Hydrolytic degradation of biodegradable poly(butylene adipate-co-terephthalate) (PBAT) - Towards an understanding of microplastics fragmentation

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Abstract :

The long-term behaviour of PBAT subjected to hydrolytic ageing is investigated in this paper. Samples were aged in water at several temperatures ranging from 80 to 100°C for different durations. Changes in physico-chemical properties were investigated through NMR, GPC, DSC and X-Ray analyses and embrittlement was assessed by tensile tests. It is demonstrated that hydrolysis of PBAT occurs first on the ester group located between the terephthalate and adipate groups leading to a decrease in molar mass. For longer ageing durations, the ester situated within the adipate group undergoes hydrolysis. An increase in crystallinity ratio and a decrease in amorphous layer thickness was observed as consequences of the chain scission process. Finally, a clear change in mechanical behaviour is noted; for the early stages of ageing, the polymer exhibits a ductile behaviour while for longer ageing durations, the polymer is brittle due to a lack of chain entanglement. This transition takes place once the molar mass of PBAT falls below 11 kg/mol, i.e. when a critical molar mass M'c is reached.

Highlights

► Hydrolysis of PBAT occurs mainly on the ester situated between the terephthalate and adipate groups ► Activation energy of the PBAT hydrolysis is 70kJ/mol ► The change from ductile to brittle behaviour due to hydrolysis can be described by a critical molar mass equal to 11 kg/mol

1. Introduction

Over the last century, polymers completely revolutionised industry due to their ease of processability and strength to weight-ratio as compared to metals. They are now found in all applications, from high performance structures to simple packageing. However, the mass production of single-use plastic is now an issue, as approximately 5 to 12 million of tons of plastics are found every year in the oceans [1-4]. The polymers commonly used, i.e. polypropylene (PP), polyethylene (PE), polyethylene terephthalate (PET), are petrosourced and their lifetime in the oceans greatly exceeds their original use. To try to fix this issue of ocean pollution by plastics, new polymers are now being investigated such as biosourced (polyhydroxyalkanoate (PHA), polylactic acid (PLA)) or biodegradable (poly(butylene adipate-co-terephthalate) (PBAT), polybutylene succinate (PBS)) materials which are designed to last in the oceans for a much shorter time. However, one issue being raised nowadays is the formation of microplastics due to fragmentation. While many studies point out this issue, little work is available concerning the understanding of the phenomenon in water. More especially, one question must be raised, do these new generation of material produce less microplastics ? To answer this question, studies on the ageing behaviour of these new polymers need to be performed.

The present study focuses on PBAT, a petrosourced biodegradable polyester-based polymer mostly used for compostable plastic bags in agriculture [5, 6]. While this material has proved to be compostable [7] [8] [9], its behaviour in contact with water is not yet completely understood. Indeed, it has been highlighted in the past that PBAT undergoes hydrolysis [10] [5] [11] [12] [13], however, degradation pathways are still unclear. PBAT has 3 types of esters within its carbon backbone meaning that hydrolysis can occur at 3 different positions. Ferreira et al suggested that hydrolysis mainly takes places on the ester bond located between the terephthalate and the adipate groups but without any clear evidence [5]. Moreover, the impact of chain scissions induced by hydrolysis on the polymer morphology and mechanical properties has not been considered in detail up to now, despite its importance in the secondary microplastics formation. In fact, to understand the mechanisms associated with polymer fragmentation, it is essential to consider the changes in mechanical behavior with time. More especially, it is hypothesised that microplastics are created by fragmentation once the polymer is brittle [14].

Despite the lack of knowledge on the impact of PBAT hydrolysis on its mechanical behavior, it is well known that chain scission induced by chemical degradation in linear polymers leads to an embrittlement of the material, i.e. the material changes from a ductile behavior to a brittle one upon ageing [15] [16] [17]. This embrittlement is usually due to a loss of entanglements within the polymer. In other words there exists a critical molar mass, named M'_c, for which the entanglement is no longer sufficient to ensure stress transfer between amorphous and crystalline phases [18]. This value has been determined in many polymers such as PET [19] [20] [21] [22], PA [23] [24] and is usually close to $5xM_e$ with M_e the molar mass between entanglements. In other words, a critical average number of

entanglements per chain of 4 is required to ensure a stress transfer between the amorphous and crystalline phases in the material.

