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Behaviour of 3D printed PLA and PLA-PHA in marine environments

G R Montalvão¹, M Moshrefi-Torbati¹, A Hamilton¹, R Machado², A João²

¹ Engineering, University of Southampton, Highfield, Southampton, SO17 1BJ, United Kingdom

² CEiiA, Avenida D. Afonso Henriques, 1825, 4450-017 Matosinhos, Portugal
E-mail: gmontalvao1998@gmail.com

Abstract. The accumulation of marine debris in the oceans has been escalating. There is an urgent need to develop new technologies that efficiently record and transmit ocean data without contributing to ocean pollution. In this study, the behaviour of Poly(lactic acid) (PLA) and Poly(lactic acid)-Poly(hydroxyalkanoate) (PLA-PHA) in marine environments was analysed in order to assess biodegradability in marine applications. 3D Printed samples were submerged completely in seawater and cyclically in a salt spray chamber. Their change in mechanical properties was evaluated by conducting uniaxial tension tests after submersion periods of up to 45 days and failure regions were observed in microscope. Contrarily to PLA's behaviour, PLA-PHA's samples suffered embrittlement and registered losses in elongation at break of around 10-18%. The alignment of salt crystals and other impurities in the failure regions suggests that embrittlement could be related with environmental stress cracking resulting from the penetration of those impurities into the polymer. Such inclusions originate residual stresses which lead to a faster and more brittle failure. Embrittlement could also be related to an increase in crystallinity caused by chain scission of amorphous regions by means of chemical degradation. Further evaluation of changes in molecular weight should be conducted to confirm the latter.

1. Introduction

Today we face the consequences of demographical growth. Around 2.4 million metric tons of plastic are trapped in garbage patches spread all over the world [1]. The United Nations Ocean Conference estimated that the oceans might contain more weight in plastics than fish by the year 2050 resulting in a tremendous impact to the world population [2]. In addition, every year Man spills hundreds of tons of oil into the oceans, devastating entire ecosystems and killing hundreds of species. With Global Warming adding to these factors, and together with the overall increase of sea temperatures, our oceans will eventually die if measures are not put into practice.

Now, more than ever, we urgently need to develop new and more capable ocean monitoring technology in order to better understand how oceans interact with marine life and how currents shape garbage patches and oil spills [3]. However, monitoring entire oceans is not a simple task. Thousands of active measuring instruments are required to create a clear image and, given the quantitative nature of such task, there is a constant need for designs that integrate new materials and techniques that will improve the environmental impact of ocean drifters.

Within this scope, the biopolymer Poly(lactic acid) (PLA) has been a focus of extensive research and has been identified as an eco-friendly alternative to traditional plastics. Not only it is biocompatible with humans, allowing its use in drug delivery and other biomedical applications, but it is also highly processable [4]. PLA offers good mechanical properties and can be utilised in various design



applications without compromising performance [5]. Its biodegradability under compostable conditions has been broadly advertised and sometimes misunderstood. In fact, PLA does not biodegrade in normal ambient conditions or marine environments [6]. Nevertheless, it is often a better environmental alternative to petrol-based polymers since its origins are completely renewable and not toxic to animal life [7].

PLA's low melting point allows its extrusion and therefore makes it suitable for Additive Manufacturing (AM) techniques as Fused Deposition Modelling TM [8]. Such techniques can easily produce many geometries and customised products at competitive prices. The use of AM in marine structures is becoming common, and more polymer filaments, with improved properties are being launched on the market regularly [9]. New polymer blends like Polylactic Acid-Polyhydroxyalkanoate (PLA-PHA) are tougher and smoother and could provide room for improvements in the biodegradability of such structures [10].

Yet, the behaviour of 3D Printed filaments in marine environments has barely been assessed. Few studies have revealed any trends on their mechanical behaviour when exposed to seawater. *Ausejo et al* (2018) reveals the influence of different printing orientations on the mechanical properties and degradation rates of PLA and PLA-PHA samples and suggests great impact of printing orientation on the final results [11]. The ageing of PLA and some other blends in seawater is also reported in *Berthé et al* (2018) but the influence of 3D Printing processing methods was not evaluated [12].

