
Chemical coupling between oxidation and hydrolysis in Polyamide 6 - A key aspect in the understanding of microplastic formation

Deshoules Quentin ^{1,2}, Le Gall M ¹, Dreanno Catherine ², Arhant Mael ¹, Priour Daniel ¹,
Le Gac Pierre Yves ^{1,*}

¹ Laboratoire Comportement des Structures en Mer, Ifremer, Centre de Bretagne, 29280 Plouzané, France

² Laboratoire Détection Capteurs et Mesures, Ifremer, Centre de Bretagne, 29280 Plouzané, France

* Corresponding author : Pierre Yves Le Gac, email address : pierre.yves.le.gac@ifremer.fr

Abstract :

The formation mechanism of secondary microplastics (issued from larger plastics) in the oceans is still an open question. However, it is commonly accepted that the chemical degradation undergone by polymers leads to their embrittlement and finally fragmentation. In the marine environment, polymers are subjected to different types of chemical and physical degradations. This study focuses on the coupling between two types of chemical degradation: hydrolysis and oxidation in the case of polyamide 6. To do so, polymer films (250 µm thick) were aged for durations up to 2 years and then characterized at the molecular scale using FTIR and at the macromolecular scale using mainly DSC and GPC. Results clearly show the existence of a chemical coupling between oxidation and hydrolysis in polyamide 6 that induces a large increase in the chain scission rate. The degradation rate is indeed 80 times faster in water with oxygen than in water without oxygen. Then, a two-stage ageing condition (first thermal oxidation in dry air and then hydrolysis in water without oxygen) was used to further study the nature of the coupling. These results have shown for the first time that a strong interaction occurs between thermal oxidation and hydrolysis of polyamide materials at the macromolecular scale.

Highlights

► Chain scission is much faster in water in presence of oxygen compared to water without oxygen. ► An increase in humidity level of air leads to an increase in degradation rate in polyamide. ► A strong chemical coupling exists between oxidation and hydrolysis in polyamide 6.

Keywords : Polyamide, Hydrolysis, Oxidation, Coupling

1. Introduction

Over the last decade, the fate of microplastics in the oceans has become a major issue for society [1-5]. This raises a significant number of scientific questions such as: How are microplastics and nanoplastics formed in the oceans? How many microplastics are in the ocean? Where do they come from? And finally, another major question, what is the effect of marine ageing on these microplastics and their behaviour? In other terms, there is a crucial need to be able to characterize, understand and model the behaviour of a given polymer subjected to ageing in the oceans. However, such ageing conditions are quite particular, as ageing in the oceans involves several ageing parameters. The polymer is at least subjected to the effects of water, UV radiation and oxygen [6]. Existing knowledge concerning the coupling between these different ageing conditions is quite limited.

In this study, we will focus on polyamide 6 (PA6) for which the decoupled ageing mechanisms are well documented in published literature. First, when the polymer evolves in a wet environment, it absorbs a significant amount of water. For example, it absorbs around 10% of water when immersed in sea water at 15°C [7]. This water absorption leads to an increase in the mobility of the macromolecular chains (plasticization) which induces a significant reduction in the glass transition temperature (T_g , from +60°C in the dry state down to -20°C in the immersed saturated state [7]) and large changes in mechanical behavior [8 - 10]. Aside from this reversible degradation in water, PA6 is also subjected to an irreversible degradation mechanism called hydrolysis. This mechanism induces a chain scission process within the amorphous phase of the polymer [11-14] that leads to a large change in the mechanical behaviour of the polymer (from ductile to brittle [15-17]). Second, PA6 can also be subjected to oxidative ageing [18-23] which leads to the formation of degradation products (imides and carboxylic acid). Upon oxidation, PA6 is also subjected to a chain scission process, which leads to an embrittlement of the material [24, 25].

Therefore, it appears that for polyamide 6, the chemical degradation mechanisms and their consequences on the mechanical properties are known. However, in the literature, only two studies we are aware of mentions a potential coupling effect between these different degradation mechanisms [26, 27new]. In first study devoted to the mechanical behaviour of polyamide fibres, Bernstein et al. highlights an increased degradation when the fibres are aged in water with oxygen compared to those aged in water without oxygen. The aim of the study was to investigate the behaviour of PA fibres under tensile loading. More especially, they studied the loss in stress at failure as well as the origin of this acceleration in degradation at the macromolecular scale. The second one, dedicated to oxygen

consumption rate in PA as function of the ageing environment (temperature and humidity) shows a large increase in the oxidation rate in presence of humidity compared to dry environment.

The aim of the present paper is to investigate and analyse the results from the ageing of polyamide 6 in different environments. First, we will confirm the major impact that oxygen has in the kinetics of degradation at the macromolecular scale while considering 3 types of ageing conditions: ageing in air, in water with oxygen and finally in water without oxygen. Second, ageing studies performed under different relative humidity conditions will confirm this coupling effect between hydrolysis and oxidation. Finally, a two-stage ageing condition (a first stage under oxidation and a second under pure hydrolysis) was carried out to identify the nature of the coupling between these phenomena.

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2. Material and methods

2.1. Material

The polymer used in this study is a neat polyamide 6 provided by Goodfellow. It was supplied in the form of polymer films with a thickness of about 250 μm . The average molar mass in number M_n , the polydispersity index PDI, and the crystallinity ratio X_c were measured to be 52.3 kg/mol, 2.4 and 20%, respectively.

