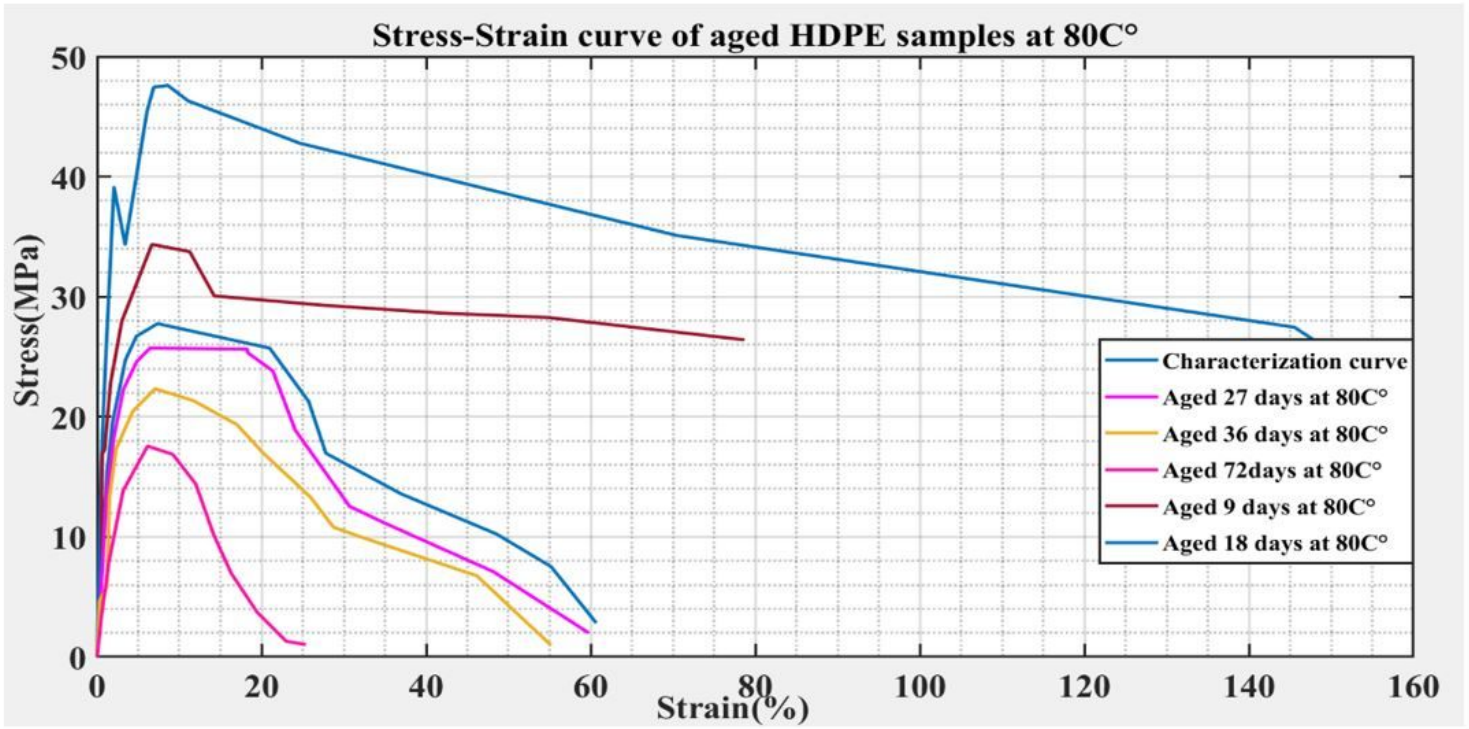


Figure 13

Changes in the mechanical behaviour of HDPE samples aged in the marine environment at 80C°.

