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# Non-Arrhenian Hydrolysis of Polyethylene Terephthalate – a 5-year Long Aging Study Above and Below The Glass Transition Temperature

Arhant Mael <sup>1,\*</sup>, Le Gall Maelenn <sup>1</sup>, Le Gac Pierre Yves <sup>1</sup>

<sup>1</sup> IFREMER, Marine Structures Laboratory, Centre de Bretagne, Plouzané, France

\* Corresponding author : Mael Arhant, email address : [mael.arhant@ifremer.fr](mailto:mael.arhant@ifremer.fr)

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## Abstract :

The hydrolysis of PET was studied over a wide range of temperatures from 25 to 105°C for duration up to 5 years in water. It was demonstrated that independent of the aging temperature, a decrease in the molar mass was witnessed due to chain scissions that occur during hydrolysis of the ester group. Above T<sub>g</sub>, it was shown that chain scissions induced an increase in degree of crystallinity and amorphous layer thickness. However, this phenomenon, chemi-crystallization, was not observed at low temperatures, i.e. below T<sub>g</sub>. This change reflects a different behaviour when the polymer is exposed to water in the glassy or rubbery state. This was highlighted by the quite different activation energies below and above T<sub>g</sub>, respectively equal to 31 ± 12 and 134 ± 4 kJ/mol.

## Highlights

► Aging of PET was studied over a wide range of temperatures from 25 to 105°C for up to 5 years of aging. ► After 5 years of aging, chemi-crystallization was not observed at temperatures below T<sub>g</sub>, i.e. when the polymer is in the glassy state. ► Activation energies for the hydrolysis rate below and above T<sub>g</sub> were found to be equal to 31 ± 12 and 134 ± 4 kJ/mol respectively. This means that an extrapolation to service temperature must be based on results obtained below T<sub>g</sub>.

**Keywords** : hydrolysis, prediction, non-Arrhenian behaviour, glass transition temperature

## **1. Introduction**

The use of PET, or PolyEthylene Terephthalate, in marine applications has become increasingly common since its first discovery in the 1940s. This is due to its durability and ability to withstand a wide range of temperatures and other environmental conditions. It was initially used to produce synthetic fibres for clothing and other textiles and is now used in

many food packaging applications [1, 2]. Its best-known application today is for plastic bottles but these have proven to be an issue for the environment, due to ocean pollution and microplastic formation [3, 4]. This can be explained by the fact that this material is highly persistent in a marine environment and that its long-term durability can hardly be predicted today. There is indeed a lack of data concerning its long-term behaviour when used in marine applications, more especially at service temperatures, typically between 4 to 35°C in a marine environment.

Despite an extensive literature on PET, there are few lifetime prediction models. Most studies performed on the hydrolysis behaviour of PET in water, i.e. the degradation of PET by water, were focused on aging at high temperatures, typically above 70°C [5, 6]. Based on these studies, activation energies for hydrolysis in the range from 100 to 130 kJ/mol can be found in literature [7-12]. However, it has been pointed out by many researchers that the activation energies determined above the glass transition temperature  $T_g$  cannot be used to extrapolate the behaviour of PET at the service temperatures [6, 13]. The  $T_g$  is indeed a transition point for the polymer, where the amorphous phase is in the rubbery state if the temperature is above  $T_g$  while it is in the glassy state when the temperature is below  $T_g$ . As a result, activation energies determined above the glass transition temperature are not applicable to service temperatures. Therefore, hydrolysis studies performed below the glass transition temperature are needed.

The slow hydrolysis rate of PET makes it difficult to study its degradation in water, as the process can take many years to identify. As a result, such data are quite rare. Back in 1998, Elias et al [14] published an aging study on PET geotextiles for aging durations up to 3.5 years at temperatures below the glass transition. Despite the great interest of such aging studies performed at low aging temperatures, data interpretation is limited because the authors

only considered mechanical properties, i.e. the consequences of aging at the macroscopic scale. Nevertheless, that study is unique and similar work has not been found in the literature. Partly due to this slow degradation rate, the mechanisms and changes associated with the hydrolysis of PET below the glass transition have not been completely understood due to the lack of experimental data. While the consequences of aging above  $T_g$  (chain scission, increase in crystallinity ratio) are now well understood and that models were developed to describe the hydrolysis rates [6, 8], no published work concerning the long-term consequences of hydrolysis below  $T_g$  at the macromolecular scale was found (using direct measurements). Therefore, several questions remain. First, it may be questioned whether chemi-crystallization can occur below  $T_g$ . This process is well known [15, 16] and involves a crystallization process that is triggered by chain scissions above  $T_g$ , i.e. when the polymer chains regain enough mobility to crystallize in the rubbery state. In the case where chain scissions happen below  $T_g$ , can chemi-crystallization take place in the glassy state? There is also a need for further research to determine with more accuracy the long-term durability of PET in water below  $T_g$  and to understand the changes associated with this slow degradation. That is the aim of this paper. Such a study involves long aging durations, here up to 5 and a half years, which provides a rare set of data.