2.2. Ageing

2.2.1. Oven

Oxidative ageing was performed in ovens (type UN55 from Memmert) at 80 and 100°C. To ensure a homogeneous degradation in the oven, a continuous convection of air was used.

2.2.2. Pressure vessels

Here, two different types of pressure vessel were used: those for ageing in water without oxygen and those with oxygen. In both cases, ageing was performed at 80 and 100°C. For those where ageing was performed without oxygen, the pressure vessels were filled with deionized water and the oxygen within the water was removed through pure nitrogen bubbling for a duration of 3 hours prior to ageing. Then, to prevent the water from boiling at 100°C, the pressure within the vessel was fixed at 10 bars. For the ageing conditions with oxygen, specific pressure vessels were designed where half of the vessel was filled with water and the other half with gas (here 98% oxygen and 2% nitrogen). The gas pressure within the pressure vessel was checked by a pressure sensor. Finally, it may be noted that each ageing condition was performed individually within a given pressure vessel, with or without oxygen.

2.2.3. Humidity

Ageing under different relative humidities (RH) was performed at 80°C in climatic chambers (Mettler): type HCP 108 for a humidity of 70% and type CTC 256 for a humidity of 98%.

2.2.4. Weight gain measurements

For some of the samples, weight gain measurements after ageing were carried out under different humidity conditions (25%, 40%, 55%, 85% RH) and immersion at 70°C. The weight gain ΔM is calculated using Eq. 1.

$$\Delta M (\%) = \frac{m_{\text{sat}} - m_0}{m_0} \times 100 \quad \text{Eq.1}$$

Where m_{sat} is the mass of a given sample that has reached its water saturation level and m_0 its initial mass measured on dried sample.

2.3 Gas Permeation Chromatography (GPC)

GPC tests was carried out by the PeakExpert company, in order to measure the changes in average molar mass by number M_n as well as the polydispersity index (PDI) during ageing. These were obtained using the Laun et al. method [28].

2.4 Differential Scanning Calorimetry (DSC)

DSC measurements were obtained using a Q200 device from TA instruments. Tests were performed under a constant nitrogen flow of 50 mL/min at a heating rate of 10°C/min from 0°C up to 250°C. The crystallinity ratio X_c was calculated using Equation 1:

$$X_c = \frac{\Delta H_f}{\Delta H_f^0} \times 100 \quad \text{Eq.2}$$

Where ΔH_f is the melting enthalpy measured during the DSC tests and ΔH_f^0 the enthalpy for a 100% crystalline material, taken here as 240 J/g [29].

2.5 Fourier Transform InfraRed spectroscopy (FTIR)

The changes in chemical structure during ageing were followed using FTIR spectroscopy in ATR (Attenuated Total Reflectance) mode with a Perkin Elmer Frontier machine. These analyses were performed at room temperature in the range from 600 to 4000 cm^{-1} using dried samples. Each spectrum was normalized using the CH_2 band at 1462 cm^{-1} which is not affected by ageing [21].

3. Results and discussion

First the results from FTIR, GPC and DSC tests are presented after ageing performed in different conditions (in water without oxygen, in air and then in water with oxygen). Then, these ageing conditions are compared in terms of chain scissions, calculated using Equation 3 below. This allows us to further investigate the degradation rate for a given ageing condition.

$$s_{amorphous} = \frac{1}{1 - X_c} \times \left(\frac{1}{M_n} - \frac{1}{M_{n0}} \right) \quad \text{Eq.3}$$

Where $s_{amorphous}$ is the concentration of chain scission (mol/kg), M_{n0} is the initial molar mass (kg/mol), X_c is the crystallinity ratio and M_n is the current molar mass (kg/mol).

Next, results from ageing under relative humidity conditions are presented. Finally, results from the two-stage ageing condition (pre-oxidation followed by a pure hydrolysis stage) are shown, to confirm the acceleration in terms of degradation that provides hydrolysis in presence of oxygen.

3.1. Ageing in water without oxygen

During immersion in oxygen free water, the polyamide undergoes pure hydrolysis degradation, i.e. chemical reaction between water molecules and amide bonds and formation of carboxylic acid. Based on FTIR results (Figure 1 a) it appears a decrease in bands situated at 3292 cm^{-1} , 1634 cm^{-1} and 1538 cm^{-1} that can be related to the consumption of amide groups situated in the amorphous phase. In the meantime, changes of bands related to the PA6 crystallinity can be observed. For example, the band situated at 2926 cm^{-1} related to CH_2 in the amorphous phase decrease whereas the band situated at 2916 cm^{-1} related to CH_2 in the crystalline phase increases (same process occurs for the band at 2856 cm^{-1} that decrease when the band at 2869 cm^{-1} increases). This increase in bands related to the crystallinity are in accordance with the increase in crystallinity ratio, see later. Carboxylic acid and amine groups formed during hydrolysis cannot be easily detect by FTIR, as already reported in [30]. A quantitative characterization of the hydrolysis process is proposed here based on the molar mass of the PA6. In fact, when hydrolysis takes place a chain scission occurs at the macromolecular scale. In Figure 1b, a clear decrease in M_n value from 53.2 kg/mol down to 32.5 kg/mol after 700 days of ageing at 80°C is observed. In the meantime, an increase in crystallinity ratio from 20% up to 32% (again after 700 days of ageing at 80°C) is observed on Figure 1.c. The first fast increase from 20 to 25% is due to the formation of monoclinic a phase in hot water (see [16] for details). Then a slow increase from 25% to 32% occurs. The latter is due to an increase in the macromolecule mobility close to the crystalline phases (a process known from the literature, named chemicrystallization). More details about the pure hydrolysis of polyamide are available in [11-17].