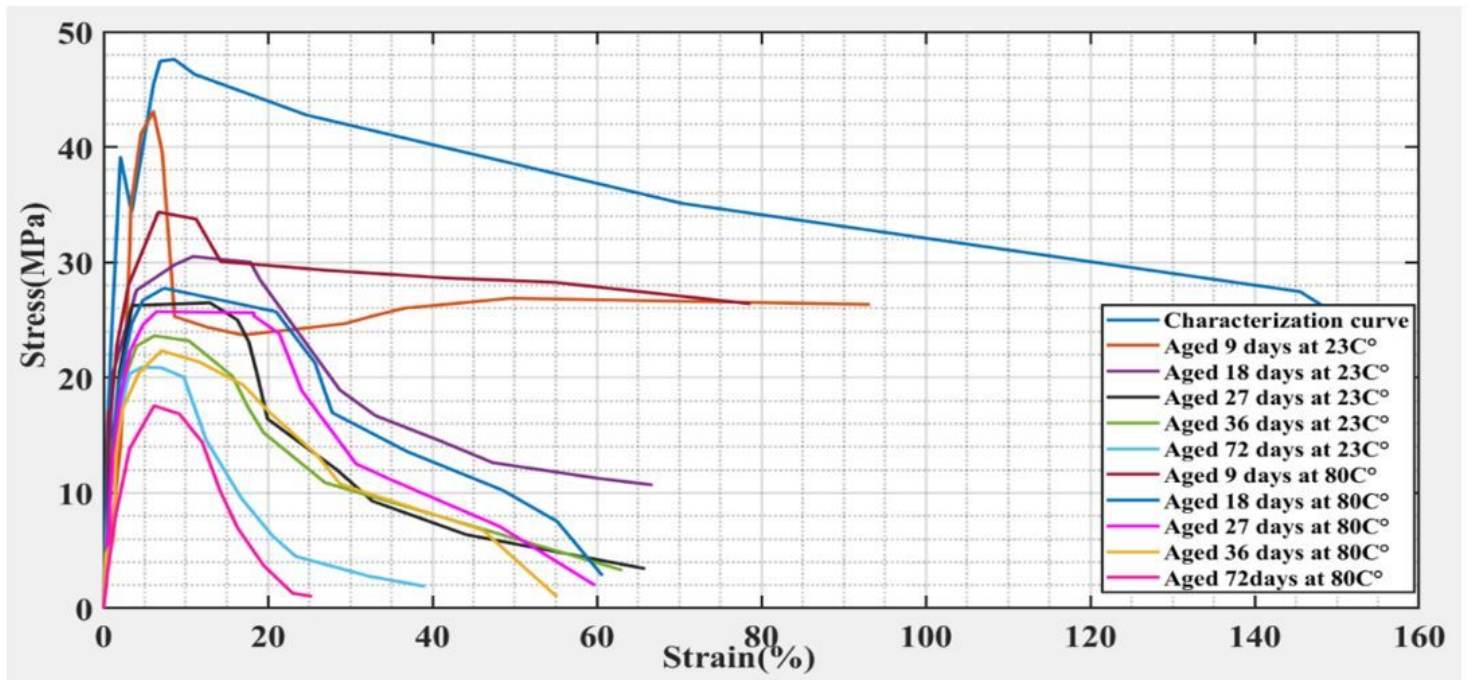


Figure 14

Comparison between the behaviour of HDPE aged at 80C° and 23C°.

