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Accelerated ageing of polylactide in aqueous environments: Comparative study between distilled water and seawater

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Abstract:

Pollution of nature by plastics is a major environmental problem and the challenge for the future is to manage the lifetime of polymers better. The aim of this study is to establish a baseline on degradation mechanism and degradation kinetics for lifetime prediction of polylactide (PLA) in a marine environment. The ageing of PLA was accelerated by raising temperature in distilled water, filtered and renewed seawater and natural seawater. Samples were immersed in distilled water for six months at different temperatures (25, 30, 40 and 50°C) in order to evaluate the influence of temperature on PLA degradation kinetics and to predict lifetime. Then, samples were immersed in seawater both in the laboratory and at sea, in order to compare the effects of environment, marine organisms and salt, on degradation. The different degradation steps were followed by gravimetry, tensile tests, scanning electron microscopy (SEM), steric exclusion chromatography (SEC) and differential scanning calorimetry (DSC). In distilled water, accelerated ageing of PLA is complex with deviation from Fickian behaviour at higher temperature. Moreover, immersion in distilled water induces morphological changes, in particular holes, which are absent in seawater at 40°C for the same immersion time. Indeed, seawater has little impact on the diffusion kinetics but affects M_∞ values, which are slightly lower compare to the distilled water uptake.

Keywords : PLA ; accelerated ageing ; hydrothermal ageing ; degradation

1. Introduction

World consumption of polymers has increased exponentially since the nineteen fifties. Polymers are used in many areas, particularly in the packaging industry. Indeed, they have many advantages like light weight, low cost and formability. However, from a life cycle point of view, they also have several drawbacks. First, they are mainly based on non-renewable resources and their price is very dependent on oil prices. Then, polymer materials have a rather short period of use, especially in the packaging

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sector. This implies high volumes of waste, whose handling is far from optimised. Nowadays, plastics which are not incinerated, landfilled or recycled are found in nature polluting for example the seas [1] and the oceans [2] and [3]. It is estimated that 80% of waste from land activity is carried by winds and rivers, the rest is derived from marine activity. The accumulation and progressive fragmentation of plastic waste lead to dramatic consequences for marine wildlife [4], [5] and [6], slowly becoming dangerous for humans, who are at the end of the marine food chain. That is why in recent years bio-based and biodegradable polymers, such as polylactide (PLA), polyhydroxyalkanoates (PHA) or thermoplastic starch (TPS), have appeared as an alternative solution in order to solve these problems. PLA is one of biopolymers which receive, currently, the most attention in the research community. PLA is synthesized by ring-opening polymerization from a cyclic monomer (lactic acid), which is produced from renewable

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resources (corn, starch...). Much attention has been paid on PLA because of their wide range in many applications like packaging [7] or biomedical for suture material or drug release delivery systems [8]. Indeed, PLA offers good mechanical properties, availability, thermoplastic processing capacity [9], the ability to biodegrade under specific conditions [10–12] and can have a favorable life cycle assessment compared to conventional polymers [13]. One of the limits remains its poor thermal stability, together with low tenacity and the relative lack of knowledge of its lifetime and degradation behaviour in aqueous environments, and more specifically in the marine environment.

Taib et al. [14] studied ageing of PLA immersed in distilled water at room temperature for 2 months, while Yew et al. [15] followed the degradation at 30°C in water (the authors do not detail the nature of water) for 1 month. The latter measured a water absorption of approximately 1% and showed that the kinetics of water absorption followed Fick's law. They also observed a decrease in stress at break of 30% after only one month. Berthé et al. [16] determined a 60% loss for the strain at break after 10 days of ageing at 65°C in the presence of 100% relative humidity (RH).

PLA ageing was also investigated in seawater at 25°C, and the degradation was insignificant even after immersion for 10 weeks [17,18]. In the same way, Zenkiewicz et al. [10] did not detect large modifications after a 9 week immersion time. Natural ageing of polymers is characterized by slow degradation kinetics and temperature is a parameter frequently employed to accelerate ageing [19]. Accelerated ageing of PLA for 3 months at two different temperatures (20 and 40°C), revealed a decrease of almost 50% of molecular weight after 3 months at 40°C in seawater [20].

Most of the articles available in the published literature deal with short term immersion (less than 100 days). Very few compare different ageing environments and accelerated ageing of PLA is also poorly studied. In the present study, ageing of PLA is investigated in several

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aqueous environments over a period of 180 days: distilled water, renewed seawater and natural seawater. Ageing time was accelerated by temperature and the degradation was followed by gravimetry, tensile tests, SEM, SEC and DSC.

The aim of this study is to establish a baseline for degradation mechanisms and degradation kinetics in order to make lifetime predictions of polylactide behaviour in seawater. This approach, based on an Arrhenius law, uses macroscopic indicators such as elongation at break [21] or the stress at break [22]. In order to use this approach natural and accelerated ageing should lead to the same microstructural changes, and there must be a single degradation process characterized by an activation energy, E_a, which is constant over the temperature range studied. This methodology, using accelerating ageing of PLA, will be discussed throughout this study and some limits of the approach will be highlighted.

2. Experimental

2.1. Materials

The polylactide (PLA) studied was a commercial grade (7001D) supplied by NatureWorks® (USA) with a D-lactide content of 4.4 % ± 0.5 (supplier's data). The material has an average molecular weight $\overline{M}_n$ = 75 000 g.mol^{-1}.

2.2. Preparation of tensile samples

PLA pellets were dried at 50°C under vacuum for 24h before processing. For the preparation of dog-bone specimens, pellets were injected using a Battenfeld HM 80/120 press. All parameters were kept constant during the injection molding process. The hopper temperature was 190°C and the profile was the following: 190-190-190-190°C. The injection pressure was 1500 bars and the mould temperature was kept at 40°C. PLA was injected in a mold designed to produce normalized specimens, 180 x 10 x 4 mm geometry (sample 1A according to NF EN ISO 527).

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2.3. Ageing conditions

Ageing tests were performed under several conditions: distilled water, filtered and renewed seawater and natural seawater. First, some PLA samples were immersed in distilled water in different containers (volume 25 L) at 25, 30, 40 and 50°C. The use of a higher temperature is not representative because PLA will be in another crystalline configuration. In a previous study at 60°C, results indicated that degradation at this temperature close to the T_g , is very rapid [20]. The distilled water was renewed each week; then, pH influence can be considered as negligible. A few drops of bactericide were added in the bath to prevent bacterial growth. Then, another series of PLA samples were immersed in baths (volume 60 L) at 25 and 40°C, with seawater pumped from the Brest estuary (France), filtered and continuously renewed. Water and salt effects were studied. Indeed, the average ocean salinity is 35 g/L and the most abundant dissolved ions in seawater are sodium, chloride, magnesium, sulphate and calcium [23]. In parallel, natural ageing tests were also performed in the Lorient harbour (France) in order to compare the results and an effect of marine bacteria is then added. Seawater temperatures during the study, from March to September 2012, were approximately between 11 and 19°C.

2.4. Characterization techniques

2.4.1. Water uptake

At selected immersion times, dog-bone specimens immersed in water were removed, washed several times with distilled water, wiped and weighed at room temperature (23°C and RH = 50%) on a weighing machine with a precision of 0.1 mg. The percentage gain at any time *t*, M_t as a result of water uptake, was determined by Eq. (1):

$$M_t(\%) = \frac{W_t - W_0}{W_t} \times 100 \quad (1)$$

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where W_0 and W_t denote, respectively, weight of dry material (the initial weight of materials prior to water exposure) and material weight after exposure to water. The maximum moisture absorption, M∞, is calculated as an average value of several consecutive measurements that show very little variation of water absorption. The weight gain resulting from moisture absorption can be modelled in terms of two parameters, the diffusion coefficient D and the maximum moisture content M∞, are given by Fick's first law in Eq. (2):

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum \frac{1}{(2i+1)^2} \exp\left(- \frac{D(2i+1)^2 \pi^2 t}{e^2} \right) \tag{2}$$

where e is the thickness of the sample. D can be calculated from the initial linear portion of the absorption curve. For $M_t/M_\infty \leq 0.5$ the function $M_t = f(\sqrt{t})$ is linear and the Fickian diffusion coefficient D is determined by Eq. (3):

$$D = \frac{\pi}{16} \frac{e^2}{t} \left(\frac{M_t}{M_\infty} \right)^2 \tag{3}$$

Commonly, this equation is used for square specimen dimension. A correction factor is needed to account for the finite width, w, and length, h, of the sample compared to its thickness, d, using Eq. (4) [24]:

$$Dc = D\left(1 + \frac{d}{h} + \frac{d}{w} \right)^{-2} \tag{4}$$

where Dc is the corrected diffusion coefficient.