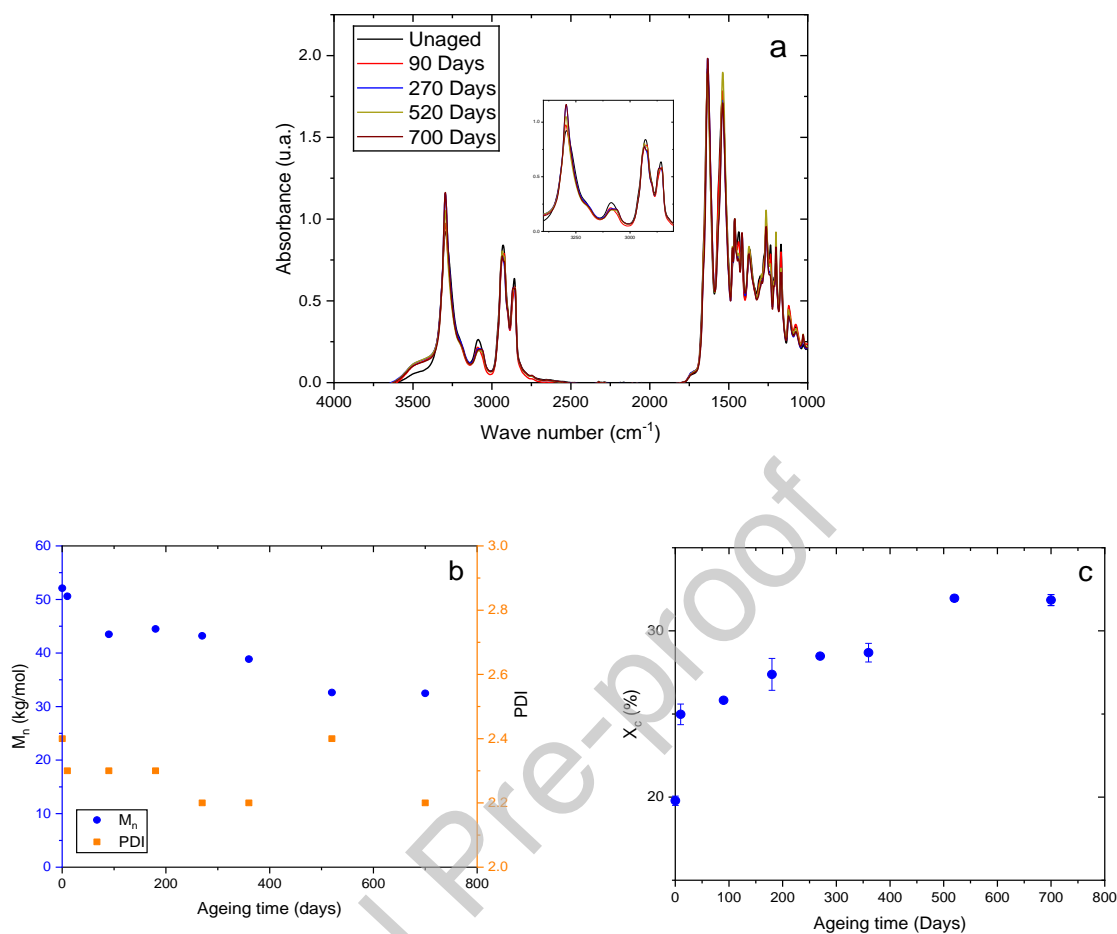


Figure 1 – Pure hydrolysis of polyamide. (a) FTIR, (b) GPC, (c) DSC results as a function of ageing time in air water without oxygen at 80°C

3.2. Ageing in air without water

In dry air, polyamide undergoes thermal oxidation. This oxidation leads to the formation of specific degradation products such as carboxylic acid (seen at 1756 and 1716 cm⁻¹ on Figure 2.a) and imide (visible at 1734 cm⁻¹, Figure 2.a), as already reported in the literature [21]. Here again, a consumption of amide groups occurs during thermal oxidation as shown by the decrease in bands situated at 3292 cm⁻¹, 1634 cm⁻¹ and 1538 cm⁻¹. The bands related to the crystalline phase also increases during ageing (2926cm⁻¹ and 2869cm⁻¹) that suggests an increase in crystallinity ratio. During thermal oxidation, a chain scission process mainly occurs as shown by the decrease in M_n (from 52.3 kg/mol down to 13.7 kg/mol after 630 days at 80°C) in Figure 2.b. Compared to the pure hydrolysis condition where a stable PDI was identified upon ageing, Figure 1.b, an increase in PDI is observed here from 2.4 up to 2.9. This suggests that crosslinking also occurs during the termination step of the oxidation. Here again, an increase in crystallinity ratio with time is observed, from 20% up to 29%, Figure 2.c. More details about the thermal oxidation of PA can be found in [18-27].