A more complex behavior is observed with PP and PE where embrittlement is explained by a decrease in the amorphous phase layer due to a decrease in molar mass [25] [26] [27]. Moreover, it should be mentioned here that because PBAT is a copolymer with 3 distinct esters groups available, in contrast to most existing work on polymer degradation, hydrolysis cannot be considered as a random reaction. Considering PBAT hydrolysis, remaining questions are related to the degradation pathways and the existence of a preferential position for the chain scission within the polymer. Moreover, what are the consequences of theses chain scissions at the macromolecular scale and on the mechanical behavior of this biodegradable polymer ? These points will be considered in this study.

First, a presentation of the material and characterization techniques are proposed. Second, the changes in physico-chemical and mechanical properties induced by ageing will be exposed and discussed. Finally, the results from tensile tests are directly linked with the molar mass results to highlight the change from ductile to brittle behaviour through the identification of the critical molar mass M'_c for PBAT.

2. Material and methods

2.1. Material

The material of interest here is a Polybutylene Adipate terephthalate (PBAT) purchased from BASF Industry under the brand Ecoflex, F Blend 1200. The chemical structure of the polymer is shown in Figure 1. It is a petrosourced copolymer made from a mix of Polybutyl Acrylate (PBA) and Polybutylene Terephtalate (PBT). Polymer films of 300 µm thickness were obtained by press forming on a Carver press at a temperature of 160°C and a pressure of 9 bar at the University of Mons. Prior to manufacture, PBAT granules were dried at 60°C. Samples are thin enough to ensure that hydrolysis is not limited by water diffusion meaning that degradation is homogenenous through sample thickness. The initial properties of PBAT after manufacture are given in Table 1.
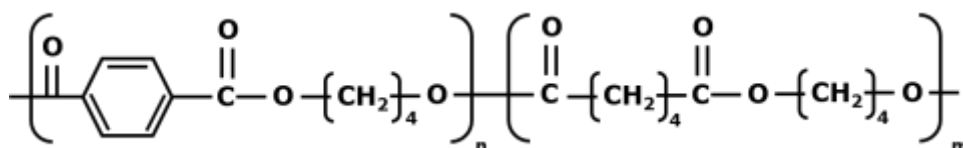

Figure 1 – Chemical structure of PBAT

4

Property	Value
Thickness (μm)	300
ρ (g.cm^3)	1.24
M_n (kg/mol)	46
X_c (%)	10

Table 1: Initial properties of PBAT measured in this study

2.2. Ageing

Ageing was performed at three different temperatures respectively from 80, 90 and 100 °C in oxygen-free deionised water in order to prevent any oxidation of the polymer as described in [28]. Ageing temperature is +/-2°C. To do so, pressure vessels were used at 10 bars to perform the ageing experiments and oxygen was removed through nitrogen bubbling for 3 hours. We have taken great care not to contaminate the water in the pressure vessels during aging by using a very low sample/water volume ratio (5.10^{-4} maximum) and by measuring the pH at the end of aging, which remains unchanged for all conditions considered here. All samples were dried in desiccators at 0% humidity after ageing at 40°C in a dessicator at 0%RH for at least 48 hours.

2.4. NMR

^{1}H NMR spectra of native and degraded PBAT in solution were performed on a Bruker Avance III HD spectrometer equipped with an inverse TCI ^{1}H/^{13}C/^{15}N cryoprobe. The spectra were recorded using a 30° pulse angle, 16 scans and a sweep width of 7500Hz. The acquisition time and recycle delay were 2.18s and 5s respectively. The raw data were apodized using an exponential line broadening of 0.3Hz prior to Fourier transformation. Chemical shifts are expressed in ppm relative to CDCl$_3$ used as reference and solvent

2.5. Gel Permeation Chromatography (GPC)

Size exclusion chromatography (SEC) was performed in CHCl3 at 30 °C using an Agilent liquid chromatograph equipped with an Agilent degasser, an isocratic HPLC pump (flow rate = 1 mL/min), an Agilent autosampler (loop volume = 100 μL, solution conc. = 1 mg/mL), an Agilent-DRI refractive index detector and three columns: a PL gel 10 μm guard column and two PL gel Mixed-D 10 μm columns (linear columns for separation of MWPS ranging from 500 to 107g/mol). Calibration was performed using polystyrene standards and samples were dissolved in

5

chloroform. Using the results from this characterization technique, it is possible to obtain the chain scission concentration in the amorphous phase after ageing using Eq.1:

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

Where M_n is the average molar mass in number, M_{n0} the initial average molar mass in number and X_c the crystallinity ratio, see [18] and [28] for details.