2.4.2. Mechanical tests

Static tensile tests were carried out in an environmentally controlled laboratory, according to ISO 527 (23°C and 50% relative humidity) on an MTS Synergie RT1000 testing machine. The loading speed was 1 mm/min. An MTS extensometer was used to measure strain, over a 25 mm gauge length. Two types of tests were performed, one on wet specimens, one on dry.

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At least five specimens were tested for each condition, and the results were averaged arithmetically.

2.4.3. Scanning electron microscopy (SEM)

Microscopy analyses were performed with a Jeol JSM 6460LV scanning electron microscope to examine the fracture surface of the PLA samples. Prior to observation, the fracture surfaces of unaged PLA and aged PLA were prepared by fracture in liquid nitrogen. Then, specimens were sputter-coated with a thin gold layer by means of a sputtering apparatus (Edwards Sputter Coater).

2.4.4. Molecular weight measurement

Sterical exclusion chromatography (SEC) was used to determine the evolution of molecular weight. The apparatus is equipped with a set of three columns: two ResiPore and one PL gel Mixed C (Polymer Labs.). The detection system is composed of a refractometer and a UV detector. Chloroform was used as eluent with a flow rate of 0.8 mL/min. The elution profiles were analysed by the Empower GPC module software (Waters). Calculations are based on calibration curves obtained from polystyrene standards ranging from 200 g/mol up to 6×106 g/mol. The weight-average molecular weight ($\overline{M}_{\mathrm{w}}$) and number-average molecular weight ($\overline{M}_{\mathrm{n}}$) are obtained from the SEC analysis. The polydispersity index (PI) was calculated as $\overline{M}_w/\overline{M}_n$. Moreover, in order to analyse an autocatalysis, the average number of random chain scissions per unit mass, n_t, was calculated by Eq. (5) [25]:

$$n_t = \frac{1}{\overline{M}_{n_t}} - \frac{1}{\overline{M}_{n_0}} \tag{5}$$

where $\overline{M}_{nt}$ and $\overline{M}_{no}$ are the number-average molecular weight at time t and at initial time, respectively.

2.4.5. Thermal analysis

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Differential scanning calorimetry (DSC) analysis was performed on samples of about 10 mg, in standard aluminium pans, using Mettler-Toledo DSC882 equipment under nitrogen atmosphere. Data were recorded at a heating rate of 20°C/min. The samples were heated from 20 to 200°C and kept at 200°C for 3 minutes. After that, the samples were cooled to -20°C and finally a second heating scan was performed from -20 to 200°C to distinguish the reversible effects from permanent changes. The crystallinity of PLA was determined by Eq. (6):

$$\chi = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_{100\%}} \quad (6)$$

where ΔH_m and ΔH_{cc} (J/g of polymer) are the melting enthalpy and the cold crystallization enthalpy, respectively. $\Delta H_{100\%}$ is the melting enthalpy for PLA of 100% crystallinity, taken to be 93.1 J/g [9].

3. Results and discussion

3.1. Accelerated ageing in distilled water

3.1.1. Water uptake

Fig. 1 shows the weight gain of PLA as a function of $t^{1/2}$ (expressed in $H^{1/2}$) at different immersion temperatures. An initial linear relationship between water uptake and square root of time is observed at 25 and 30°C, followed by plateau saturation, indicating a typical Fickian behaviour. Data for the saturation plateau at 25 and 30°C, are respectively 0.59% and 0.62% (Table 1). These values are a little lower than those found in the literature but diffusion coefficients are similar [14,15,26]. PLA grades are not the same and morphology is known to affect the water uptake [27,28]. Processing can also induce morphological changes.

Due to moderate polarity induced by the presence of ester bonds [29], PLA absorbs higher water content than conventional commodity polymers such as PP or PE (0.2% at room

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temperature [24,30]) which are quite hydrophobic, but lower than some polyamides (for polyamide 11, M_∞ is around 1.6 % in pH 7 immersion at 50°C [31]).

Figure 1 and Table 1

At 40°C, a deviation from Fickian behavior is observed. Indeed, after a plateau similar to those observed at lower temperatures, i.e. 25 and 30°C, around 0.76%, a sharp increase in water absorption occurs after about 100 days. This trend is also observed at 50°C, but occurs earlier (after 15 days). This increase, already observed in the literature, indicates degradation within the polymer and is attributed to several phenomena. First, it may be due to the generation of holes in the PLA associated with osmotic cracking phenomena [16,32]. The increase may also be linked with the creation of diffusion paths induced by cracks [33]. Another explanation could be the hydrolysis process products such as carboxyl groups, which have a strong water affinity [34].

Using Eq. 3, Fickian diffusion coefficients were calculated (Table 1), based on the hypothesis that the experimental plateau observed is the saturation plateau. A linear relation (R^2=0.98) is noted between lnD and the inverse of temperature (Fig. 2), suggesting that these coefficients obey an Arrhenius law (Eq. 7):

$$D = D_0 \exp\left(-\frac{E_a}{RT}\right) \tag{7}$$

Figure 2

The activation energy E_a is obtained from the slope of the linear fitting of lnD vs T^{-1} and is estimated at 30 kJ/mol. Very few published values are available but E_a has been found to range from 40 to 80 kJ/mol [35]. This slightly lower E_a value could be explained by several reasons: the different kinds of aqueous environments, the grade of PLA used or the processing conditions which modify the polymer morphology. In distilled water, the absence of many components such as mineral salts could facilitate the diffusion of water within the matrix and the energy required is therefore lower.

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These results indicate that temperature can be used within a limited range for accelerated ageing of PLA, but lifetime prediction is more difficult. One of the initial assumptions for accelerated aging is not respected because structural changes occur at higher temperature, despite the narrow temperature range.

3.1.2. Mechanical properties

Tensile tests were carried out on the aged PLA samples in the wet state and after drying. Fig. 3 shows the mechanical behaviour of PLA samples after 6 months in distilled water at 25, 30 and 40°C and after 15 days at 50°C. The degradation rate of PLA at 50°C is very fast, and after one month, tensile tests were not possible due to the very brittle nature of the aged samples.

Figure 3

An initial elastic linear behaviour is observed, whatever the ageing temperature. After 6 months of immersion at 25°C, ductility increases for wet PLA (Fig. 3a.). After drying, behaviour returns to the initial state. At 30 and 40°C after 6 months, PLA is less ductile in wet tests and the strain at break decreases. However, in the dry state, PLA recovers partially its initial properties at 30°C but becomes completely brittle at 40°C. These variations confirm the irreversible nature of the degradation. At 50°C, all changes are intensified. After only 15 days, ductility increases and failure strain exceeds 20%. In the dry state, a significant decrease in stress at break is observed and brittle behaviour is noted.

The evolutions of global dry mechanical properties as a function of the temperature and immersion time are presented in Fig. 4 and property percentage losses are shown in Table 2. As shown in Fig. 4a, at 25 and 30°C the stress at break remains constant during ageing. At 25°C, the increase in strain is observed after 2 months of immersion and is constant over time (Fig. 4b). Nevertheless, at 30°C, the increase in failure strain is significant after 1 month of immersion (+47%) but drops after 6 months (-42%). After 6 months at 40°C, the stress and

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the strain at break were greatly reduced, -85 and -92% respectively, with a sudden drop observed in the failure stress after 4 months (Fig. 4a). For these three temperatures and after 6 months, the Young's modulus increases compared to the initial properties but values remain relatively similar. After only 15 days at 50°C, the stress and the strain at break decrease, with a loss of 12% and 50% respectively and Young's modulus remains quite constant.