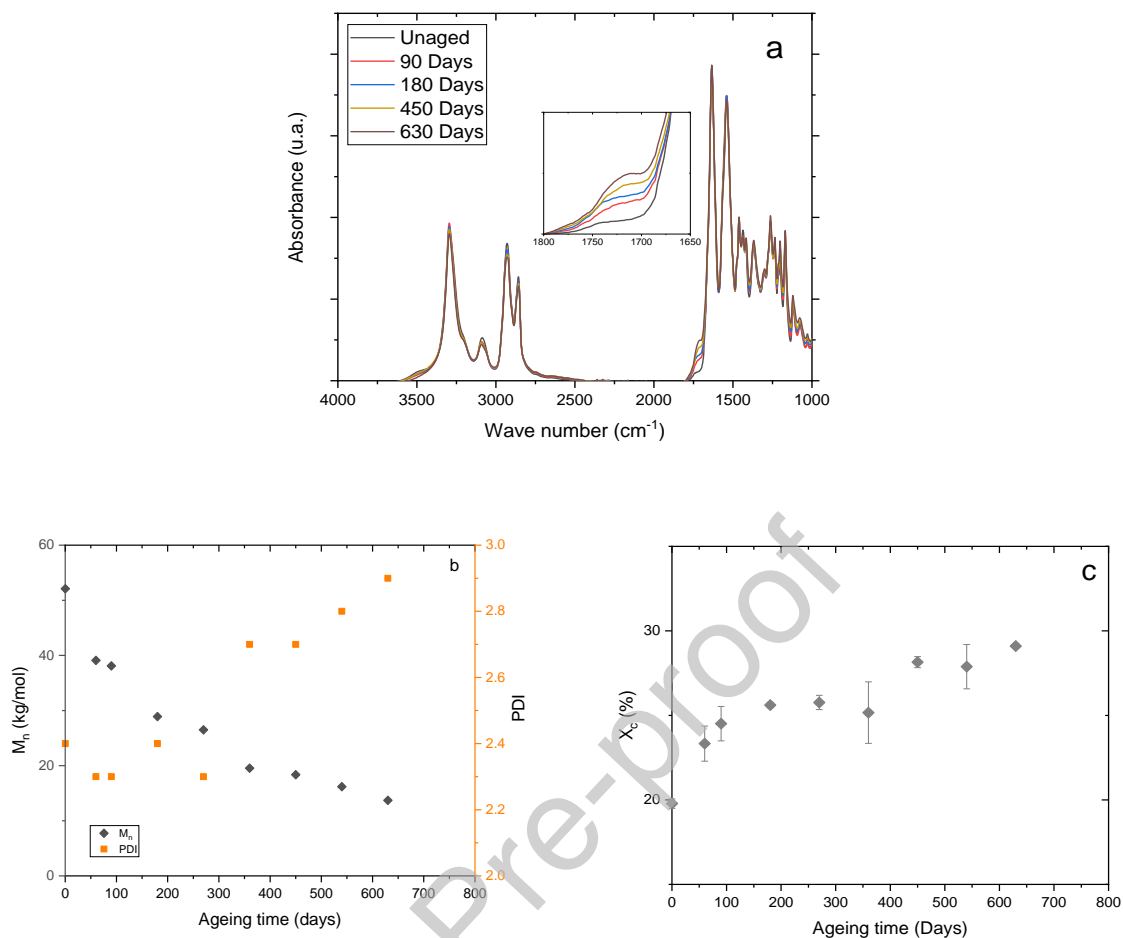


Figure 2 – Thermal oxidation of polyamide. (a) FTIR, (b) GPC, (c) DSC results as function of ageing time in air at 80°C

3.3. Ageing in water with oxygen

When immersed in water with oxygen, polyamide undergoes chemical degradations due to both hydrolysis and oxidation. Based on FTIR results from Figure 3.a, it appears that the carbonyl peak evolves are formed during ageing. This suggests an oxidative degradation of the polymer. Formation of a new peak at 1756cm⁻¹ is observed during ageing in water with oxygen, this peak is commonly attributed to isolated carboxylic acid. Here again a chain scission process is observed with a decrease in molar mass from 52.3 kg/mol down to 13.5 kg/mol after 28 days of ageing at 80°C, Figure 3.b. An increase in crystallinity ratio is also identified on Figure 3.c (from 20% up to 29%). If we consider a 20 kg/mol loss upon ageing at 80°C, around 600 days are needed under pure hydrolysis conditions, about 200 days in air and only 15 days in water with oxygen. Such a difference is highly significant. From these results, it clearly appears that the degradation rate is much faster when the polymer is placed in water with oxygen, compared to thermal oxidation and pure hydrolysis. The following sections are therefore devoted to the confirmation of this acceleration in degradation rate when PA6 is immersed in water with oxygen due to an increase in oxidation rate.