2.6. Differential Scanning Calorimetry (DSC)

The crystallinity ratio X_c was determined by DSC using Q200 equipment from TA Instrument. Samples of about 10 mg were heated up to 200°C at a rate of 10°C/min under a nitrogen flux. The crystallinity ratio χ_c was then calculated using Equation 2.

$$\chi_c = \frac{\Delta H_f}{\Delta H_f^0} \times 100$$
Eq.2

Where ΔH_f is the measured enthalpy and ΔH_f^0 the enthalpy of a 100% crystalline PBAT, equal to 114 J/g [29].

2.7. X-Ray measurments

Wide angle X-Ray scattering (WAXS) and Small-angle X-ray scattering (SAXS) were performed using a Xeuss 2.0 apparatus (Xenocs) equipped with a Cu Kα radiation micro source (λ=1.54 Å). The distance between the specimen and the detector was 12 cm for WAXS and 1.5 m for SAXS). The system was calibrated using silver behenate and diffraction patterns were recorded on a Pilatus 200k detector. The integrated intensity profiles were computed from the 2D patterns using the Foxtrot software. Standard corrections (i.e. background substraction, dark current removal…) were applied to patterns before their analysis.

From these patterns, the long period L_p was determined using Eq. 3 according to Bragg's law:

$$L_p = \frac{2\pi}{q_{max}}$$
Eq.3

Where L_p is the long period expressed in nm and q_{max} the maximum correlation peak also expressed in nm. From this measurement, the amorphous layer thickness l_a can be calculated using Eq. 4 and Eq.5.

$$l_a = L_p - l_c$$
Eq.4

$$l_c = X_c \frac{L_p \rho_a}{\rho_c - X_c(\rho_c - \rho_a)}$$
Eq.5

6

Where l_c is the crystalline layer thickness. ρ_a and ρ_c are the amourphous and cryustalline densities and are respectively equal to 1.23 g.cm^{-3} and 1.36 g.cm^{-3} [30].

2.8. Tensile tests

Tensile tests were performed on H3 dog-bone specimens (test length is 10mm and width is 4 mm) on a universal Instron testing machine 5966 using a 500 N load cell at room temperature, with a crosshead speed of 2 mm/min. During the tests, strain was recorded with a video extensometer (AVE2). Prior to testing, all samples were dried in dessciators at 40°C and 0% humidity for at least 48 hours. Three specimens were tested for each condition.

3. Results & discussion

3.1. Nature of the degradation at the molecular scale

PBAT is a polymer with three types of ester as shown in Figure 1. These three esters can undergo hydrolysis when the material is in contact with water. It is thus a question here, initially, of clarifying the nature of the hydrolytic degradation of the polymer. For this purpose, NMR analyses were performed on PBAT before and after ageing at 100°C for several durations. Let us first focus on the results related to the unaged sample presented in Figure 2. A detailed attribution of the different peaks is available in [10]: the peaks located at 8.09 ppm and 2.33 ppm are attributed to aromatic groups in terephthalate and -OCOCH$_2$- in adipate groups respectively. By peak integration, it is thus possible to assess the molar fraction n and m values presented in Figure 1 respectively equal to 0.46 and 0.54.
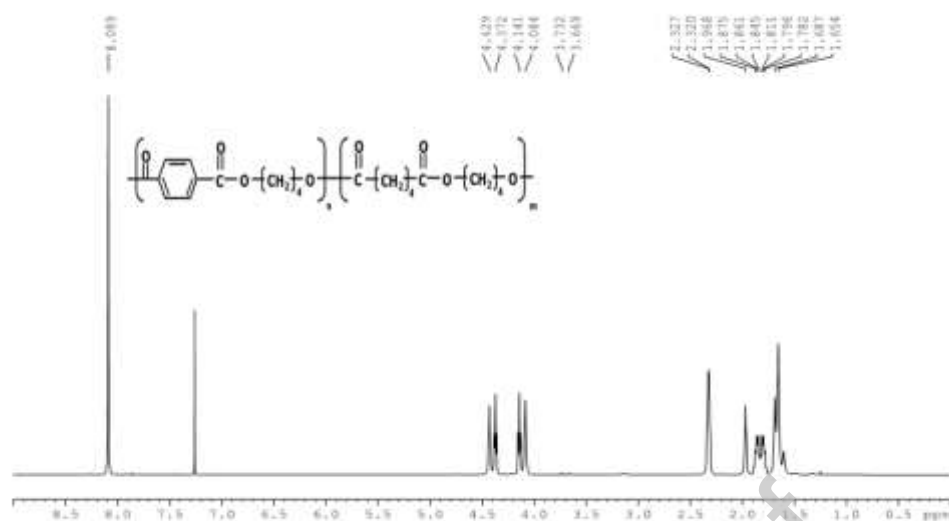
Figure 2 – ^{1}H NMR spectra of unaged PBAT used in this study.