In this study, we report the changes in mechanical properties and failure behaviour of 3D printed PLA and PLA-PHA samples when exposed to two different marine environments: complete submersion in seawater and cyclic submersion in a salt spray chamber for up to 45 days and 15 wet/dry cycles, respectively. The influence of different printing densities on the overall behaviour of samples was also evaluated.

2. Experimental

2.1 Specimens and Experimental set-up

A total of 28 samples were printed in a Leapfrog Creatr HS printer using Fused Deposition Modelling TM as the Additive Manufacturing method. From those 28 specimens, 14 were made from PLA filament, supplied by Filament2Print® while the remaining 14 were made from PLA/PHA filament produced and supplied by ColourFab®. The infill densities of specimens were evenly split between 40 and 80% so that half of both PLA and PLA/PHA samples would have an infill percentage of 40% whereas the other half would have an infill percentage of 80%. The samples can then be split into 4 different experimental groups:

- PLA40: 7 samples of PLA with 40% Printing Density
- PLA80: 7 samples of PLA with 80% Printing Density
- PLAPHA40: 7 samples of PLA-PHA with 40% Printing Density
- PLAPHA80: 7 samples of PLA-PHA with 80% Printing Density

Where 1 sample from each group worked as the control sample - were not exposed to any marine environment.

The samples were printed with only one outside wall. This way the penetration of water was enhanced, allowing for a greater exposure of the material to the surrounding environment. The geometry of the samples was chosen in accordance with the ISO-527 standard – 'Standards for Uniaxial Tension Tests of Polymers' and filaments were deposited in an arrangement of 45° relative to the x-axis (loading direction) as represented in figure 1 [13].

With the aim of assessing the behaviour of the material in marine conditions, the samples were submitted to two different marine environments: complete submersion in the Atlantic sea and simulated cyclic submersion in a salt spray chamber. Uniaxial Tensile Tests and Microscopic Observation were used to evaluate the change in mechanical properties and failure behaviour.

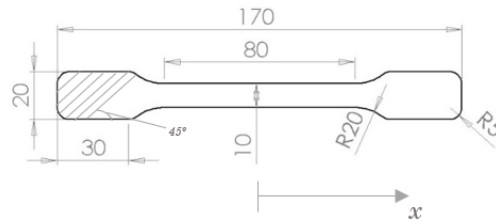


Figure 1. Geometry of the testing samples ([mm]; symmetric about the centre of area).

2.2 Complete Submersion in Sea

ASTM D6691 underlines the methodology and standards required to assess the increase of carbon content in a marine-simulated as an indicator of the rate of degradation of polymer specimens [14]. These include complex experimental set ups that could not be established in the context of this project. Instead, to simulate the environment at which an ocean drifter buoy is exposed, twelve samples were identified using colourful tape and were placed underwater just below surface, secured by a nylon net and attached to a boat dock by a nylon cable as illustrated in figure 2.

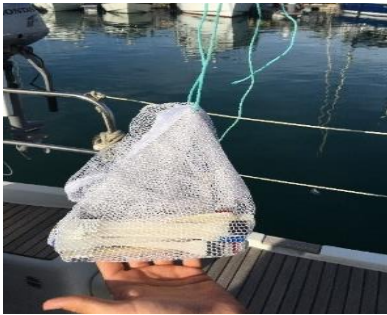


Figure 2. Samples subjected to complete submersion collocated inside a nylon net. A nylon cable was attached to the net and the samples were secured to a boat dock. The system rested just below surface exposed to all the natural phenomena (light, rain, current, humidity...). Location coordinates: 38.676579, -9.317849, Atlantic Ocean, Portugal, Lisbon.

After 15 days of submersion, a total of 4 samples (one from each group) were recovered from the marine environment and were placed in a Aralab ® Environmental Testing Chamber, where they were left to dry at 25°C for 24 hours. The samples were then submitted to uniaxial tensile tests to determine their properties. The same procedure was repeated with the remaining samples after a period of 30 and 45 days of submersion.