First, the PET material and experimental techniques used in this study are presented. Then, results from physico-chemical characterizations (molar mass, crystallinity ratio, amorphous layer thickness and chain scission concentration) are presented at temperatures above and below the glass transition. Finally, the hydrolysis kinetics have allowed the determination of activation energies below and above  $T_g$ .

## **2. Materials and methods**

### *2.1. Material*

The material used in this work is a Polyethylene terephthalate commonly used in the plastic bottle industry (Ref: Silar 874 C80). It was received in the form of 200  $\mu\text{m}$  thick polymer films obtained by extrusion. The initial crystallinity of this material was 7% but for this study, the polymer was recrystallized in vacuum at 110°C for 30 min. This resulted in a polymer with a stable morphology with a new initial crystallinity of 33%. Following this, the density, initial molar mass and polydispersity index were measured to be equal to 1.37  $\text{g}\cdot\text{cm}^{-3}$ , 35 kg/mol and 2.1, respectively.

## 2.2. Differential Scanning Calorimetry (DSC)

To measure the changes in crystallinity ratio during aging, DSC tests were performed after all aging conditions on Q200 equipment from TA Instruments. Samples of around 10 mg were heated from 0°C up to 300°C at a heating ramp of 10°C/min. The degree of crystallinity  $X_c$  (in %) was then determined based on the measured melting enthalpy  $\Delta H_f$  (in J/g) and the theoretical melting enthalpy for a 100% crystalline PET,  $\Delta H_f^0$ , obtained from literature and equal to 188 J/g [17], Eq.1. For each aging condition, one sample was tested.

$$X_c = \frac{\Delta H_f}{\Delta H_f^0} \times 100 \quad \text{Eq.1}$$

## 2.3. Aging

Aging was performed at different temperatures, ranging from 25°C up to 105°C in oxygen-containing de-ionised water for durations up to 5 and a half years. From 25 up to 90°C, aging was conducted in de-ionised water tanks at atmospheric pressure. However, at temperatures equal or above 100°C, it was performed in pressure vessels at a pressure of 15 bars so that

water remains liquid. After all aging stages, specimens were dried at 40°C in desiccators at a relative humidity of 0%. The dry  $T_g$  was found to be  $84 \pm 1$  °C. However,  $T_g$  after saturation at 25°C in water was measured at  $68 \pm 1$  °C as shown in Figure 1.

As its name suggests, the  $T_g$  is a transition temperature. There are several ways to define the glass transition temperature from DSC [18] such as the  $T_{g \text{ onset}}$  or the  $T_{g \text{ inflection}}$ . Here, the  $T_g$  value of 68°C after water saturation corresponds to the value at the inflection point. However, Figure 1 shows a DSC scan performed on a PET sample fully saturated with water. It is apparent that the transition actually starts at a much earlier stage, i.e. at 58°C and ends at around 75°C. This is important here, as aging studies performed at 60°C within this work are considered to be above  $T_g$ . Further discussion on this will be given later in the paper.

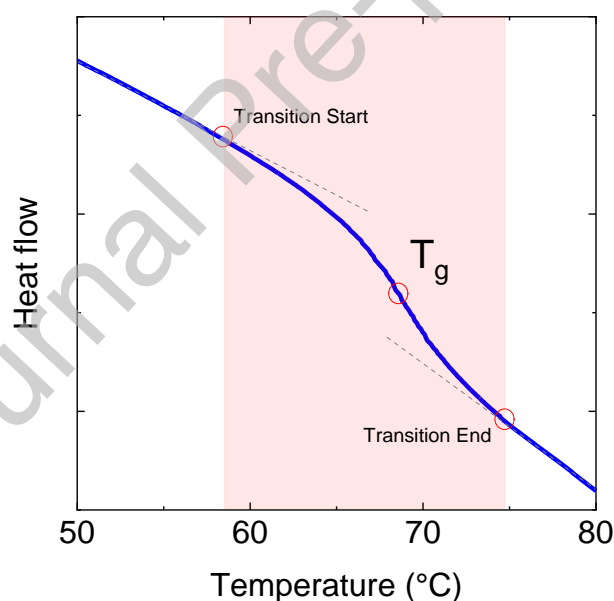


Figure 1: DSC scan - PET saturated with 0.8% of water at 25°C

#### 2.4 SAXS measurements (Small Angle X-ray Scattering)

SAXS measurements were performed on Xeuss 2.0 (Xenocs) apparatus using a Cu K $\alpha$  radiation source with a wavelength  $\lambda$  of 1.54 Å. The distance between the detector and the specimen was 1.5 meters.