Figure 4

These mechanical results show a reversible degradation at short times and at lower temperature. Indeed, the plasticization of the PLA by water is reversible [7] and the loss of properties is quite small after 6 months at 25°C. Temperature increase promotes a premature loss of properties, which could be linked with water uptake (Fig. 5). A quasi-linear relationship can be found below 1%, weight gain for all temperatures. From this point on, the phenomena become irreversible and the ageing temperature clearly accelerates the PLA degradation. Loss of linearity between water uptake and stress at break is observed at 40 and 50°C and this is explained by a different diffusive behaviour. On the Fig. 1, the sudden increasing, after saturation plateau, corresponds to a water uptake threshold. This deviation compared with standard Fickian models leads to a fall of stress at break (Fig. 4b).

Figure 5 and Figure 6

The SEM images in Fig. 6d reveal the appearance of holes within PLA after 6 months at 40°C and this can explain the sudden increase in water uptake observed after 4 months (Fig. 1). It appears here that during hydrolytic degradation the PLA undergoes bulk degradation, as previously noted [36,37]. Indeed, a hydrolysis reaction takes place homogeneously throughout the sample. The formation of lactic acid oligomers, which directly follows from the chain scission, increases the carboxylic acid end groups concentration and then leads to a heterogeneous degradation. Oligomer products near the surface are rapidly evacuated while those formed in the bulk stay inside, and promote autocatalysis in the heart of the sample.

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Modeling to develop a lifetime prediction will be complex because degradation becomes heterogeneous. Moreover, degradation kinetics differs at higher temperature, despite the narrow range of temperature used.

3.1.3. Molecular weight analysis

Measurements of molecular weight enable permanent changes due to chemical ageing to be detected and can be directly linked with dry mechanical properties. Table 3 shows the evolution of molecular weights of PLA samples as a function of ageing time and temperature.

Table 3

A reduction of $\overline{M}_n$ by 10% and 15% is observed at 25 and 30°C respectively after 180 days' immersion, indicating a small proportion of chain cleavage. This confirms the results obtained using tensile tests. At 40°C, $\overline{M}_n$ decreases with the immersion time with a drop of 65% after 6 months. After only one month at 50°C, $\overline{M}_n$ is reduced by 60% compared to the initial value. Polydispersity index values (Table 3) also provide information on the distribution of chain lengths and on the chain cleavage mechanism. At 25°C, the evolution of the polydispersity index is negligible, while a slight decrease is observed at 30°C. At 40°C after 6 months and at 50°C after only one month, the polydispersity index decreases significantly, indicating different chain cleavage kinetics, which will make modelling difficult. For temperatures above 30°C, the random chain cleavages are caused by the hydrolysis of ester functions introducing a polymer weakening, as discussed previously.

Fig. 7 represents the average number of random chain scission (n_t) per unit mass for PLA as a function of immersion at different temperatures (Eq. 5). No change is observed at 25 and 30°C. At 40 and 50°C, the increasing n_t value can be explain by an autocatalytic process linked to the formation of lactic acid oligomers, which directly result from these chain scission processes, increasing the concentration of carboxylic acid end groups in the medium.

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The catalysis degradation is confirmed by results obtained by SEM (Fig. 6d) and by the increase of water uptake.

Figure 7

The formation of lactic acid oligomer, estimated by determination of acid group contents contained in the PLA samples after 6 months' immersion at 25, 30 and 40°C and after only 1 month at 50°C, confirmed these results (not shown here). At 25 and 30°C, no significant difference was observed in the acid group content for unaged PLA or aged PLA. However at 40°C, greatly significant increase was noted, by a factor 3 after 6 months' immersion, confirming the higher degradation rate observed with the SEC results. At 50°C, the increase in the acid group amount is similar to that measured for the sample aged at 40°C but for a much shorter immersion time (i.e. after 1 month).

All the results obtained from molecular weights, average number of random chain scission and acid group content highlight a progressive acceleration in the PLA degradation up to a temperature of 40°C, which is followed by a strong acceleration when the ageing temperature reaches a value close to 50°C. The water uptake results correlate with these observations. Moreover, the hydrolytic degradation of PLA is a self-catalysed process when temperature increases. Carboxylic acid chains formed in the bulk facilitate autocatalysis in the heart of the sample. This is a further complication for a prediction tool [38].

3.1.4. Thermal properties

Table 4 summarizes the thermal properties of PLA after 6 months at 25, 30 and 40°C, and after 1 month at 50°C, obtained by DSC first and second heating scans.

Table 4

At 25 and 30°C after 6 months in distilled water, the melting and cold crystallization temperatures remain constant during the first heating while a slight reduction of glass transition is observed. For the second heating, the T_g values decrease slightly which confirms

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the reversible degradation for long time immersion. At 40 and 50°C, all the transition temperatures decrease significantly. These lower temperatures may make residual stress relaxation easier and lead to microstructural changes which can also facilitate the increase of water uptake [39]. The melting enthalpy shows a clear increase, for example at 40°C from 2 to 37 J/g. This can be related to the significant decrease in the PLA molecular weights under these conditions, as shown by SEC. The remaining PLA chains then have higher mobility and they can reorganize themselves more easily which leads to an increase of the melting enthalpy and degree of crystallinity [16,40]. In addition, after 1 month of immersion at 50°C, a duplication of the melting peak appears (not shown here), which is a phenomenon already observed in the literature and corresponds to the formation of some oligomers during degradation and development of different crystal populations [41,42]. Moreover, the disappearance of a cold crystallization peak at 50°C after 30 days can also be ascribed to the increasing crystallinity of PLA with degradation time [43]. We can assume that macromolecular chains are less mobile in these conditions and this may suggest that crystallization threshold is reached after PLA ageing for 30 days at 50°C.

The evolution of the global crystallinity (χ_c) of the PLA chains during hydrolysis can be deduced from the evolutions of both ΔH_{cc} and ΔH_m. Initially, χ_c is very weak, i.e. between 1 and 2 %, indicating a quasi-amorphous structure explaining why PLA is totally transparent before ageing (Fig 8). Based on the first scans, crystallinity increases at all temperatures except at 40°C. The hydrolytic chain cleavage proceeds preferentially in amorphous regions, but for long ageing times crystalline lamellae may also be affected by the hydrolysis, leading therefore to a decrease of the crystallinity ratio [25]. During the second heating, crystallinity remains constant. Indeed, PLA is totally melted after the first scan and there is no recrystallization during cooling. However, melting and cold crystallisation enthalpies

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regularly increase with the temperature of immersion, attributed to the higher molecular mobility of shorter chains.

Moreover, an increase in the relative opacity of samples with aging time is observed (Fig. 8a), caused by a molecular reorganization induced by chain scission [44], and confirmed by SEC and DSC results. At 25°C and after 6 months, samples maintain the same appearance as before ageing. These results suggest that the degradation is very low at this temperature and confirm the lack of structural changes. Some modifications in the visual aspects begin for the PLA aged after 6 months at 30°C. Sample whitening in the distilled water is clearly accentuated with ageing time and temperature.

Figure 8

In this section, we have shown that hydrolytic degradation of PLA even in distilled water is a complex mechanism, due to the polymer morphology and its temperature sensitivity. This is not in itself surprising, as PLA is a biodegradable polymer under specific conditions [12]. However, after analyzing the effects of distilled water uptake on PLA samples at different temperatures, in order to envisage the use of this polymer in marine applications it is essential to extend this study to examine the influence of the environment. Two ageing temperatures were selected, 25 and 40°C, and aging in seawater both in the laboratory and at sea has been performed.