During hydrolytic ageing, changes in NMR spectrum are observed, Figure 3. A first observation is that ageing leads to the formation of two new triplets as noted at 3.6 and 3.7 ppm in Figure 2. These new peaks can be attributed to the formation of -CH$_2$OH groups respectively attached to terephthalate and adipate groups [[10]. This suggests that for up to 5 days of ageing, chain scission occurs mainly on the ester bond located between the terephthalate and the adipate groups. For longer ageing durations (from 6 to 14 days) a new peak located at 2.33 ppm is also appeared during ageing. This new peak can be attributed to CH2-COOH groups [10]. This indicates that the ester located within the adipate group also undergoes hydrolysis but only for a high level of degradation (see below).
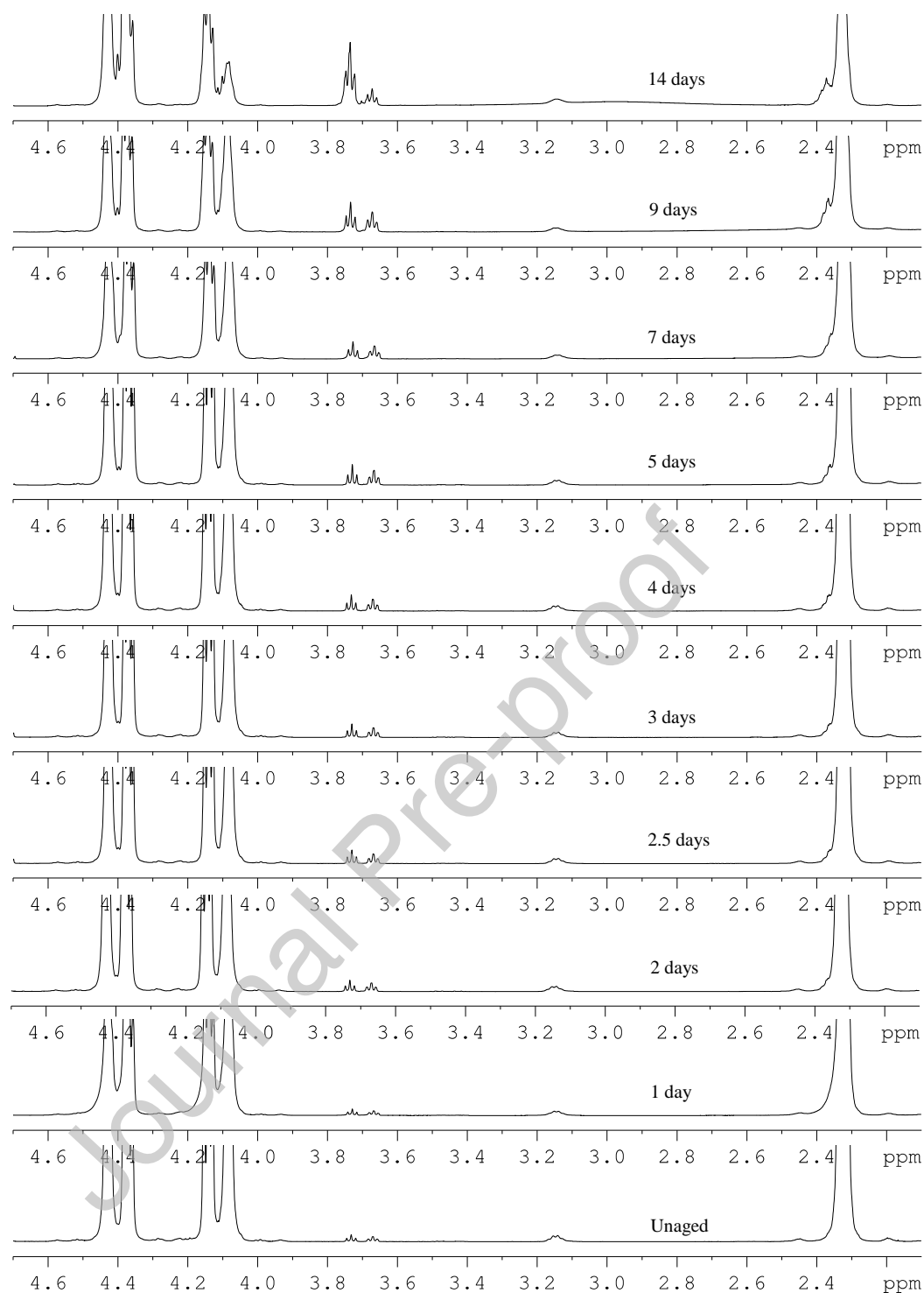
Figure 3 – ¹H NMR spectrum of PBAT as function of ageing duration at 100°C in water. Ageing duration is specified on each spectra)