Using the SAXS results, the long period  $L_p$  (in nm) was determined based on Bragg's law, Eq.2:

$$L_p = \frac{2\pi}{q_{max}} \quad \text{Eq.2}$$

Where  $q_{max}$  is the maximum correlation peak in nm. Based on the long period calculation, the amorphous layer thickness  $l_a$  and the crystalline layer thickness  $l_c$  can be calculated using Eq. 3 and Eq.4:

$$l_c = X_c \frac{L_p \cdot \rho_a}{\rho_c - X_c(\rho_c - \rho_a)} \quad \text{Eq. 3}$$

$$l_a = L_p - l_c \quad \text{Eq. 4}$$

Where  $\rho_a$  and  $\rho_c$  are the amorphous and crystalline densities, equal to 1.335 g.cm<sup>-3</sup> and 1.445 g.cm<sup>-3</sup>, respectively. One sample was tested per aging condition.

## 2.5. Gel Permeation Chromatography (GPC)

GPC tests were performed by the Peakexpert company located in Tours, France, using the Laun et. al method [19]. Samples of approximately 10 mg were dissolved in 4 mL of hexafluoroisopropanol (HFiP) for 24 hours at room temperature. The GPC calibration was performed using poly(methyl methacrylate) PMMA standards with molar mass ranging from 800 to 1,600,000 g/mol. Average molecular weights are therefore expressed as PMMA equivalents. One sample was tested per aging condition.

Based on molar mass measurements, it is possible to assess the chain scission concentration in the amorphous phase ( $s_{amorphous}$ ) as a function of aging using Eq.5.

$$S_{amorphous} = \frac{1}{1 - X_c} \times \left( \frac{1}{M_n} - \frac{1}{M_{n0}} \right) \quad \text{Eq.5}$$

Where the chain scission concentration is expressed in mol/kg and the molar mass  $M_n$  and initial molar mass  $M_{n0}$  in kg/mol.

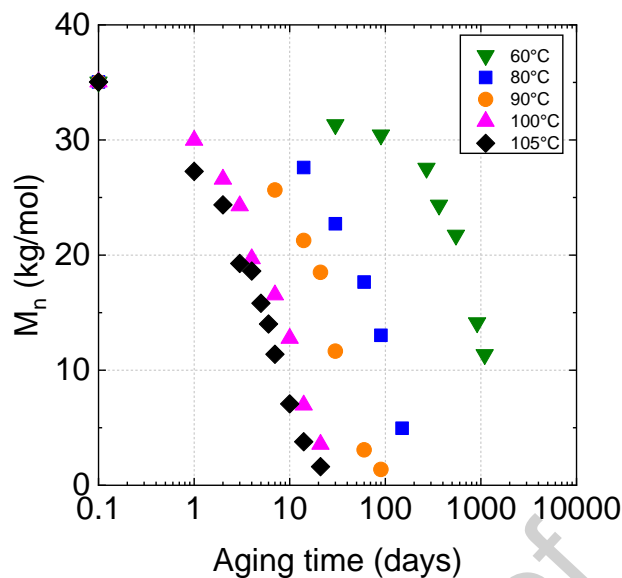
### 3. Results & discussion

First, the behaviour of PET at temperatures above  $T_g$  will be examined. Second, emphasis will be placed on the behaviour of PET at temperatures much closer to the usual service temperature, i.e. below  $T_g$ . Finally, the hydrolytic kinetics obtained above and below  $T_g$  are compared and discussed.