3.2. Influence of seawater ageing

3.2.1. Water uptake

Fig. 9 compares the weight gain of PLA plotted as a function of square root of immersion time (expressed in $H^{1/2}$) in natural seawater, in distilled water and renewed and filtered seawater at 25 and 40°C.

At 25°C and under natural conditions, the evolutions of water absorption are very similar (Fickian behavior) to the one at 40°C in seawater. The behavior of the PLA aged at 40°C in

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seawater differs from distilled water with the sharp increase of water absorption around 120 days. This observation can be correlated with the difference in sample morphology observed in Fig 6c and 6d. The SEM images clearly reveal the appearance of many cavities and holes of different shapes and sizes. The ageing effects are much more pronounced for the PLA samples aged in distilled water, which are characterized by a higher degradation rate, compared to the samples aged in seawater for the same period. The accelerated ageing in seawater could be easier to use in a lifetime prediction of PLA because the structural changes are similar.

The saturation plateau and the diffusion coefficients are lower in seawater than in distilled water (still with the assumption of the intermediate plateau) but we can note they are in the same range (Table 5). Moreover, values in seawater are higher than published values [20]. Regarding the results for the immersion in a natural environment, the value of the plateau is 0.47 % and the diffusion coefficient associated is 0.37 10^{-7} cm²/s but immersion temperature is lower than in laboratory tests.

Figure 9 and Table 5

Temperature has an influence on the value of the plateau as it facilitates the water diffusion within the PLA. The marine eco-system has a little impact on the diffusion kinetics but affects the M_∞ value. Different mineral salts present in seawater (around 3.5%) may explain this difference. Moreover, ageing in seawater is similar to that in distilled water if we consider an immersion inferior at 120 days. Modeling of ageing in seawater, using distilled water, is therefore possible in this time window.

3.2.2. Mechanical properties

The influence of immersion in seawater on tensile behavior of PLA specimens after 6 months at 25 and 40°C was also investigated, and was compared to the behavior of the specimens aged in distilled water (Fig. 10).

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Figure 10

At 25 and 40°C, mechanical behaviour is similar for both aging environments. Regarding the evolution of mechanical properties (Table 2), for the strain at break at 25°C, an increase from 3.4 to 6.9% is observed after 6 months of immersion in the dry state, this is similar to the results of Le Duigou et al. [20]. At 40°C, the stress at break of PLA decreases significantly after 6 months' immersion but with a larger reduction in distilled water (85% versus 70% in seawater). The reduction in properties of PLA in sea water, smaller than in distilled water, can be attributed to the difference in water absorption (Fig. 9a) and to the different morphology observed by SEM.

In each immersion medium, the Young's modulus tends to slightly increase with time, this could be explained by an increase in the crystallinity. Considering the natural ageing, PLA properties do not evolve significantly, confirmed by SEM images (Fig. 6b) despite an extremely slow drop in strain at break over time. As a result it will be difficult to establish a correlation with the accelerated test values in order to make a lifetime prediction, even after 6 months of immersion.

Considering the accelerated ageing in seawater and distilled water, the nature of the aqueous medium significantly affects the polymer properties. Degradation is faster in distilled water as has already been noted previously [45,46]. Possible reasons are the role of mineral salts which facilitate the diffusion of seawater within the polymer and/or a lower pH of distilled water, ≈6 against ≈8 for seawater, which can promote hydrolytic degradation [35]. However, despite a more aggressive degradation in distilled water, the ageing temperature appears to be the main parameter affecting the mechanical property changes.

3.2.3. Molecular weight analysis

$\overline{M}_n$ and $\overline{M}_w$ of PLA specimens aged in natural conditions do not change significantly after 6 months and the polydispersity index remains constant (Table 6). At 25°C, slight changes

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occur between both environments with a PI constant. At 40°C, $\overline{M}_n$ and $\overline{M}_w$ reductions of 65 and 73% in distilled water and 75 and 77% in seawater, are measured respectively. Moreover, there is a difference between the polydispersity index, lower in distilled water, which suggests that kinetics of chain cleavage are different and it this correlates with the lower degradation in seawater. Critical molecular weight, corresponding to an "end of use" criterion, can be determined by plotting the evolution of stress at break versus evolution of molecular weight (not shown here) and is, in each environment, close to 30 000 g/mol.

Table 6

The evolution of acid values for PLA specimens aged in natural seawater, in renewed seawater and distilled water at 25 and 40°C (not shown here), follows the same trends.

3.2.4. Thermal properties

Table 7 shows the influence of degradation time on thermal transitions (T_g, T_c and T_m) as well as enthalpies (ΔH_{cc}, ΔH_m) and crystallinity (χ_c). Regarding the first heating, for PLA samples aged in natural conditions and at 25°C in both environments, the evolution of transition temperatures are almost the same, whatever the immersion medium. For the second heating, a slight decrease in T_g is observed while T_{cc} and T_m do not evolve, despite a slight increase in enthalpy ΔH_{cc} and ΔH_m. However, the increase in crystallinity is more important in distilled water.

Table 7

At 40°C, the immersion environment appears to have a stronger effect on the thermal properties of PLA. The most critical case is obtained in distilled water with a decrease in T_g of about 15°C during the first heating, this effect is not observed at the same temperature in the marine environment. This significant variation of T_g in distilled water can be linked to the water uptake which is more important in distilled water than in seawater (see Fig. 9), inducing an higher plasticizing effect, as already observed by Balzer et al. [47]. Similarly, T_{cc} and T_m

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were greatly reduced after 6 months in distilled water while in seawater, only a decrease of T_{cc} is noted. In addition, there is much less difference between the two environments in the second heating because the influence of water on the polymer is removed. Changes observed in Fig. 8b such as the whitening of specimens do not depend on the immersion environment but only the temperature.

3.3. Prediction of long term immersion behavior

When immersed in water, PLA first absorbs water with a Fickian behavior up to a maximum water up take of about 0.8%. The presence of this water leads to a plasticization of the polymer, a decrease in T_g is observed indicating an increase in molecular mobility. This enhancement of molecular motion leads to a large increase in the elongation at break and a decrease of stress at break. A linear relationship between stress at break and water content in PLA can be observed, for a 0 to 1% water content range. When samples are dried, mechanical behavior is equivalent to that of unaged samples.

However, irreversible degradation also occurs when PLA is immersed in water for longer times or higher temperatures [48]. In fact, at 40°C and 50°C (for the immersion durations studied here) hydrolysis occurs in the PLA, leading to an irreversible chain scission that induces changes in terms of mechanical behavior and an increase in crystallinity due to a chemi-crystallization process [48,49]. Chemi-crystallisation is the phenomenon linking crystallinity and chain scission. Indeed, in semicrystalline polymers the chain scission process occurs only in the amorphous phase by freeing new chain segments which have higher mobility and can reorganize themselves. Irreversible embrittlement of the material is observed when tests are performed in both wet and dry conditions, this is a typical consequence of chain scission mechanisms [20]. Moreover, at the same time as embrittlement, a large water uptake is recorded, corresponding to the observation of holes within the bulk of samples. This

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could be explained by an osmotic process, which has already been observed in other hydrolysable polymers [16,25,32].

These observations suggest that, as long as hydrolytic degradation remains limited, water absorption in PLA can be predicted using a Fickian behavior with a linear Arrhenius law for water diffusion kinetics. Moreover, under these conditions mechanical behavior of the polymer can be assessed using a linear relationship between water uptake and stress at break. When hydrolysis occurs, life time prediction is no longer straightforward and competing factors including autoacceleration and osmotic degradation will require more detailed analysis.

4. Conclusions

In this work, accelerated ageing of PLA has been performed in different aqueous environments (distilled water, filtered and renewed seawater in the laboratory, and natural seawater at sea). Ageing is accelerated by the temperature in order to establish a baseline for PLA lifetime predictions in a marine environment.