2.3 Cyclic Submersion in Salt Spray Chamber

The remaining 12 samples were exposed to several wet/dry cycles in order to simulate the cyclic submersion to which some of the parts from common marine structures are exposed to. On each cycle the samples were placed inside a salt spray chamber for 5h and the standard practices described by the ASTM B117 - Standard Practice for Operating Salt Spray (Fog) were followed [15]. A Dry Corrosion Test Cabinet (DCTC) 1200 from ACS@The was used.

The DCTCTM machine simulates salty and corrosive environments that can be applied to any kind of surface. A 120-liter salt solution tank contains the solution that is then pumped and mixed with compressed air to be atomized and sprayed on the samples, simulating partial submersion of the samples. After a 5-hour wet period the samples were left to dry for 18-20 hours at ambient conditions, inside the laboratory. At this stage the samples were not exposed to UV light. All samples were carefully labelled and weighed before testing. Tensile tests were conducted each 5 wet/dry cycles, having this way gathered information on the tensile response of the samples after 5, 10 and 15 cycles.

2.4 Uniaxial Tensile Tests

To conduct the tensile tests, the standard practices described by the norm ISO527 were followed and an MTS Landmark Servohydraulic Test System equipped with two 627 Hydraulic Wedge Grips was used.

The load and displacement were analysed using the MTS Elite Software®. The width and thickness of all samples were measured using a caliper rule prior to testing. All failures were photographed. The room temperature was kept at 22°C throughout the tests. An extensometer was used to measure the change in length of the specimen so that the strain and other parameters could then be derived as follows:

2.4.1 Yield Stress, MPa. For PLA-PHA samples this parameter was calculated in accordance with the definition given by the norm ISO527, which defines yield stress as the “first stress at which an increase in strain occurs without an increase in stress”. For PLA, a brittle polymer that does not present a well-defined yield stress value, the offset yield stress was calculated instead. The method for determination of the offset yield stress consists on drawing a line parallel to the elastic domain of the material which intersects the strain axis at 0.2%. The intersection of such line with the stress-strain curve gives the Offset Yield Point.

2.4.2 Ultimate Tensile Strength, MPa. The maximum tensile stress sustained by a sample during the tensile test. Calculated in accordance with the standard practices described in ISO527.

2.4.3 Young’s Modulus, MPa. Calculated in accordance with ISO527 which defines Young’s Modulus as the “ratio of the stress difference σ_2 minus σ_1 to the corresponding strain difference values ϵ_2 minus ϵ_1 = 0,0025 minus ϵ_1 = 0,0005”. Young’s Modulus, E is then given by the following equation:

$$E = (\sigma_2 - \sigma_1) / (\epsilon_2 - \epsilon_1) \quad (1)$$

2.4.4 Elongation at Fracture, %. Tensile strain at break. Calculated as described in the norm ISO527.

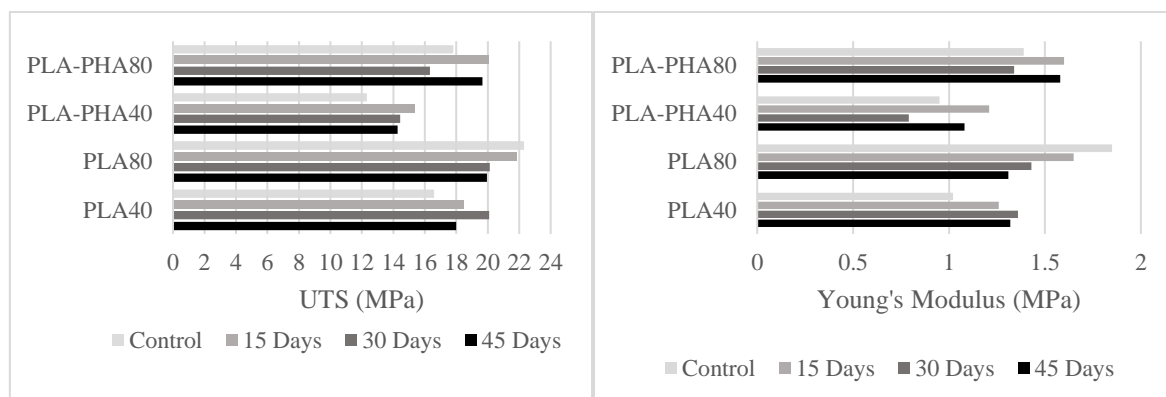
2.5 Microscopic Observation

Failures were observed in a Nikon Eclipse microscope. The NYSElement Software package was used to process data.