#### 3.1. Consequences of hydrolysis above $T_g$

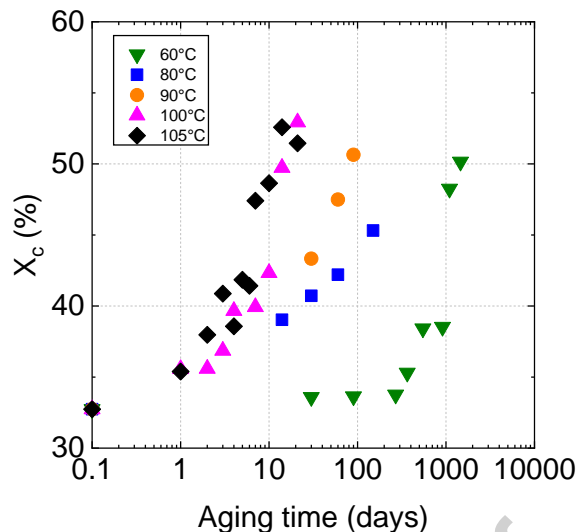
Figure 2 first shows the molar mass as a function of aging time, for aging conditions above  $T_g$ . Independent of the aging temperature, a significant decrease in molar mass is observed and the lower the temperature, the slower the decrease in molar mass. Such a result is common and has been discussed previously [12, 20, 21]. Hydrolysis indeed leads to chain scission within the amorphous phase of the polymer, involving a decrease of the molar mass. It may be noted that no changes in polydispersity index were measured during aging.





**Figure 2: Effect of aging on molar mass above  $T_g$**

The effect of aging on the degree of crystallinity is now presented in Figure 3. For all temperatures investigated, an increase in crystallinity is observed. This phenomenon is, again, known from the literature [12] and is associated with the so called chemi-crystallization process. In the case observed here, chain scission takes place when the amorphous phase of the polymer is in the rubbery state ( $T > T_g$ ), meaning that the amorphous polymer chains are mobile. This mobility, coupled with the broken polymer chains, allows for the creation of new crystallites, leading to an increase of the degree of crystallinity, as observed on Figure 3.

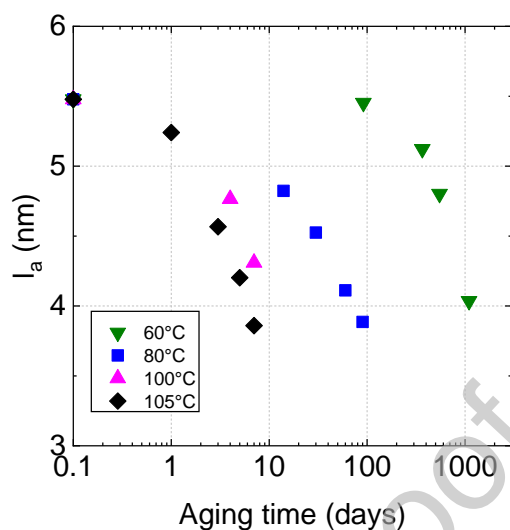


**Figure 3: Effect of aging on crystallinity above  $T_g$**

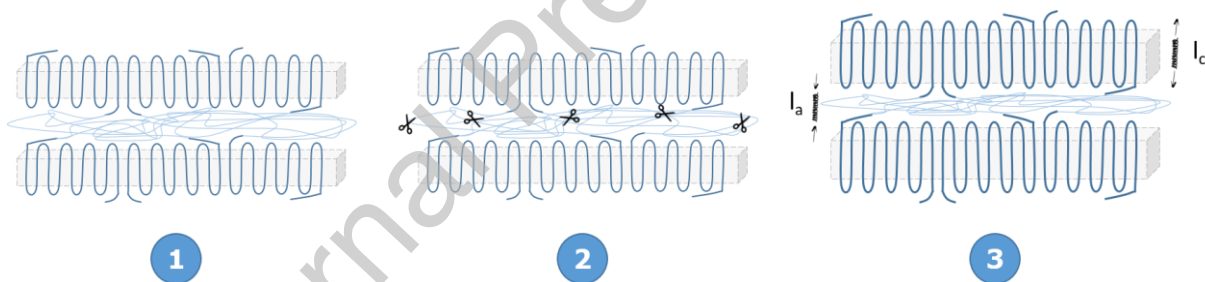
Figure 4 shows the change in amorphous layer thickness as a function of aging time. For all temperatures, a decrease is observed. Here again, this phenomenon is related to the chemi-crystallization process. To better understand this, Figure 5 provides a diagram explaining the different stages leading to chemi-crystallization. At first (1), the unaged polymer has a given chain length  $M_n$  and a degree of crystallinity  $X_c$ . When the polymer is then immersed in water (2), the polymer chains are shortened due to hydrolysis (represented here with scissors on the diagram). Due to this, the regained mobility of the polymer chains allows a reorganization and new crystallites can be created (3). Actually, the initial crystallites strengthen themselves, which induces a thickening of the initial crystallite and therefore a decrease of the amorphous layer thickness (represented on the diagram).

It may also be noted that in this work, a two-phase system was assumed with a semi-crystalline and an amorphous phase. However, it has been demonstrated that PET actually follows a three phase system [22-24], where the amorphous phase actually contains a rigid and a mobile phase. Nonetheless, this does not change the amorphous layer thickness

determined here, but is an interesting parameter to be followed in future work, more especially when considering the mechanical behavior of the polymer.