First, the water uptake within PLA in distilled water is temperature dependant and follows Fickian behaviour at 25 and 30°C while a deviation from Fickian behaviour is noted at 40 and 50°C. Using the intermediary plateau to determine diffusion coefficients, a linear relation appears between log D and the inverse of temperature. However, SEM images (particularly figure 6d), show important structural changes with temperature. The loss of linearity between mechanical properties and water uptake reveal that degradation mechanisms are modified above 40°C, as confirmed by SEC and DSC, and underline the complexity of lifetime prediction for this material.

The influence of the environment has also been shown and the degradation rate is faster in distilled water than in seawater. One reason is the lack of mineral salts which facilitates the

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diffusion of water within the polymer. Seawater uptake, following Fickian behaviour, has little influence on the diffusion kinetics but affects M_∞ values, which are slightly lower compared to the distilled water uptake values. Concerning mechanical properties after aging at 40°C in the two environments, PLA is degraded after 6 months in both but SEM images show different degrees of degradation.

The initial aim of this work was to develop a lifetime prediction methodology for PLA in the marine environment. Data acquired during this study do not yet allow such predictions to be made, as the limited temperature range which allows acceleration without introducing new damage mechanisms does not allow a correlation with marine conditions. In one sense this is encouraging, as it shows that PLA can be used for at least 6 months in seawater with little degradation. Further work is underway to extend the study, in particular by the use of thin film specimens which should enable more rapid saturation to be attained and core/surface differences to be limited.

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Figure captions

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Fig. 1. Evolution of water uptake as function of the square root of immersion time at 50, 40, 30 and 25°C for PLA samples immerged in distilled water.

Fig. 2. Identification of the diffusion coefficient of distilled water in the PLA for different ageing temperatures.

Fig. 3. Evolution of tensile behaviour of PLA specimens aged in distilled water at 25, 30 and 40°C after 6 months and at 50°C after 15 days, before (a) and after drying (b).

Fig. 4. Evolution of dry mechanical properties of PLA specimens aged in distilled water at 25, 30 and 40°C after 6 months and at 50°C after 15 days: stress at break (a), strain at break (b) and Young modulus (c).

Fig. 5. Evolution of stress at break versus water uptake in distilled water at different temperature.

Fig. 6. SEM micrograph of the fractured surface of unaged PLA (a), of PLA aged in natural seawater (b) and after 6 months immersion at 40°C in seawater (c) and distilled water (d). (Red circles show few hole apparition)

Fig. 7. Average number of random chain scissions per unit mass for PLA as a function of immersion time at different temperatures.

Fig.8. Visual aspect before and after the degradation in distilled water (a) and in sea water (b) at different temperatures.

Fig. 9. Comparison between water uptake as a function of square root time at 40°C in distilled or seawater (a) and at 25°C in distilled or seawater and with natural ageing (b).

Fig. 10. Influence of environment on mechanical tensile behaviour of PLA specimens after 6 months in immersion at 25 and 40°C and in immersion in natural seawater, before (a) and after drying (b).

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Table 1. Equilibrium water uptake and Fickian diffusion coefficients for PLA specimens aged in distilled water.

T (°C)	M_∞ (%)	D .10^{-7} (cm²/s)	D_c .10^{-7} (cm²/s)
25°C	0.59 ± 0.03	0.48	0.24
30°C	0.62 ± 0.03	0.57	0.28
40°C	0.76 ± 0.03	0.75	0.37
50°C	1.01 ± 0.02	1.05	0.52

Table 2. Mechanical properties of PLA before and after ageing in different aqueous environments and the evolution of properties.

T (°C)	Immersion condition	Immersion time (days)	E (MPa)		σ_b (MPa)		ε_b (%)	
	unaged		3487 ± 127		54.7 ± 3,4		3.4 ± 0,8	
	natural ageing in seawater	180	3997 ± 71	+ 15%	56.9 ± 2,79	+ 4%	2 ± 0,2	- 41%
25	distilled water	180	4317 ± 120	+ 24%	50.2 ± 0,8	- 8%	6.9 ± 0,8	+ 103%
	seawater	180	4086 ± 122	+ 17%	51.4 ± 2,9	- 6%	5.2 ± 1,2	+ 53%
30	distilled water	180	4068 ± 132	+ 17%	50.1 ± 1,2	- 9%	2 ± 0,02	- 42%
40	distilled water	180	4032 ± 125	+ 16%	8 ± 2,5	- 85%	0.3 ± 0,1	- 92%
	seawater	180	4427 ± 293	+ 27%	16.5 ± 1,9	- 70%	0.4 ± 0,01	- 88%
50	distilled water	15	3432 ± 205	- 2%	50.3 ± 1,5	- 12%	1.7 ± 0,03	- 50%

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Table 3. Evolution of number-average molecular weight ($\overline{M}_n$), weight-average molecular weight ($\overline{M}_w$) and polydispersity index (PI) of PLA samples as a function of temperature in distilled water.

T (°C)	Immersion time (days)	$\overline{M}_n$ (g.mol^{-1})	$\overline{M}_w$ (g.mol^{-1})	PI
	0	75 000	149 500	1.99
25°C	180	66 300	132 000	2.05
30°C	180	64 100	113 000	1.81
40°C	180	26 400	40 900	1.55
50°C	30	29 700	46 400	1.56

Table 4. Evolution of thermal transitions of PLA samples aged in distilled water.

	Immersion times (days)	**1st heating**						**2nd heating**					
		T_g (°C)	T_{cc} (°C)	ΔH_{cc} (J/g)	T_m (°C)	ΔH_m (J/g)	χ_c (%)	T_g (°C)	T_{cc} (°C)	ΔH_{cc} (J/g)	T_m (°C)	ΔH_m (J/g)	χ_c (%)
	unaged	65	126	3.1	152	1.7	1.3	57	126	0.8	150	1.6	0.7
25°C	180	60	125	7	155	17.1	10.8	55	127	9.2	153	10	0.9
30°C	180	58	124	11	153	18.8	8.4	53	122	13.6	149	15.8	2.4
40°C	180	51	92	35	148	36.9	2.0	51	123	15.5	146	17	1.6
50°C	30	47	-	-	150-155*	34	-	53	100	29.3	147-153*	30.2	0.8

*Corresponding to a double melting peak

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Table 5. Equilibrium water uptake and Fickian diffusion coefficients for PLA specimens aged in distilled and seawater at different temperature.

		M_∞ (%)	D.10^{-7} (cm²/s)	D_c.10^{-7} (cm²/s)
	natural ageing	0.47 ± 0.02	0.37	0.18
25°C	distilled water	0.59 ± 0.03	0.57	0.28
	sea water	0.52 ± 0.02	0.54	0.26
40°C	distilled water	0.76 ± 0.05	0.75	0.37
	sea water	0.74 ± 0.03	0.73	0.36

Table 6. Evolution of number-average molecular weight ($\overline{M}_n$), weight-average molecular weight ($\overline{M}_w$), and polydispersity index (PI) of PLA samples as a function of aqueous environment.

			$\overline{M}_n$ (g.mol^{-1})	$\overline{M}_w$ (g.mol^{-1})	PI
	unaged	0	75 000	149 500	1.99
	natural ageing	180	75 600	141 000	1.93
25°C	distilled water	180	66 300	132 000	2.01
	sea water	180	58 000	127 000	2.19
40°C	distilled water	180	26 400	40 900	1.55
	sea water	180	18 000	35 000	1.94

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Table 7. Evolution of thermal transitions of PLA samples for the natural and accelerated ageing at 25 and 40°C after 180 days in immersion.