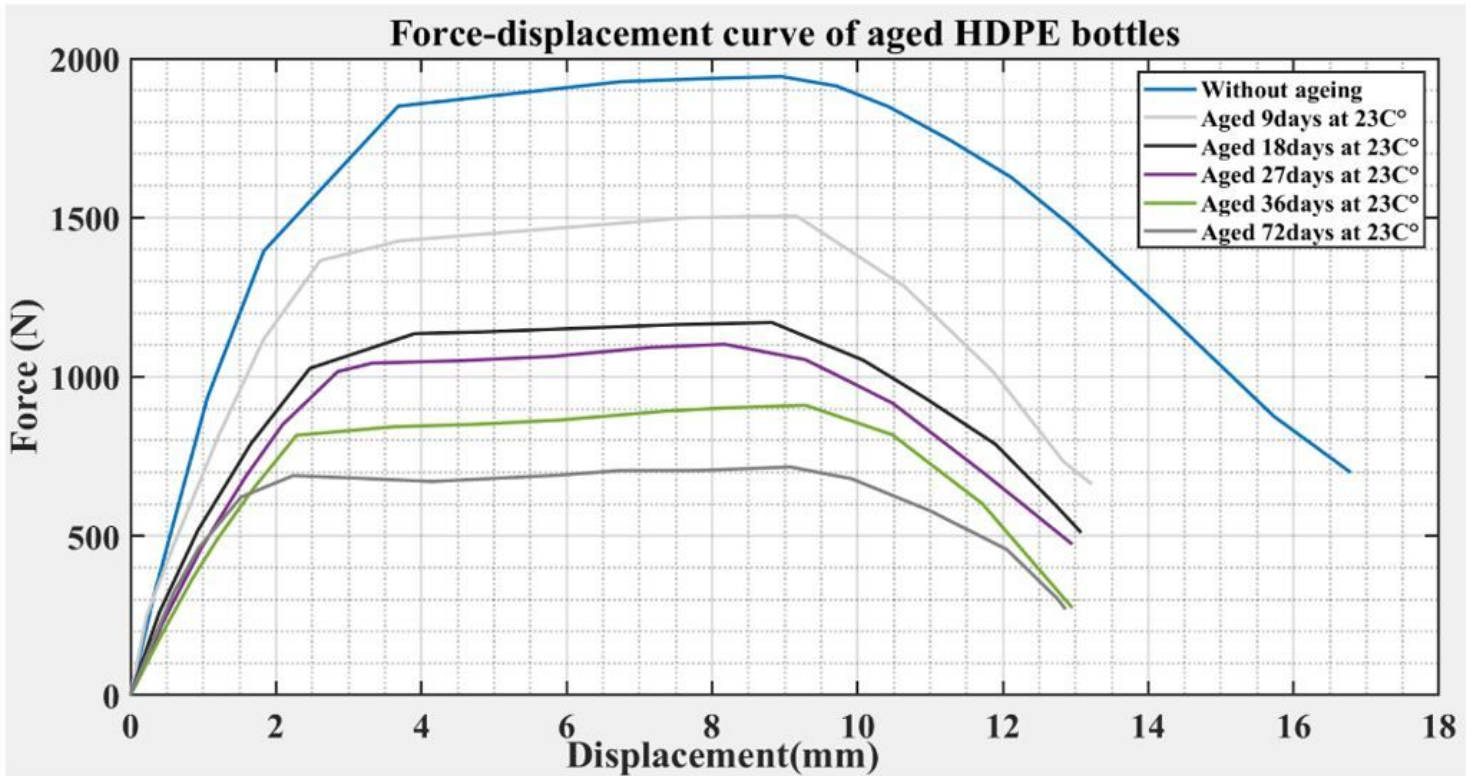


Figure 15

Force-displacement curves obtained by compressing HDPE bottles aged at 23°C.