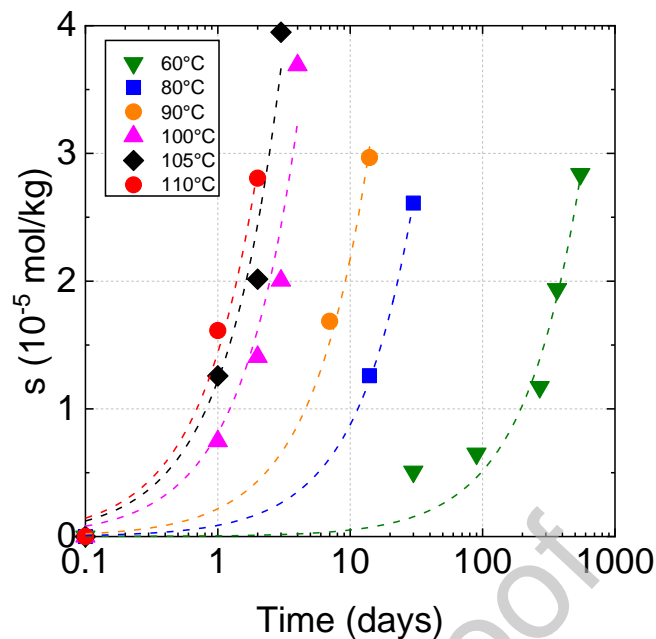


**Figure 4: Effect of aging on amorphous layer thickness above  $T_g$**



**Figure 5: Diagram representing the chemi-crystallization process in the rubbery state**  
**(1) Unaged semi-crystalline polymer with the representation of its two phases: crystalline phase and amorphous phase**  
**(2) Hydrolysis leads to chain scission in the amorphous layer**  
**(3) Chain scission provides additional mobility to polymer chains which induces an increase of  $X_c$  and a decrease of  $l_a$**

Based on these physico-chemical changes induced by aging at high temperatures, it is possible to calculate the chain scission concentration based on Eq. 5. Results are shown in Figure 6. It is observed that whatever the aging temperature, an increase in chain scission concentration is observed. Also, the changes in chain scission concentration as a function of aging time appear linear (a linear fitting curve was indeed used in Figure 6 despite the x-axis being represented on a log scale).



**Figure 6: Effect of aging on chain scissions above  $T_g$  – Dotted lines represent a linear fit**

To summarize, the hydrolysis of PET at high temperatures induces:

- A loss in the molar mass induced by an increase in chains scission concentration
- An increase in the degree of crystallinity
- A decrease in the amorphous layer thickness

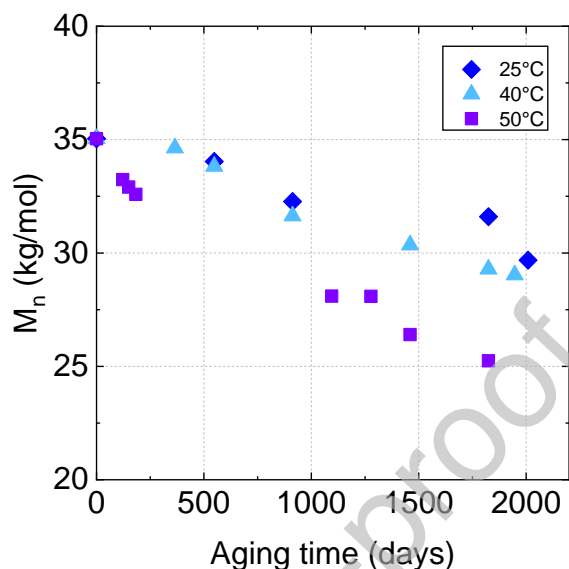
It may be noted that these results are similar to existing published results [12, 20].

### 3.2. Consequences of hydrolysis below $T_g$

Now that the consequences of hydrolysis at high temperatures have been presented, we will focus on hydrolysis at low temperatures, i.e. below  $T_g$ . It should be underlined that these results were obtained over an aging period of 5 and a half years, making them quite unique.