3. Results

3.1 Complete submersion in sea

The bar charts in figure 3 reveal the variation of the various mechanical properties over 45 days in sea.



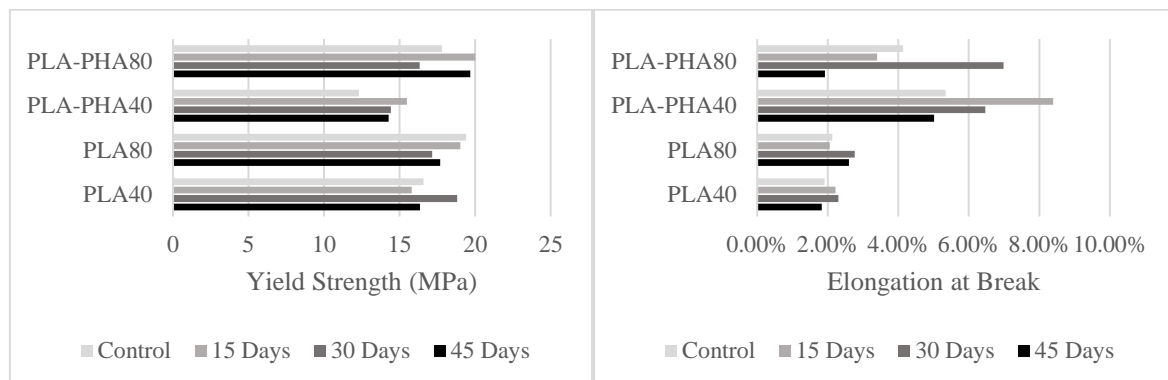


Figure 3. Mechanical properties of the samples over the various submersion periods. Upper left – Ultimate Tensile Strength, Upper Right – Young's Modulus, Bottom Left – Yield Strength and Bottom Right – Elongation at Break.

3.1.1 Control Group – no exposure to marine environments. For both control samples of PLA and PLA-PHA, an increase in the infill percentage lead to enhancement in material performance under the applied tension. For the PLA control samples, an infill percentage of 80% revealed an increase in the Ultimate Tensile Strength (UTS) of around 29% when compared to an infill percentage of 40%. Other properties such as the Young's Modulus, Elongation at Fracture and Yield Strength were also improved by 81%, 12% and 17%, respectively, when infill percentage was increased to 80%. For PLA-PHA control samples, a positive change in the UTS of around 44% was also observed for the same change in infill percentage whereas the Young's Modulus and Yield Strength were both increased by 45%.

When comparing the two polymers, prior to any exposure to marine environments, the results from the tensile tests show greater elongation at fracture for PLA-PHA, which indicates a more ductile response to failure.

3.1.2 15, 30 and 45 days of complete submersion. The data reveals a general increase in brittleness after 15 days for all samples apart from PLA80 which shows almost no change in the UTS and a decrease in the Young's modulus of 0,20 MPa. The biggest change in mechanical properties after 15 days in seawater was registered by PLA-PHA with 40% infill, which revealed an increase in UTS on the order of 24%. Overall, the increase in brittleness was sharper for PLA-PHA for this time period.

A general loss of properties was observed after 30 days of complete submersion. Apart from PLA40, all samples saw a decrease in their UTS and Young's Modulus. The biggest change in properties was again registered by the PLA-PHA samples, which revealed decreases in their Young's Modulus of around 35% and 16% for respective infill densities of 80 and 40%. PLA-PHA80 also revealed a substantial increase in elongation after that same period. The behaviour of PLA with 40 percent infill, that had previously been in harmony with the behaviour of PLA-PHA samples, revealed a continuous embrittlement. On the other hand, PLA80, which had previously shown little change in behaviour after 15 days in sea, revealed a decaying UTS and Young's Modulus, and a slightly bigger elongation at break after a month of submersion.