		1st heating						**2nd heating**					
		T_g (°C)	T_{cc} (°C)	ΔH_{cc} (J/g)	T_m (°C)	ΔH_m (J/g)	χ_c (%)	T_g (°C)	T_{cc} (°C)	ΔH_{cc} (J/g)	T_m (°C)	ΔH_m (J/g)	χ_c (%)
	unaged	65	126	3.1	152	1.7	1.7	57	126	0.8	150	1.6	0.7
	natural ageing	61	126	9.1	153	11.4	2 .4	54	124	11.8	150	13.4	1.7
25°C	distilled water	60	125	6.1	155	17.1	13.5	55	126	9.0	153	10.4	1.7
	seawater	63	126	6.4	152	10.7	4.7	55	126	7.8	150	8.9	1.1
40°C	distilled water	51	92	34.5	148	36.9	2.6	51	122	15	146	16	1.5
	seawater	62	105	34.1	154	35.8	1.8	51	122	19.8	147	21.4	1.6

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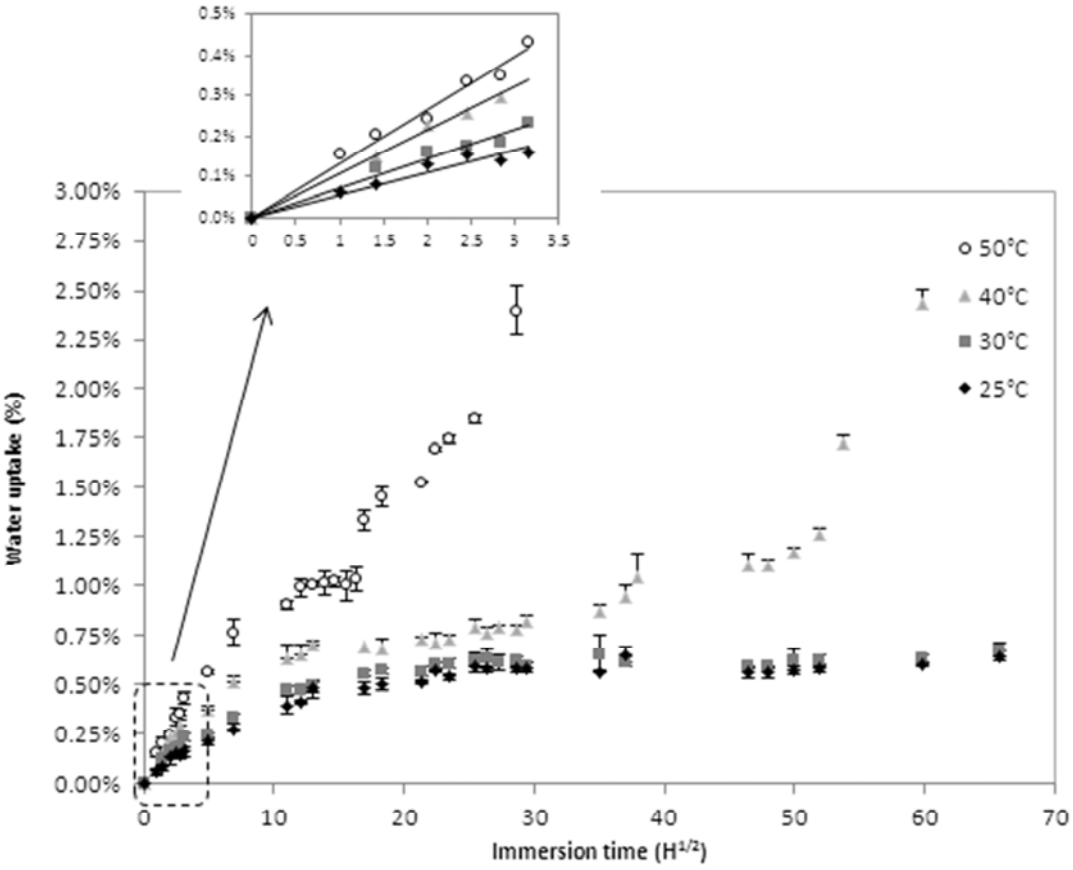

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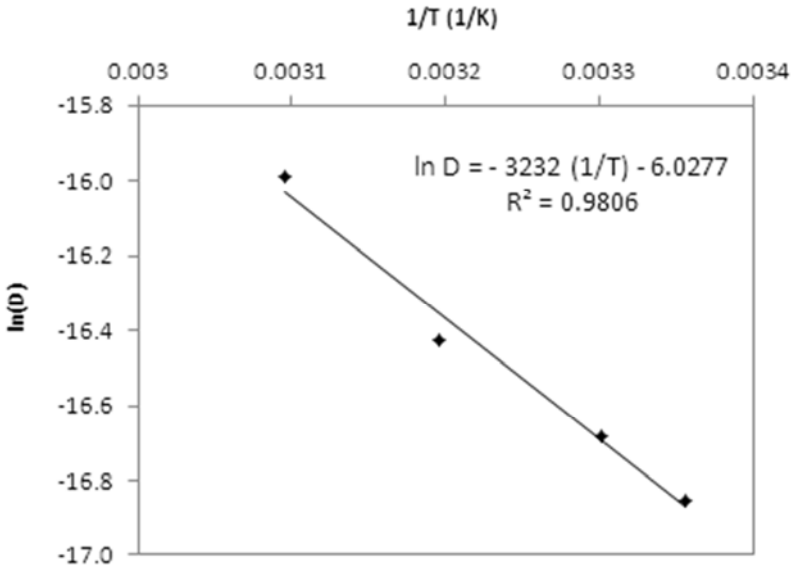

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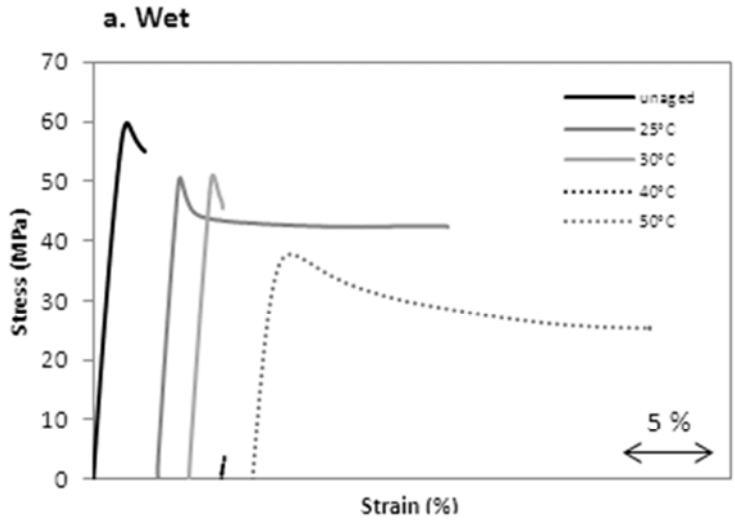