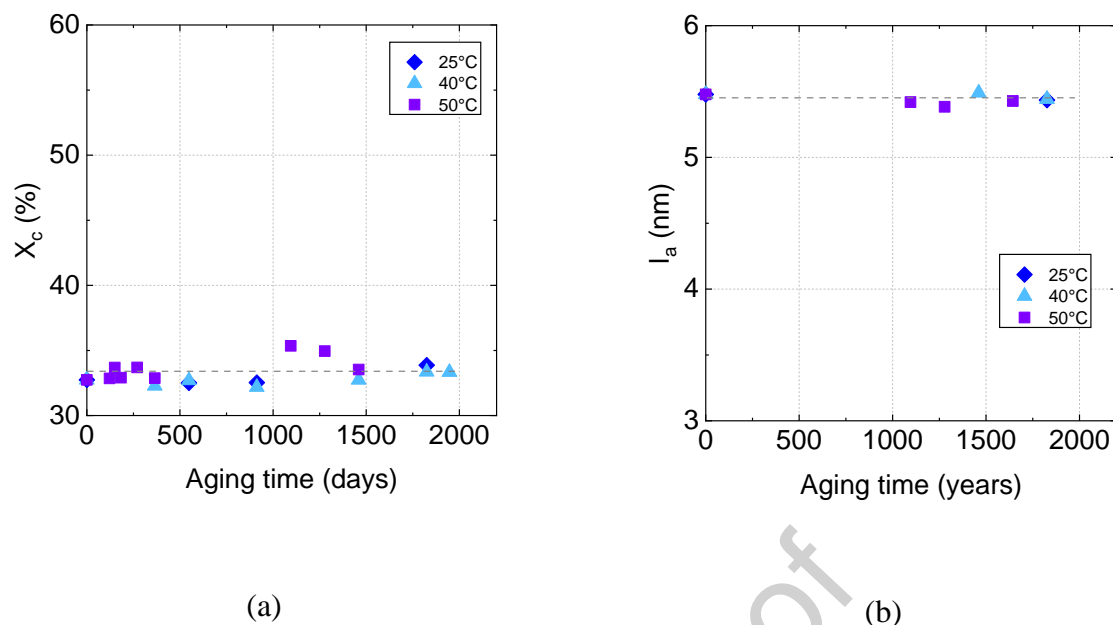
First, the changes in molar mass as a function of aging time are shown in Figure 7. A decrease in the molar mass is observed, however, at a much slower rate than that observed at high temperatures. While it takes less than two weeks to reach a molar mass below 30 kg/mol at

80°C, it takes about 5 years to reach the same molar mass value at 40°C. However, a decrease in molar mass is observed even when PET is immersed at low temperatures, as demonstrated by Figure 7.



**Figure 7: Effect of aging on molar mass below  $T_g$**

An interesting question can now be raised. Can chemi-crystallization take place when the polymer is in the glassy state? To answer this, Figure 8.a and Figure 8.b provide results concerning the degree of crystallinity and amorphous layer thickness as a function of aging time at low temperatures, respectively. For ease of understanding, the y-scales used in these two figures are similar to those used in the previous section, i.e. for aging conditions above  $T_g$ . For both figures, no changes are observed over the aging duration investigated here, despite the loss in molar mass shown in Figure 7. To fully conclude on the existence of chemi-crystallization in the glassy state, longer aging durations are needed. However, based on the results shown here, i.e. after aging in water for 5 years, chemi-crystallization does not seem to happen. This may be explained by the fact that the shortened amorphous polymer chains are not mobile in the glassy state, which does not allow a rearrangement of the crystalline phase.

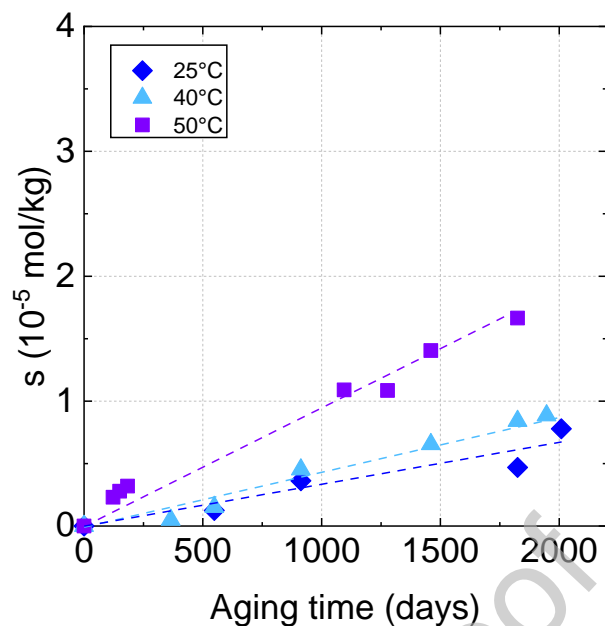


**Figure 8: Effect of aging below  $T_g$  on (a) degree of crystallinity (b) amorphous layer thickness**

Similarly to the calculation performed at high temperatures, the chain scission concentration at low temperatures is presented in Figure 9 as a function of aging time. It is observed that the chain scission concentration increases linearly for the three temperatures investigated and that again, the higher the temperature, the faster the rate of chain scissions.