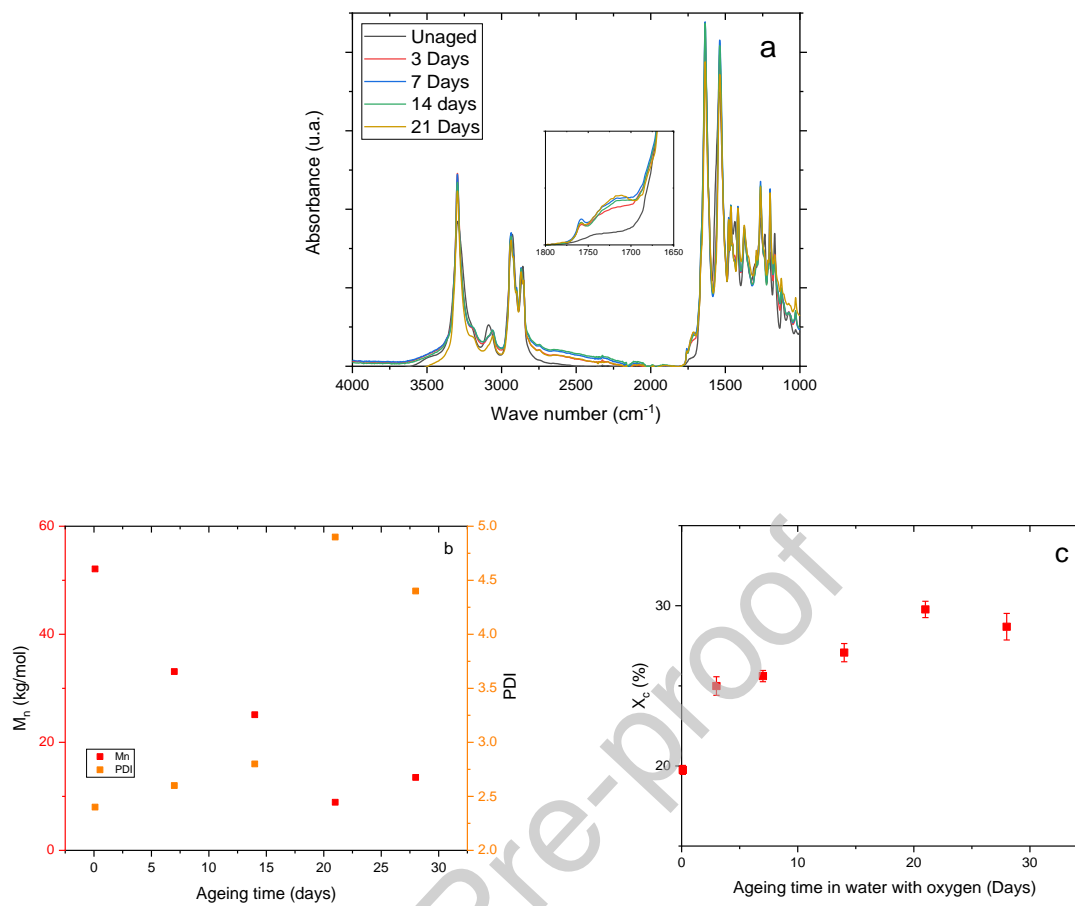


Figure 3 – Degradation of polyamide in water with oxygen. (a) FTIR, (b) GPC, (c) DSC results as function of ageing time in water with oxygen at 80°C

3.4. Impact of the environment on chain scissions

In order to study the impact of the environment on the chemical degradation of polyamide 6 in terms of kinetics both decrease in molar mass and increase in crystallinity ratio during ageing at 80°C are plotted in Figure 4. It can be observed here that degradation in water with oxygen is much faster than in air and water without oxygen.

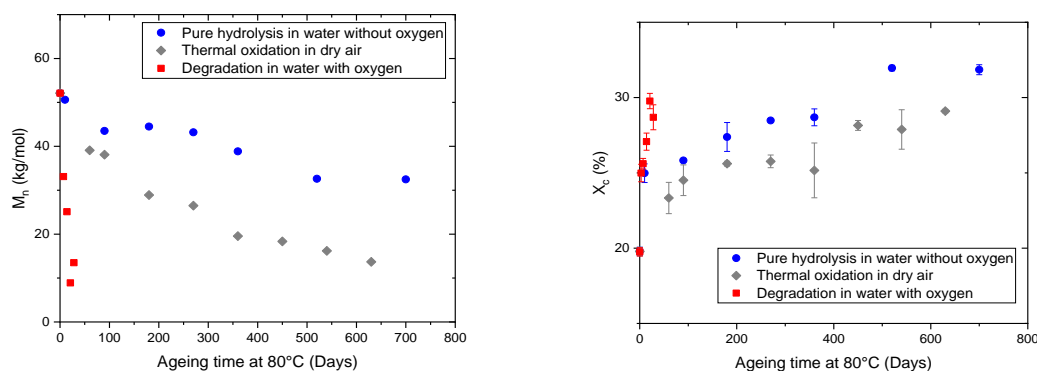


Figure 4 – Changes in molar mass (a) and crystallinity ratio (b) during ageing at 80°C as function of the environment

Because both M_n and X_c change during ageing, we will focus now on the number of chain scissions that occur within the polymer. In the past, it has been shown that chain scissions occur only in the amorphous phase when considering semi-crystalline polymers. We have thus chosen to consider chain scissions in the amorphous phase of the PA6 (calculated with Eq.3) to consider chemical degradation at the macromolecular scale in a quantitative manner. In Figure 5 a chain scission in the amorphous phase is plotted as a function of ageing time when samples are immersed in water without oxygen (blue dots in Figure 5.a) and with oxygen (red squares in Figure 5.a). This confirms that the degradation is much faster in water with oxygen. As an example, at 80°C, the ageing duration needed to reach 0.01 mol.L^{-1} of chain scissions is 7 days in the presence of oxygen in water whereas this takes about 1.5 years in the absence of oxygen. Therefore, the presence of oxygen in water increases the degradation rate by a factor around 80, indicating that the acceleration factor induced by the presence of oxygen is significant. This behavior can be explained by the fact that both hydrolysis and oxidation occur when samples are placed in water with oxygen. However, in a quantitative way, if we consider now the sum of chain scissions induced by thermal oxidation in air and hydrolysis in water without oxygen (plotted in triangles on Figure 5.b), it clearly appears that this sum is much lower than the chain scissions in water with oxygen for a specific ageing duration. This provides clear evidence of an increase in degradation rate when PA6 is immersed in water with oxygen compared to water without oxygen. This result is in accordance with existing data [26] in the literature based on mechanical considerations but this behavior is highlighted for the first time at the macromolecular scale. But also results from Gijsman et al. [27] that clearly show an acceleration of the oxidation rate when samples are in a humid environment compared to dry air. In order to study this coupling between oxidation and hydrolysis further, ageing was performed at several humidity levels.