After 45 days all samples revealed a loss in Elongation at Break. However, none of the samples demonstrated a significant loss of mechanical properties. The behaviour of the PLA samples was in fact, very similar to the ones from the previous 30-days period while PLA-PHA's properties were more proximate to the ones from the 15-Days period. General embrittlement was observed.

3.2 Cyclic submersion in salt spray chamber

The bar charts in figure 4 reveal the variation of the various mechanical properties over the various wet/dry cycles.

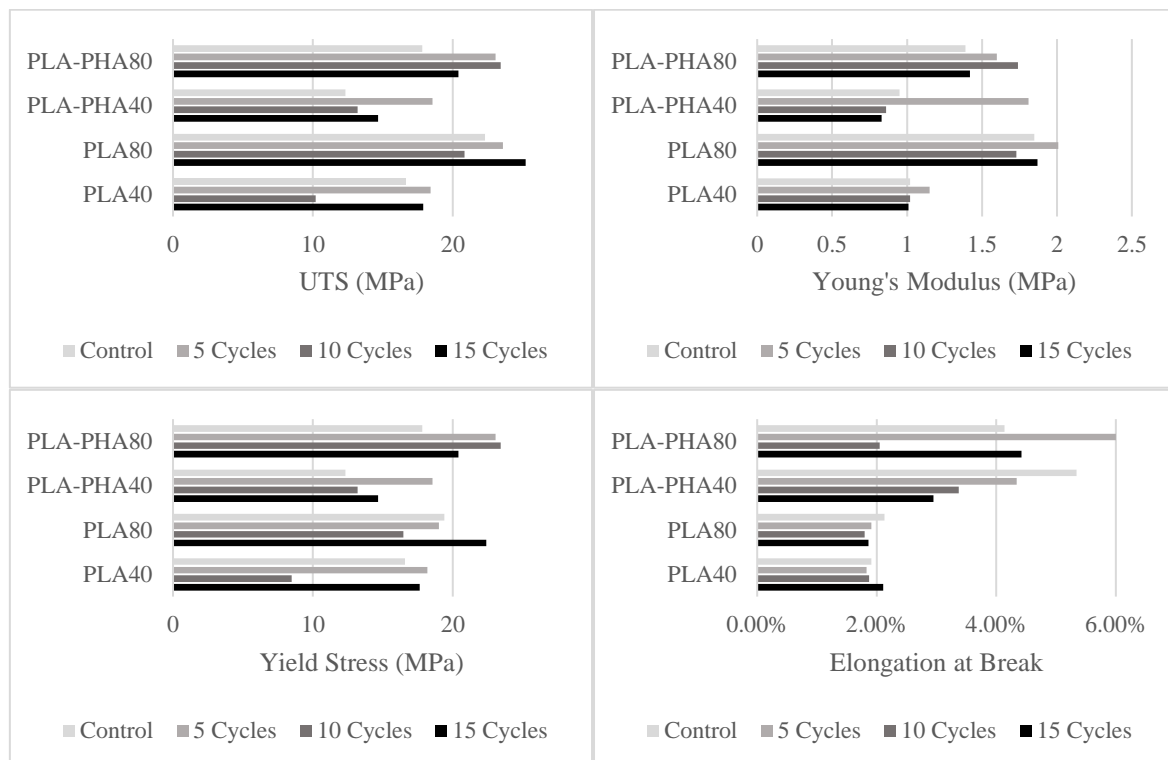


Figure 4. Mechanical properties of the samples over 5, 10 and 15 wet/dry cycles. Upper left: UTS, Upper Right: Young's Modulus, Bottom Left: Yield Strength and Bottom Right: Elongation at Break.

The data above reveals a general embrittlement of samples, which is again more pronounced for PLA-PHA samples. PLA samples were not significantly affected when exposed to the salinity chamber, some minor embrittlement is observed but it is not conclusive. On the other hand, a great rise in the UTS for both PLA-PHA40 and PLA-PHA80 is observed. This embrittlement also reflects on a general reduction in the elongation of PLA-PHA samples: PLA-PHA40 presented the most conclusive data and registered an average loss of elongation of around 18%. Samples from the other testing groups have also shown some loss in elongation which was sometimes contradicted by slight occasional increases on that parameter. The visual appearance of sample failures reveals, in accordance with the results from complete submersion in seawater, a great embrittlement in the PLA-PHA's behaviour.