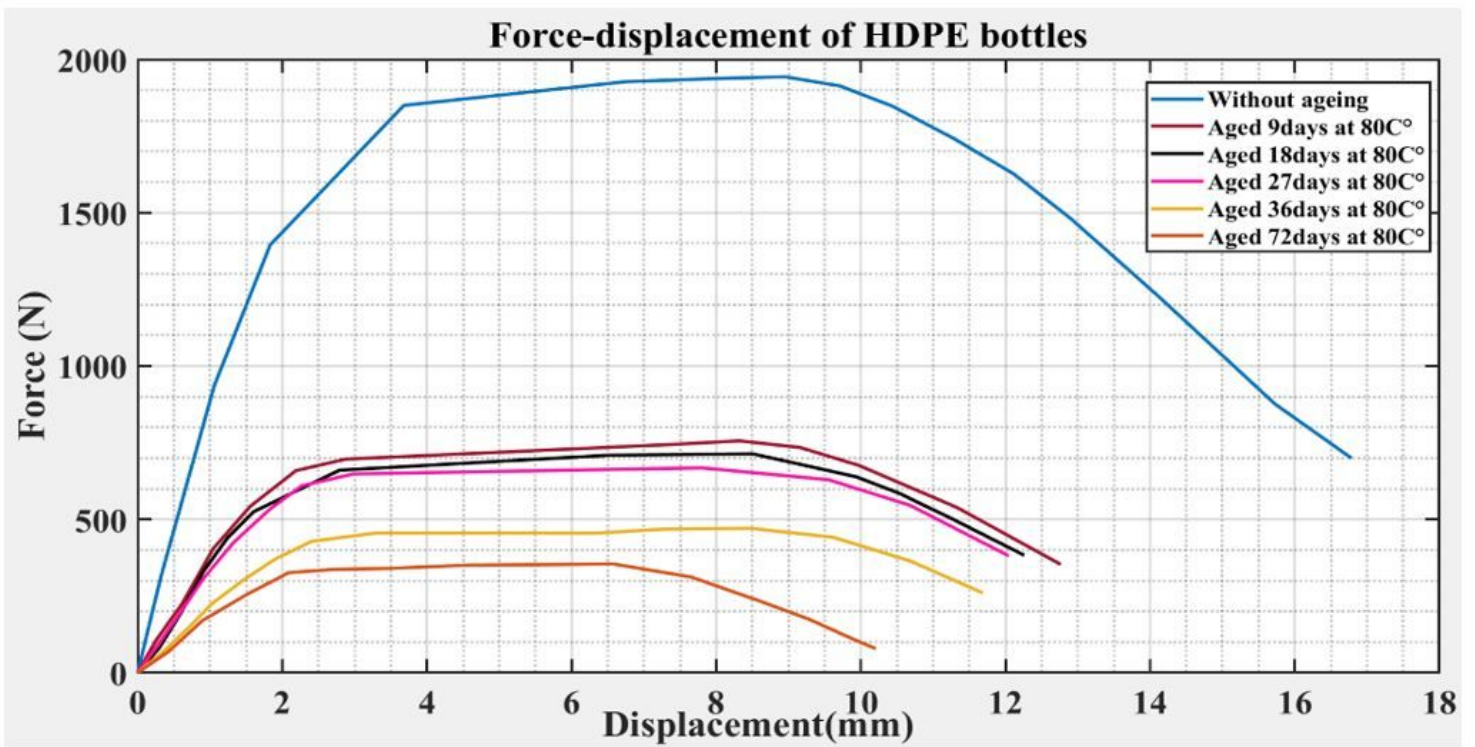


Figure 16

Force-displacement curves obtained by compressing HDPE bottles aged at 80°C.

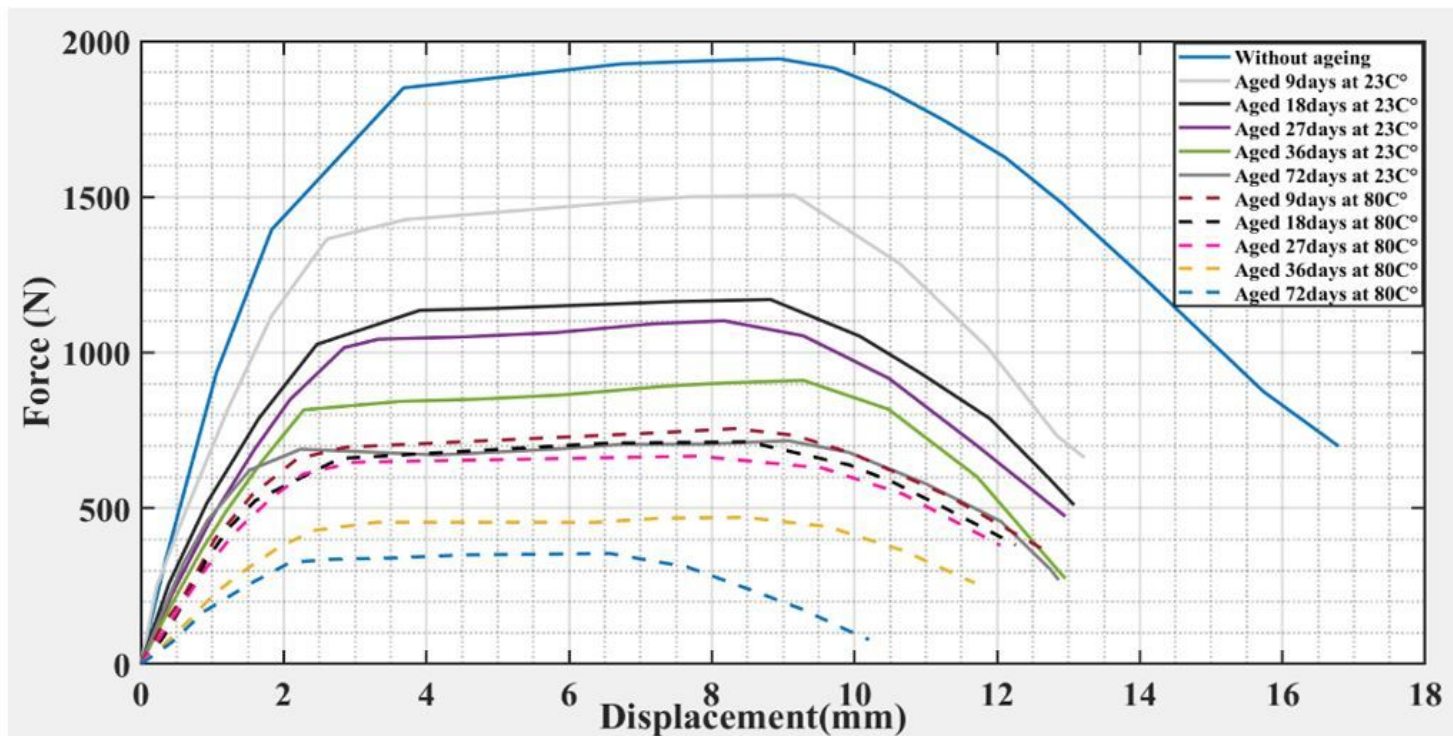


Figure 17

Comparison of the mechanical behaviour under compression of HDPE bottles aged at 80°C and 23°C.