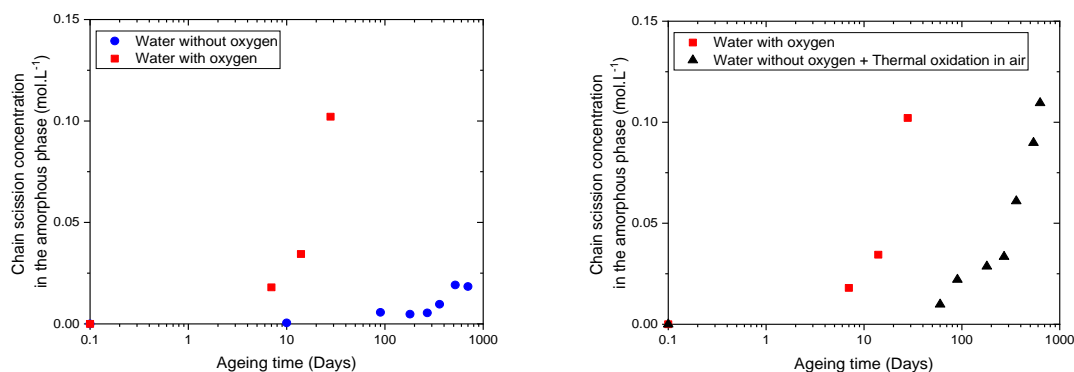


Figure 5 – Chain scission in polyamide 6 as a function of ageing time at 80°C for 3 different environments (water only where only hydrolysis occurs, dry air where only thermal oxidation occurs and in water with oxygen)

3.5. Confirmation of the coupling between oxidation and presence of water

In order to study the chemical coupling between oxidation and hydrolysis in detail, PA6 samples were aged in humid air at 3 levels: 70%, 98% and 100% (the latter corresponds to immersion). Chain scissions as a function of ageing time are plotted in Figure 6, for a temperature of 80°C. Changing the moisture content in the air leads to a change in the water concentration within the amorphous phase of PA6, which is independent of ageing in dry air as shown in Figure 6. Moreover, it is known that the hydrolysis kinetics depend on the water concentration in the material. Ageing at different humidity levels allows us to modify the hydrolysis kinetics while keeping the oxidation rate constant if there is no impact of oxidation on water uptake; this point has to be checked here before considering the results in Figure 7. It has been already shown several times in the literature that oxidation leads to the formation of polar degradation products that can induce an increase in the amount of water absorbed by the polymer (and therefore the hydrolysis rate). Here, water absorption as a function of the humidity level does not change significantly with oxidation level of the polymer, Figure 7. Results presented in Figure 5 clearly show that chemical degradation of PA6 is much faster when samples are placed in a humid environment compared to dry air. Furthermore, the higher the humidity level, the higher the degradation rate. These results confirm that there is a coupling between the hydrolysis and oxidation of PA6. In order to better understand this process, two-stage ageing conditions were pursued, results are shown in the next section.

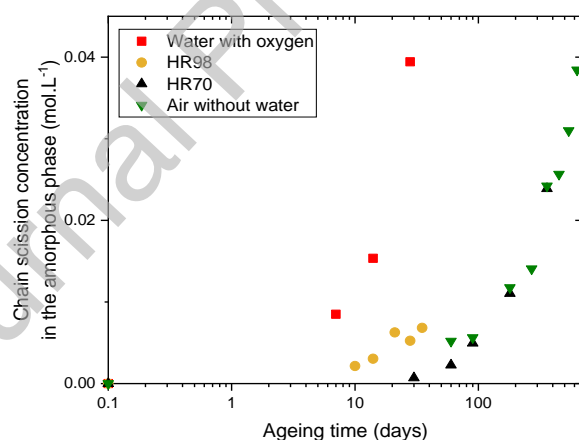


Figure 6 – Chain scissions as a function of ageing time for 4 different environments (water with oxygen, humidity of 98%, humidity of 70% and water without oxygen)

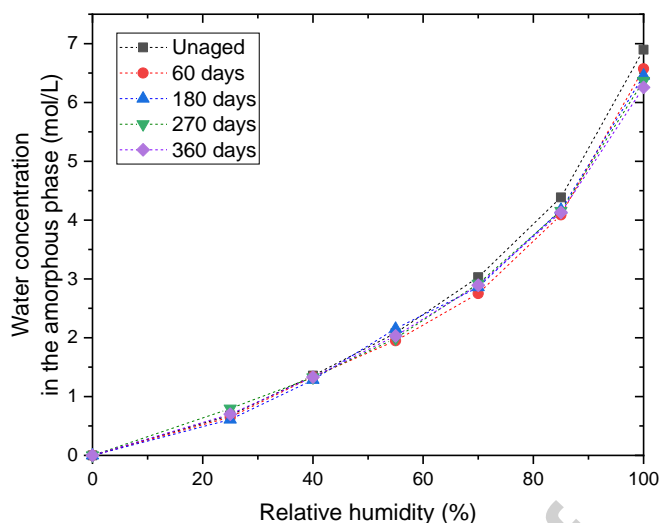


Figure 7 – Water concentration in the amorphous phase as a function of relative humidity after thermo-oxidative ageing at different ageing times at 80°C in dry air