3.3 Microscopic observation – failure evaluation

The embrittlement of samples, previously suggested by the tensile tests, was clearly noted in the microscopic observations. As figure 5 reveals, PLA-PHA control samples revealed long necking regions which are linked to the strain recovery response of the material. After just 15 days in sea that ductile behaviour was lost almost completely, and it was very hard to find any plastic deformation on the failure of individual filaments, as figure 6 illustrates.

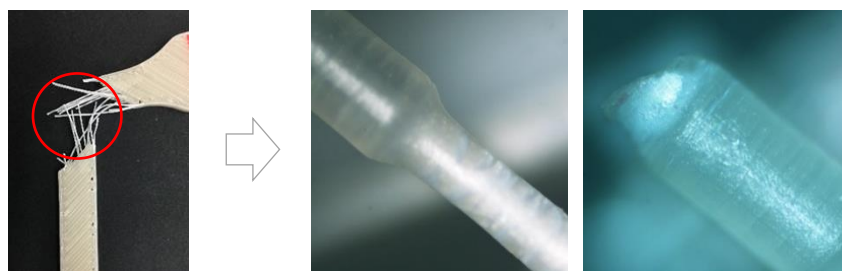


Figure 5. 5x Amplified necking and failure regions of PLA-PHA control sample. Necking region and plastic deformation clearly visible. The necking regions reveal a decrease in transparency.

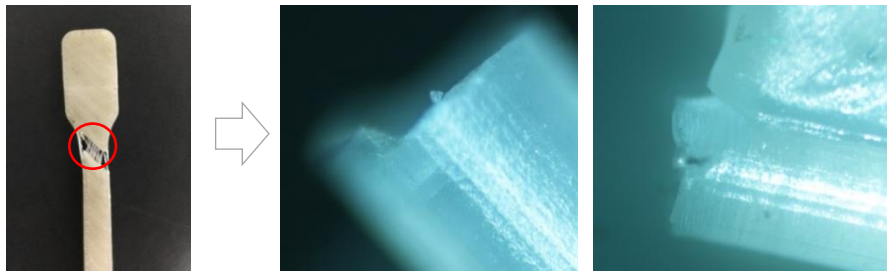


Figure 6. 5x Amplified necking and failure regions of PLA-PHA after submersion in sea. At the left-hand side, no necking is observed nor plastic deformation and the material looks uniform with no stripes or chain reordering. At the right-hand side some necking and striping is observed but much reduced.

For PLA no changes in failure behaviour could be identified, since the material presented, from the beginning, a brittle response to failure. Very little necking or plastic deformation was observed in PLA's samples.

As expected, impurities were preferably accumulated in the available free space between the different 3D Printed layers and different filament sections. A relatively large accumulation of salt and biofouling was observed for both polymers and printing densities of the samples that were submerged in seawater. On the other hand, samples from the salt spray chamber revealed greater accumulation of salt which was obviously offset by the almost non-existing fouling concentrations (the chamber's-controlled environment and isolation from UV light prevents the proliferation of any living mechanisms). The accumulation of salt was uniform for both polymers and densities and it was proportional to the time of submersion.

On the failure regions, orientation of impurities was observed in the same direction as the applied load.

4. Discussion

The results from both complete and cyclic submergence tests reveal an embrittlement for PLA-PHA samples revealing average losses in elongation at break of around 10-18%. The change in behaviour was sharper for sample submitted to the salt spray chamber than for the one submerged in seawater: PLA-PHA80 showed great increases in the UTS of around 6 MPa during the first 10 salinity cycles, accounting for 40% of the initial value, and PLA-PHA40 saw a decrease of 18% in elongation.

Samples of PLA, on the other hand, have not revealed any conclusive trends on mechanical behaviour. In fact, many times opposite behaviours were registered from test to test. The broad variance of data led us to conclude that no major changes have been experienced on the mechanical properties of PLA.

The results do not reveal a major influence of printing density on the change in mechanical properties of both polymers.