To conclude on the consequences of hydrolysis at low temperatures, it is observed that:

- There is a decrease in molar mass during aging below  $T_g$ . However, the hydrolysis rate is much slower than above  $T_g$ .
- No changes in degree of crystallinity and amorphous layer thickness were observed over the 5-year aging study.

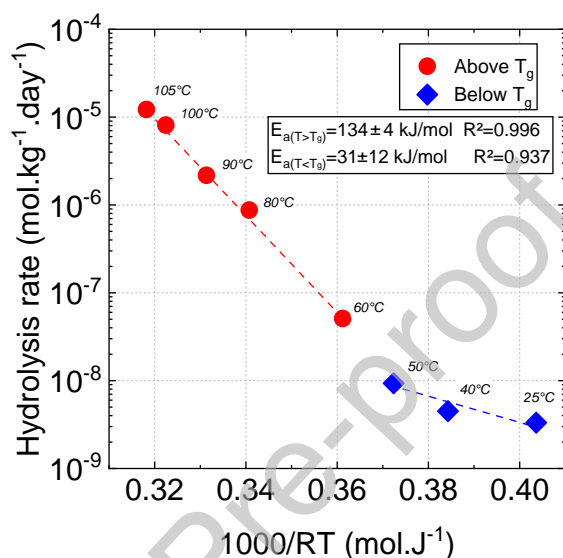


**Figure 9: Effect of aging on chain scissions below  $T_g$**

### 3.3. Non-Arrhenian hydrolysis

The previous sections demonstrated that the consequences of hydrolysis were different when the polymer evolves at temperatures above and below  $T_g$ . While chain scissions can happen whatever the aging temperature, no chemi-crystallization was observed below  $T_g$ . Based on Figure 6 and Figure 9, the hydrolysis rate  $K$  can be determined based on the slope of  $s_{\text{amorphous}}=f(\text{aging time})$ . To try and explain this, Figure 10 shows  $K$  as a function of  $1000/RT$ , to investigate whether the hydrolysis rate follows the Arrhenius law below and above  $T_g$ . It is observed that a single linear curve is not observed, which demonstrates that the hydrolysis rate in PET does not follow the Arrhenius law. Actually, a change in slope is identified at a temperature between  $60^\circ\text{C}$  and  $40^\circ\text{C}$ . This is consistent with the fact that aging at  $60^\circ\text{C}$  can be considered as being above  $T_g$ . Chemi-crystallization was indeed observed at  $60^\circ\text{C}$  because it was not below  $T_g$ . However, it may be noted that the point at  $50^\circ\text{C}$  lies nicely on the linear fit above  $T_g$ , so it again raises questions concerning the range of  $T_g$ . As stated in section 2.2 and

2.3,  $T_g$  was determined at  $10^\circ\text{C}/\text{min}$  the transition begins as low as  $58^\circ\text{C}$ . However, Langevin et al [25] showed that the value of  $T_g$  is highly dependent of the heating rate. They were able to show that when the heating ramp is divided by 10 (from 20 K/min down to 2.5 K/min), a change in  $T_g$  of  $10^\circ\text{C}$  was witnessed. So in our case, it is possible that the glass transition starts at an even lower value than  $58^\circ\text{C}$ .



**Figure 10: Temperature dependence of hydrolysis rate determined from Figure 6 and Figure 9**

Nevertheless, based on these two linear plots above and below  $T_g$  shown in Figure 10, the two activation energies  $E_a$  can be determined and are respectively equal to  $134 \pm 4$  kJ/mol and  $31 \pm 12$  kJ/mol. This is evidence that the hydrolysis rate in PET does not follow the Arrhenius law. The non-Arrhenius behaviour of polymers subjected to oxidative aging has already been described in the literature for polymers such as Polyethylene [26, 27], Polypropylene [28], PA6.6 [29] and elastomers [30, 31]. However, fewer results are available concerning hydrolysis. The activation energy above  $T_g$  is in the range of published values, between 100-130 kJ/mol [7-12].



A change in  $E_a$  below  $T_g$  was also witnessed by White et al. [32], where they performed a study on PET films aged at temperatures ranging from 90 to 40°C at 95% relative humidity. By measuring the drops using an indirect method (i.e. intrinsic viscosity), they were able to show a discontinuity in the Arrhenius plot around  $T_g$ , where an activation energy of  $126 \pm 13$  kJ/mol was found above  $T_g$  and of  $54 \pm 17$  kJ/mol below  $T_g$ .