Based on NMR results it has thus been demonstrated that hydrolysis occurs first on the ester located between the terephthalate and the adipate groups. Then for high levels of degradation the ester situated within the adipate group undergoes hydrolysis. The next section is devoted to changes induced by hydrolysis at the macromolecular scale.

9

3.2. *Impact of hydrolysis at the macromolecular scale*

It is well known that hydrolysis leads to chain scission in polymers, the average number molar mass of PBAT will be then investigated. Moreover, in semicrystalline polymers, chain scission can lead to changes in the crystalline structure, so this point will be considered based on both X-Ray and DSC analyses.

3.2.1. *Effect of ageing on molar mass*

The average molar mass of PBAT before and after ageing was measured by GPC for all temperatures investigated within this study. Results are presented in Figure 4 and show that for all temperatures, a clear decrease in molar mass occurs. Indeed, on Figure 4.a, a shift from lower towards higher retention time is observed with ageing at 100°C and this is directly related to a decrease in molar mass. On Figure 4.b, at 100°C, the molar mass decreases from 46 kg/mol down to values below 3 kg/mol after 10 days of ageing. This decrease in M_n is due to chain scission within the polymer that occurs for all the ageing temperatures considered here due to hydrolysis. As expected, an increase in ageing temperature leads to a faster decrease in the average molar mass value. It is worth noting that the M_n value appears to reach a plateau for long ageing durations at a very low value of Mn (3 kg/mol). This suggests that the reversible hydrolysis reaction (saponification) may be neglected for PBAT, which is in accordance with existing knowledge on polyester hydrolysis [21]. In the meantime, it appears that polydispersity index (PDI) remains almost constant during ageing with a value close to 3. As only chain scission occurs during hydrolysis large changes in PDI were not expected.
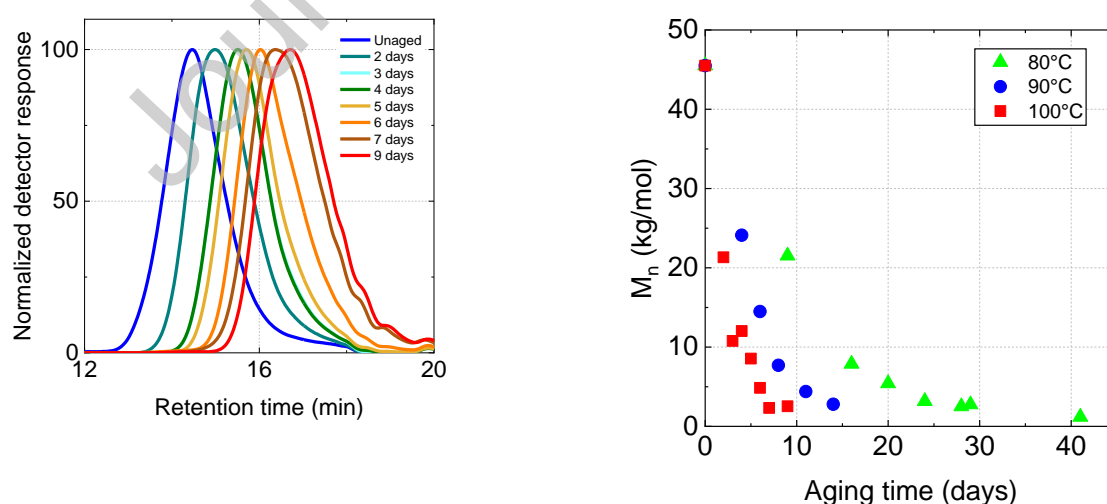