In agreement with our results, previous research has also registered substantial decreases in the Elongation values of polymer samples when these were submitted to aqueous environments. Such decrease in strain at break was sometimes justified by an increase in crystallinity resultant from polymer degradation and erosion [16]. The hydrolysis of bio-polymers like PLA and PHA attacks amorphous regions resulting in the so mentioned increase in crystallinity and in the consequent reduction on the ductile behaviour [17].

The change in crystallinity can be evaluated by measuring the change in molecular weight, Mw, over the degradation period. Although it was not possible to address such procedure in the scope of this study, previous literature reveals that PLA presents no change in molecular weight when submerged in seawater at temperatures of around 25°C [6]. This indicates that, for that period, no chain cleavage occurs. Further evaluation of the changes in Mw of PLA-PHA would then reveal if the same happens for this blend.

Nevertheless, there are various degradation mechanisms that could be contributing to this change from ductile to brittle behaviour. Thermal ageing and weathering are probably the main causes for polymer erosion. Elevated temperatures and UV radiation provide enough thermal energy to activate and break ester and amide bonds present in biopolymers like PLA and PHA [18]. Yet, samples that were submitted

to the controlled environment of the salt spray chamber were never exposed to either UV or high temperatures. These samples revealed the same change in mechanical properties than those submerged in sea. In fact, although not clearly demonstrated by the stress-strain curves, samples from the salt spray chamber have revealed an even more brittle behaviour than those submerged in seawater. It is therefore concluded that the change in mechanical properties does not arrive from thermal activation of chain bonds. More plausible causes would be Chemical Degradation combined with Environmental Stress Cracking (ESC).

Chemical degradation refers to the already mentioned process of hydrolyses to which thermoplastic biopolymers are commonly exposed. Such process breaks the ester and amide bonds present in the monomer structure leading to chain cleavage which could result in loss of ductile behaviour [18]. Again, changes in Mw should be evaluated to take any further conclusions on whether there was chain cleavage in PLA-PHA's samples.

ESC refers to the penetration of fluid and impurities in the polymer. Those impurities then dissolve creating localised stresses and promoting cracking [18]. The microscopic images indeed revealed the penetration of salt crystals and other impurities in the surface of both polymers. A lot of surface scratching and penetration was observed. Small imperfections and voids that pre-existed in the samples could have facilitated the penetration of salty water. Salt crystals were then allowed to grow beyond the volume of those voids pushing the surrounding material and originating residual stresses that most probably led to cracking. The fact that the samples from the cyclic submersion presented greater embrittlement points out that ESC was possibly the main degradation mechanism behind this behaviour since the growing of salt crystals was enhanced during the dry periods of cyclic submersion. Furthermore, the orientation of impurities was also identified near failure regions. Contrarily to what the orientation of these impurities first suggests, salt crystals (impurities) were not stretched and oriented during tension, but the surrounding material was. The presence of impurities in the previously described small voids could have initiated higher surrounding stresses that lead to localised plastic deformation on the surrounding material when this is pulled apart, leading to an increase on the volume of the void and ultimately leading to failure.

5. Conclusions

A transition from a ductile behaviour to a brittle response was observed for PLA-PHA samples. Printing density of samples has not had a major influence on the behaviour. Nevertheless, the use of lower infill percentages would present less material to any final design purposes and would then lead to faster deterioration.

Furthermore, cyclic submersion in the salt spray chamber had a bigger impact on the behaviour of samples. This was perhaps related to the existence of dry periods that allowed the impurities present in the aqueous solution to dissolve, originating bigger stress profiles along the samples.

Overall, PLA-PHA blend was more sensitive to the marine environment which, on top of the described eroding mechanisms, could be related to chain scission and therefore biodegradation. Further evaluation on the changes in molecular weight should be conducted to assess the level of degradation of this polymer.

Comparatively to previous studies, the use of 3D Printing as the manufacturing process greatly amplified the response of the polymers to the various marine environments, specially PLA-PHA, revealing that the total surface area of polymer is crucial on the uptake of water and eroding mechanisms [18].

Finally, it is concluded that if the degradation rate of polymers is to be accelerated concerning the suitability for biodegradable marine structures - parameters like surface roughness, overall crystallinity and ratio of wet/dry periods are crucial and should be considered.

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