Elias et al [14] performed an aging study over a 3-year period on PET geotextiles immersed in distilled water at pH=7 at temperatures ranging from 50 to 80°C. The degradation due to hydrolysis was highlighted by the loss in tensile strength observed on their PET geotextiles. Based on these results, they were able to show that the activation energy below  $T_g$  was indeed lower than that observed above  $T_g$  with a measured value of 79 kJ/mol. However, this value is higher than the one found in this work. Three main reasons can explain this. First, their study was performed on PET geotextiles, which are different from the PET films used here as the polymer is drawn. Second, this value is based on changes in mechanical behaviour and more especially the stress at break, that is a consequence of the hydrolysis at the macroscopic scale (and there is no evidence that changes in the mechanical behaviour are the same above and below  $T_g$  especially due to the increase in crystallinity during aging). Third, this value was obtained at temperatures between 50 and 80°C. The  $T_g$  of their PET was 80°C and it is not specified whether this value was obtained in the dry state or when the geotextiles were fully saturated with water. If obtained in the dry state, the  $T_g$  would drop when the polymer is fully saturated with water and the geotextile would surely be in the rubbery state at 80°C. If obtained after water saturation, there is also a chance that the polymer would be in the rubbery state since the  $T_g$  represents a transition range and not a discrete value, as demonstrated by the results of this work.

Nonetheless, they were able to demonstrate that the activation energy was different at low temperatures based on mechanical considerations (tensile strength). In our work, based on

physico-chemical considerations, it was also demonstrated that the activation energies were different above and below  $T_g$ . These results confirm that the hydrolysis rate of PET does not follow the Arrhenius law.

Based on results obtained above  $T_g$ , an activation energy of hydrolysis is 134 kJ/mol was found. In literature, this value is usually used to extrapolate hydrolysis rate at 25°C (here, for PET, the value would be  $1.3 \cdot 10^{-10}$  L/mol/day). In reality, the actual hydrolysis rate was measured in this study to be equal to  $3.3 \cdot 10^{-9}$  L/mol/day, i.e. a value that is 26 times faster. This difference is explained by the fact that aging is performed below  $T_g$ . This highlights a difficulty to make lifetime predictions based on results obtained above  $T_g$  of the polymer. Finally, based on the literature, it may be of interest to clarify the definition of non-Arrhenius behaviour. While the overall reaction rate may not appear to follow an Arrhenius behaviour due to the influence of multiple competing processes, each of these individual processes may still exhibit an Arrhenius behaviour. At the macroscopic scale, it is possible that the combined effects of these processes lead to non-Arrhenius behaviour, but each individual process can still be described by a single linear Arrhenius function. In polymer aging, curved behaviour is often observed and associated with non-Arrhenius behaviour, but this may not be correct if both processes involved can be described by a single linear function. In fact, the sum of two linear functions results in their combined curvature, so great care must be taken. In this work, additional data precision may be needed to fully determine whether the observed behaviour is non-Arrhenius or simply the sum of two linear Arrhenius plots. Further investigation is required to address this aspect.

#### 4. Conclusion

In this paper, the long-term behaviour of PET films in water was studied over a 5-year period at different temperatures, ranging from 25 to 105°C. Whatever the aging temperature, a drop in the molar mass was observed and associated with the hydrolysis of the amorphous phase of the studied PET. Then, while chemi-crystallization was clearly observed at temperatures above  $T_g$ , no changes in either the degree of crystallinity or the amorphous layer thickness were witnessed below  $T_g$ . Based on these results, it was possible to determine the chain scissions concentration and hydrolysis rates for all the temperatures investigated in this work. It was shown that the activation energies below and above  $T_g$  were significantly different, with a value above  $T_g$  of 134 kJ/mol and below  $T_g$  of 31 kJ/mol. This new result will allow reliable prediction of the hydrolysis rate at service temperature and more especially lifetime prediction of PET in the framework of microplastic formation. Future work will now focus on the effects of hydrolysis on the mechanical behaviour of PET below  $T_g$ . More especially, it will be interesting to investigate whether embrittlement occurs at the same molar mass as above  $T_g$  and to clarify the role of chemi-crystallization on embrittlement. Further work is also needed to explain the decrease in activation below  $T_g$ . To do so, experiments with different aging medium (humidity, NaOH...) will be performed to try and answer this open question.

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## Credit Author Statement

Mael Arhant : Conceptualization, Methodology, Investigation, Writing, Review & Editing

Maelenn Le Gall : Conceptualization, Methodology, Investigation, Writing, Review & Editing

Pierre-Yves Le Gac : Conceptualization, Methodology, Investigation, Writing, Review & Editing

**Declaration of interests**

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

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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