3.6. Chemical coupling between oxidation and hydrolysis

From the previous results, it appears that when hydrolysis and oxidation are combined, the degradation rate is much faster than in the case of pure oxidation or pure hydrolysis. During thermal oxidation, chemical products such as carboxylic acid and imides are formed (oxidation products). Imides can then undergo hydrolysis. Such a process would lead to an increase in the number of chain scissions within the polymer. To check this hypothesis, decoupled ageing was performed.

- First, samples were oxidized in air at 100°C (pre-oxidation, PO) for several durations up to 75 days in order to produce samples with several concentrations of oxidation products.
- Second, these samples were placed in water without oxygen at 100°C.

Results concerning the changes in M_n for a sample pre-oxidized in an oven for 75 days at 100°C (red dots) and then subjected to pure hydrolysis at 100°C (blue dots) are presented in Figure 8. These results are compared to those obtained from the pure hydrolysis of an unaged specimen (blue dots) at 100°C. We observe that after the pre-oxidative stage of 75 days, the molar mass decreases from 52.3 kg/mol in the unaged state down to 18.3 kg/mol. At this stage, a significant number of carboxylic acids and imides are created. Afterwards, this same sample aged for 75 days in an oven is placed under pure hydrolysis conditions (water without oxygen). It appears that during this second ageing stage, the molar mass continues to decrease down to 8.6 kg/mol.

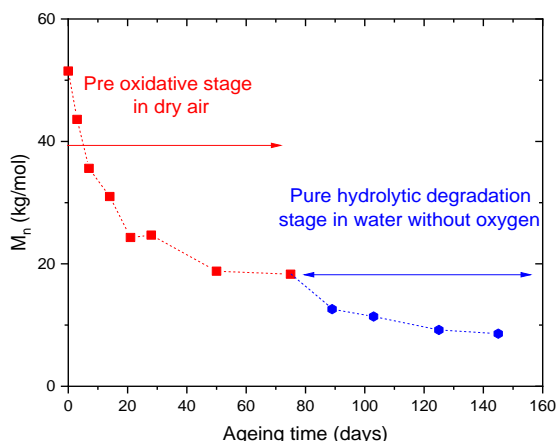


Figure 8 – Two-stage ageing condition with first thermal oxidation in dry air and then hydrolysis in water without oxygen

These results from molar mass measurements can then be translated into the number of chain scissions in the amorphous phase during the pure hydrolysis stage (after the pre-oxidation stage). Results are presented in Figure 9 for different pre-oxidation durations (7, 14, 28, 50 and 75 days). There is a clear increase in chain scission rate when samples are oxidized before immersion. The more the oxidation products, the higher the chain scission rate during immersion at 100°C in oxygen-free water. In order to have a better understanding of the origin of the degradation in PA6; we measured the concentration of the imide group during the immersion in water without water oxygen of a sample previously oxidized in dry air. For this purpose, a deconvolution of the FTIR spectra is necessary, an example is shown in Figure 10a. Then the area of the band at 1734cm⁻¹, relative to the imide, is followed over the time of immersion in water without oxygen, the results are shown in Figure 10b. A rapid drop in imide concentration is visible during immersion showing that hydrolysis of this chemical group seems to be involved in the degradation process of PA6. This result is supported by existing work in literature [31, 32].

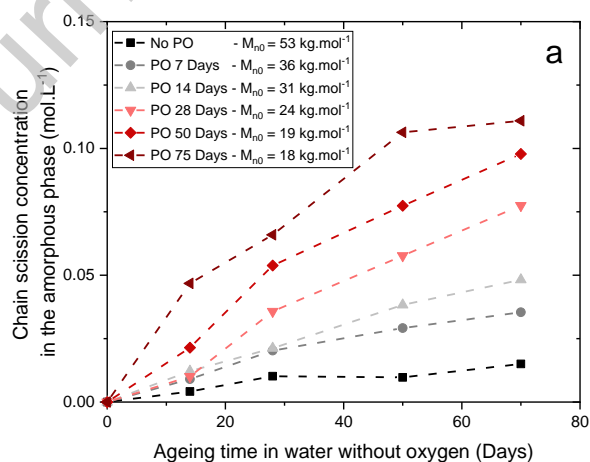


Figure 9 – Chain scission in the amorphous phase of PA6 immersed in water without oxygen at 100°C after oxidation in air at 100°C for several durations (M_n indicates the molar mass value after the oxidative ageing stage)