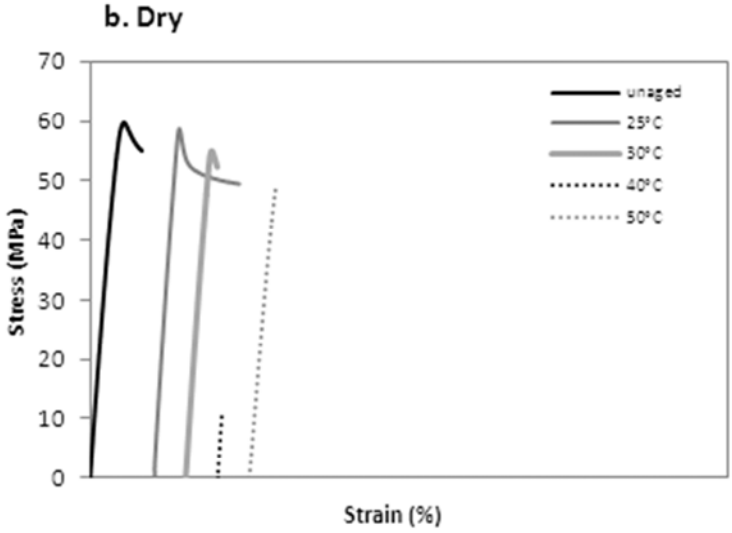

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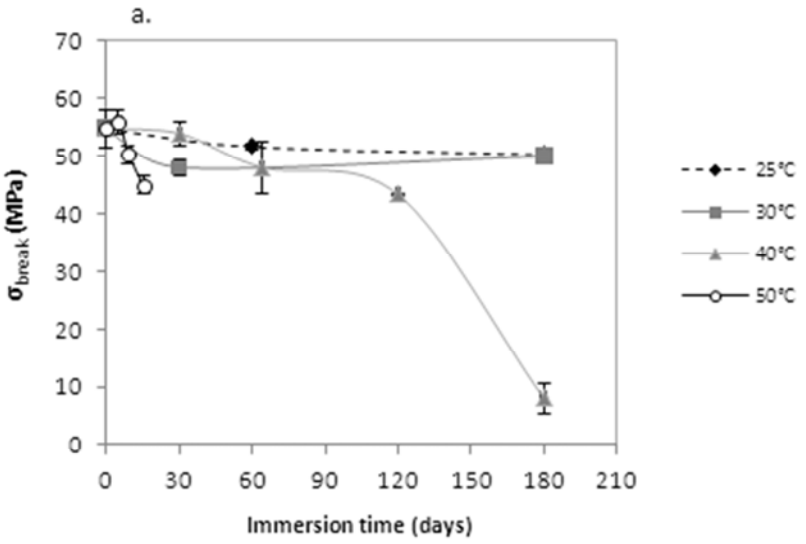

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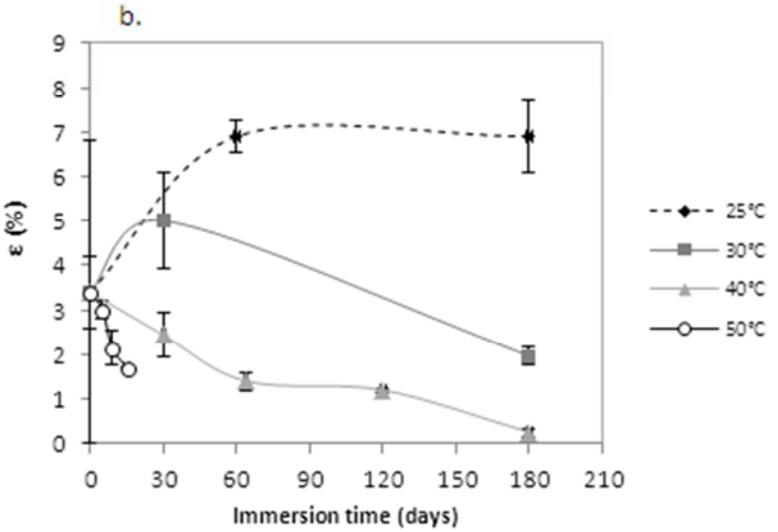

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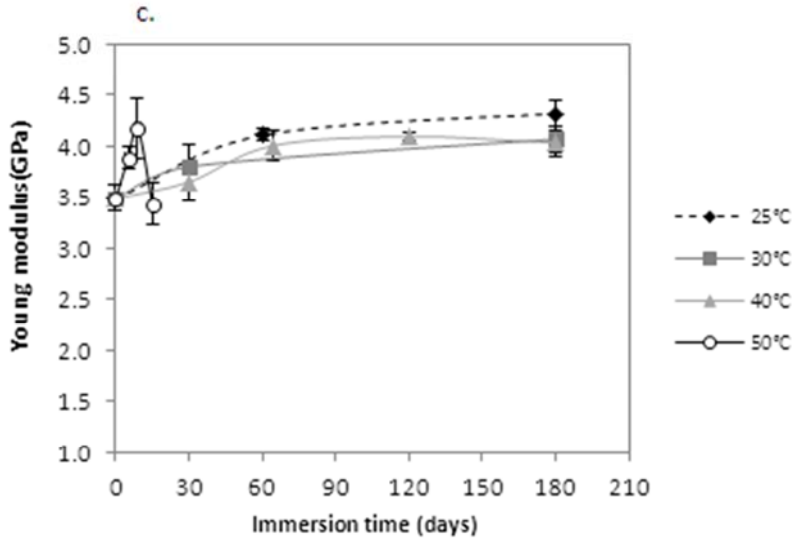

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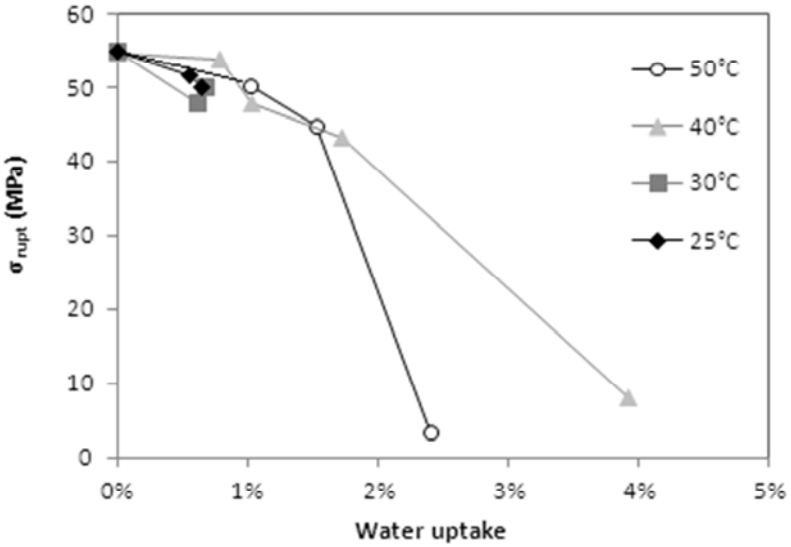

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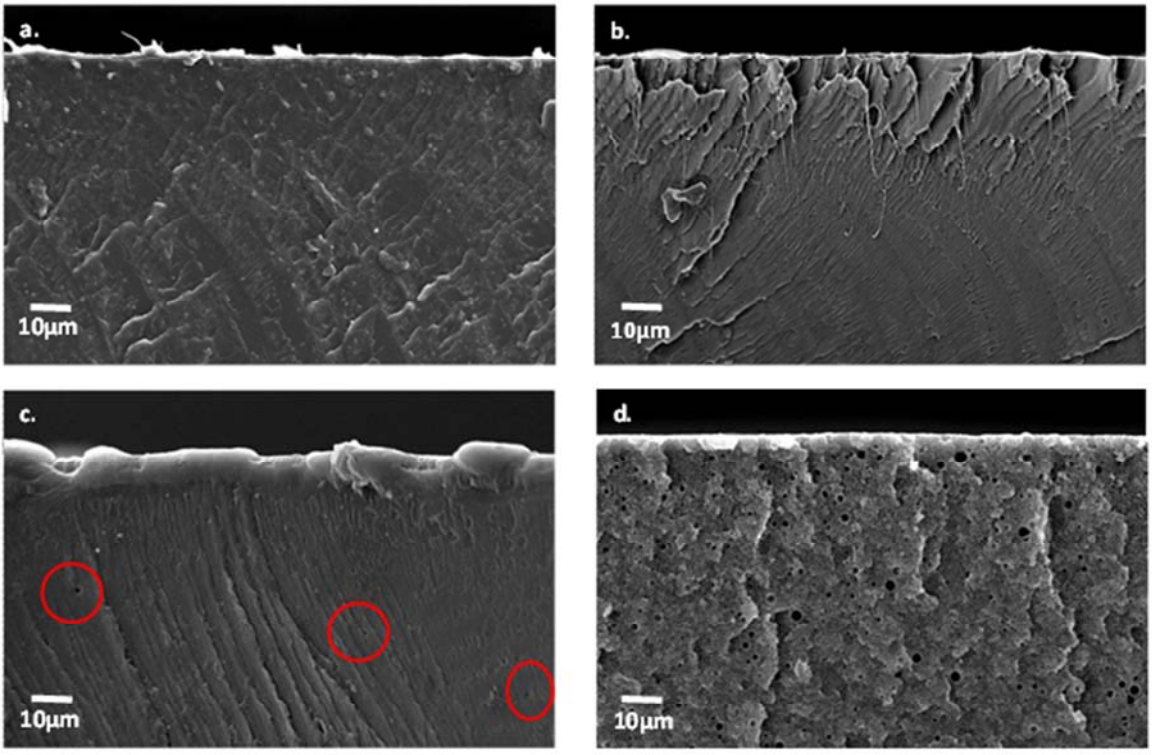