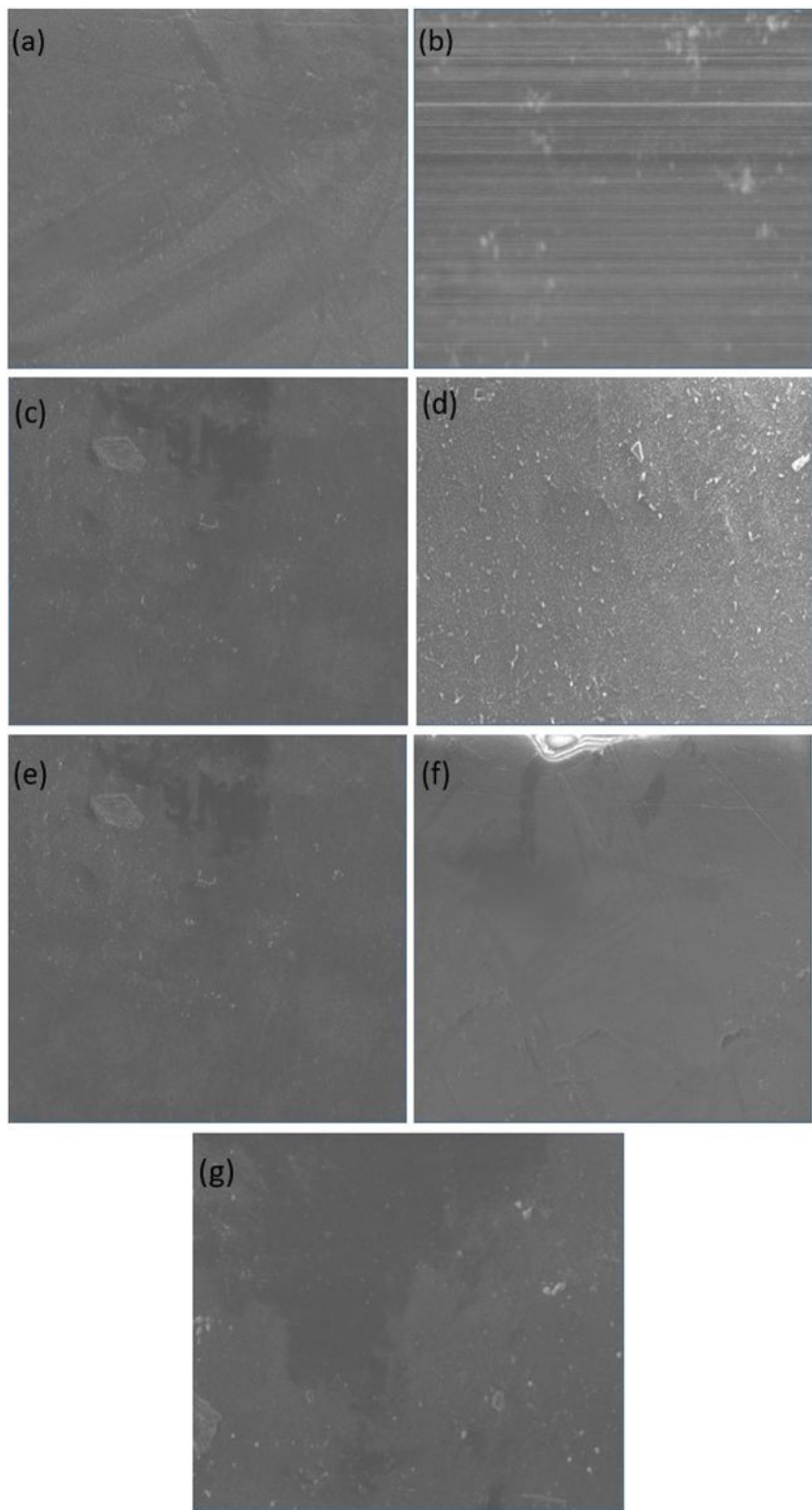


Figure 18

SEM results of specimens: (a) unaged (b): aged 18 days at 23C° (c): aged 18 days at 80C° (d): aged 36 days at 23C° (e): aged 36 days at 80C° (f): aged 72 days at 23C° (g): aged 72 days at 80C°.