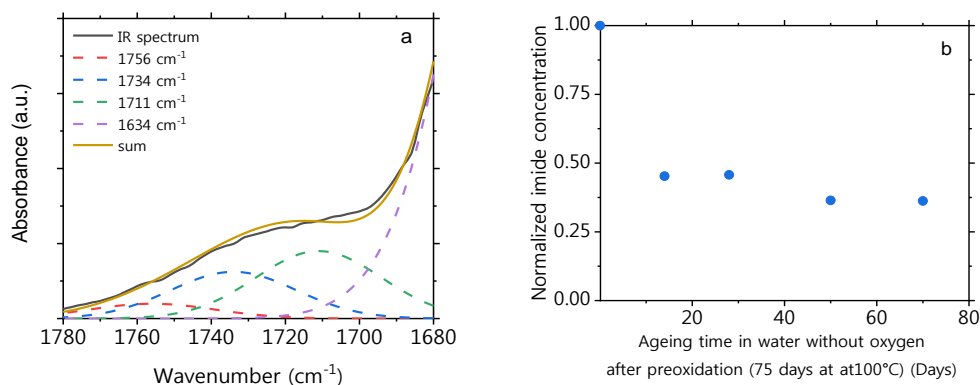


Figure 10 – Deconvolution of FTIR spectrum after thermal oxidation for 75 days in dry air at 100°C (a) and decrease in imide concentration as function immersion time in water without oxygen after preoxidation (b)

However, even if the hydrolysis of the oxidation products leads to an increase in the chain scission rate, this process does not explain our results in water with oxygen in Figure 4. To fully confirm this hypothesis, it would be of particular interest to perform ageing tests in water with different oxygen concentrations. As a major conclusion, there is clear evidence of an increase in the degradation rate when polyamide 6 is subjected to both hydrolysis and oxidation, as demonstrated by Figure 11 below. It is worth noting that data presented in Figure 11 comes from ageing performed at 100°C (whereas in Figure 4, it is 80°C). Based on our results and in contradiction with results obtained by Bernstein, et al. [26] chain scission due to thermal oxidation is faster than pure hydrolysis. This behavior may come from the fact that the PA used in this study has a very low amount of stabilizers and so more sensitive to oxidative degradation. Moreover, it is important to keep in mind that data for pure hydrolysis after oxidation plot in Figure 11 are only chain scission during the immersion, chain scission during the thermal oxidation process is not considered here. This is a significant result, that highlights the need to consider all types of degradation when a given polymer is immersed in water.

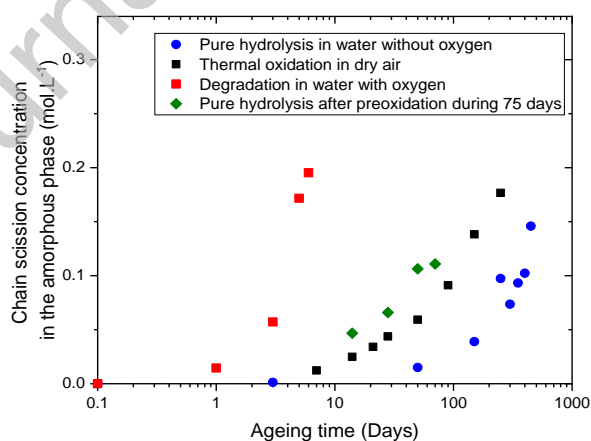


Figure 11 – Chain scissions as a function of the ageing environment at 100°C

4. Conclusions

Polyamide 6 degradation has been studied in oxygen free water where only hydrolysis occurs, in dry air where only thermal oxidation occurs and in water containing oxygen. Aged samples were

then characterized by FTIR, DSC and GPC. The degradation rate was assessed by considering the number of chain scission within the amorphous phase of the PA6 as a function of ageing time. The results obtained here clearly show a large increase in the degradation rate when both oxidation and hydrolysis occur in the polymer (i.e. in water with oxygen) compared with either pure oxidation (in dry air) or pure hydrolysis (in water without oxygen). This finding means, from a practical point of view, that future studies on polyamide hydrolysis need to consider the impact of the oxygen content in the ageing cells.

A chemical coupling between oxidation and hydrolysis has been highlighted for the first time in PA6 at the macromolecular scale using sequential ageing: first thermal oxidation and then pure hydrolysis. Results show a hydrolysis of imide groups formed during the oxidation and hence an increase in chain scission rate. Nonetheless, the increase in the degradation rate due to this chemical coupling is not of the same order of magnitude as the results in water with oxygen. Therefore, this result in itself does not fully confirm this hypothesis.

However, even if the exact coupling mechanisms between water and oxygen are not yet fully understood, this study highlights for the first time at the macromolecular scale an increase in the degradation rate due to an increase of the oxidation rate as already shown in [27]. This means that, at least for polyamide 6, coupling between several sources of ageing has to be considered very carefully, and needs further study in the future, especially when considering accelerated ageing for understanding of microplastic formation in the oceans.

Macroplastics at sea are subjected to different sources of ageing such as UV, water, oxygen and the living environment. Furthermore, in this specific case, plastics have no end of life; they will undergo significant levels of degradation that may lead to their fragmentation into micro plastics. Those plastics have been observed everywhere in the seas, from the coast to the artic, on the surface to the deepest seafloor [33-34]. Depending where they are the degradation mechanisms will be different, i.e. UV do not reached deep seafloor but are important on the surface. The majority of the current studies on the ageing of polymers in the oceans focus on a single type of degradation for the sake of simplification of laboratory experimental set up and the understanding of the degradation. The study proposed here shows that couplings between the different sources of ageing can occur. It is therefore necessary to consider these couplings in order to understand the fragmentation mechanisms of micro plastics in the marine environment and to propose predictive models.

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