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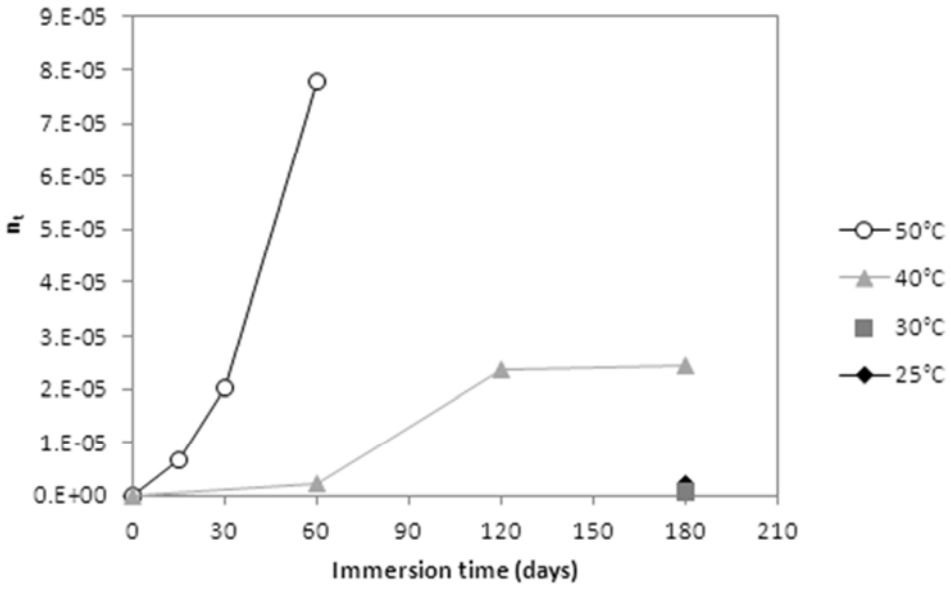

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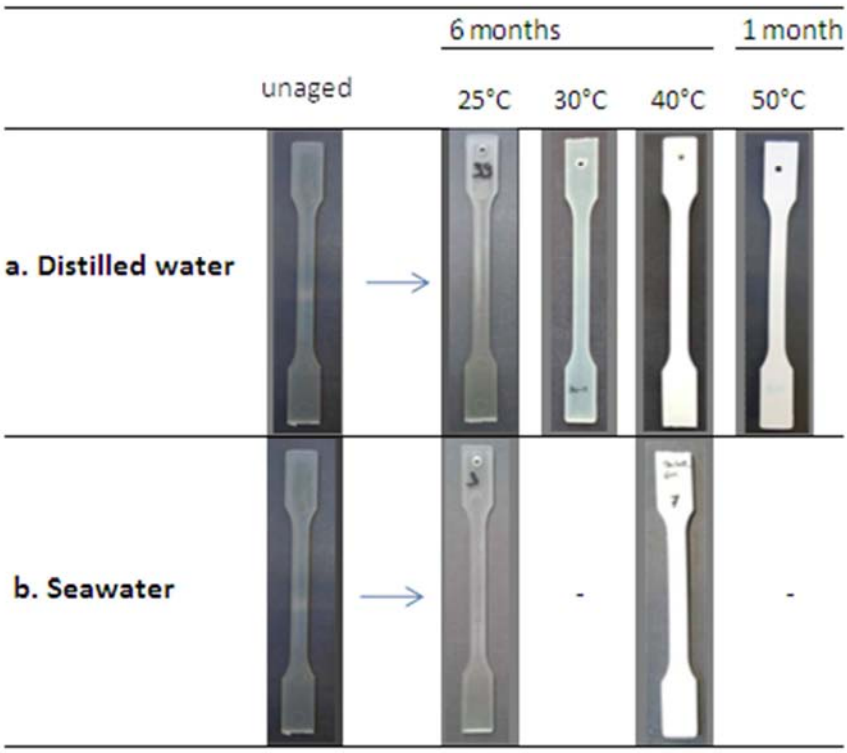

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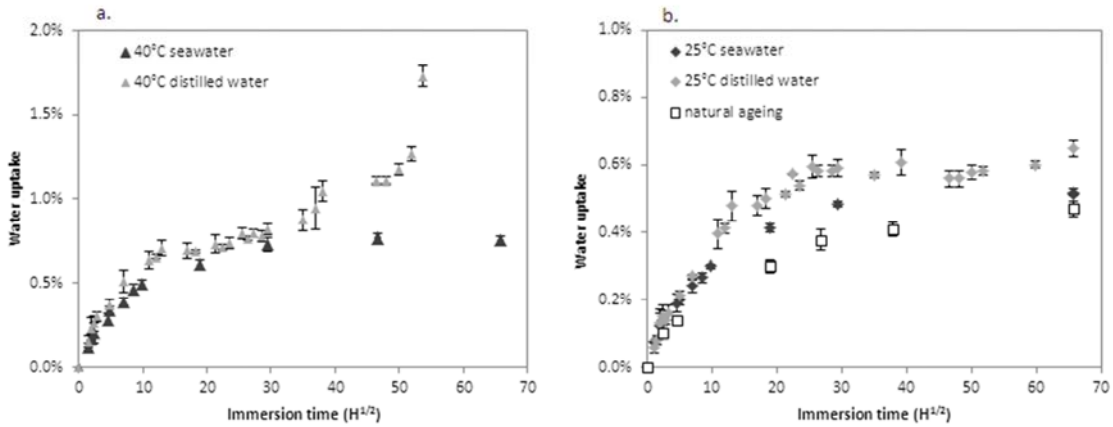

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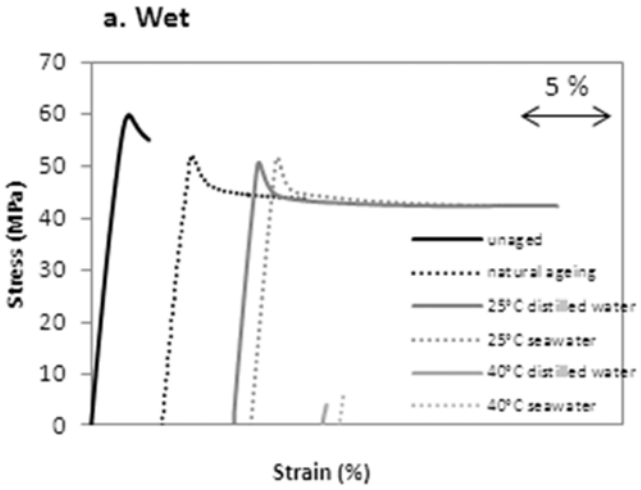

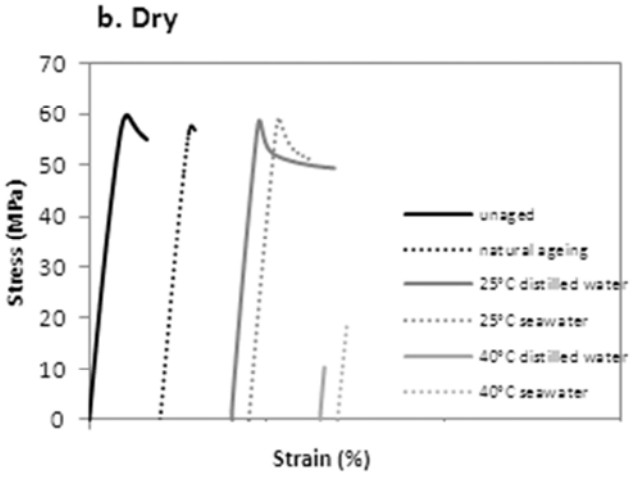

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