Figure 4 – (a) Changes in GPC retention time as a function of ageing at 100°C (b) Decrease in M_n as a function of ageing time at 100, 90 and 80°C

It clearly appears that the hydrolysis of PBAT highlighted in the previous section leads to chain scission within the polymer; this behavior is in accordance with existing knowledge. Furthemore, it is interesting to recall that for up to 5 days of ageing at 100°C, PBAT hydrolysis induces chain scission mainly located on the ester bond situated between the terephthalate and the adipate groups. This reaction is thus responsible for the large decrease in M_n from 46 to 5 kg/mol (that corresponds to about 20 repetition of monomers) and is probably the main reaction to consider for the description of the drop in mechanical properties (see below). Let us now consider the impact of hydrolysis on the crystalline phase.

3.2.2 Effect of ageing on crystallinity

- *Crystallinity ratio*

During the hydrolysis of PBAT at 100°C, changes in thermal properties are noted, particularly concerning the melting peak that is typical of the crystalline phase, as shown in Figure 5.a. It is observed that the longer the ageing duration the broader the melting peak due to an increase in crystallinity ratio. This behaviour can be explained by the well know chemi-crystallization process that can be described as follows: due to chain scission (as seen in section 3.2), an increase in macromolecular mobility occurs. This allows for the smaller chains to be included within the crystalline phase, which induces an increase in crystallinity ratio. This increase has been oberved at all the temperatures investigated within this study, Figure 5.b. For all temperatures considered in this study, an increase is indeed noticed.
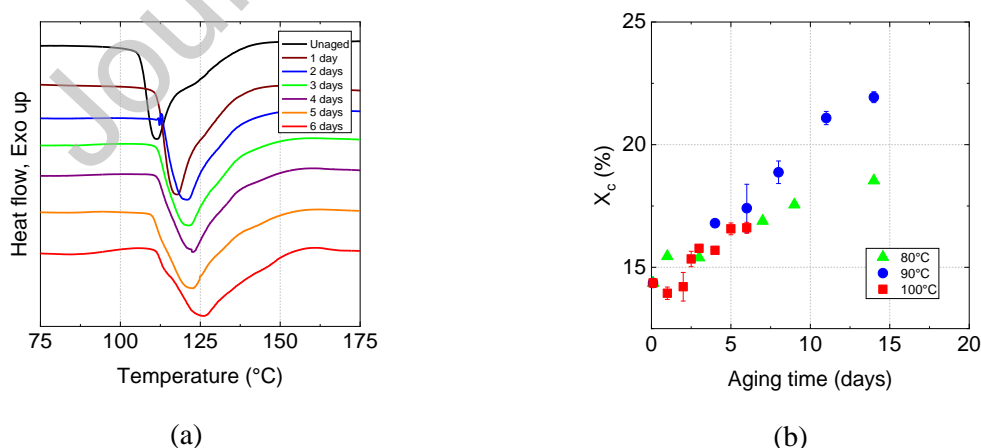

(a)   (b)

Figure 5 – DSC curves for various ageing durations at 100°C in water (a) Change in X_c as a function of ageing time at 100, 90 and 80°C

It clearly appears here that hydrolysis in PBAT leads to an increase in crystallinity ratio within the polymer. The remaining question now is how hydrolysis affects the nature of the crystalline phase.

- Nature of the crystalline phase

It was previously shown that there is an increase in crystallinity ratio with ageing, it is now of particular interest to investigate whether a change in crystalline phases occurs. To do so, WAXS patterns are first plotted in Figure 6 for different ageing durations at 100°C. The positions of the peaks are the same as the ones encountered in the case of PBT homopolymer [31] which indicates that only the PBT sequences crystallize in this material.

Based on WAXS patterns it appears that the nature of the crystalline phase is not affected by hydrolysis at 100°C.
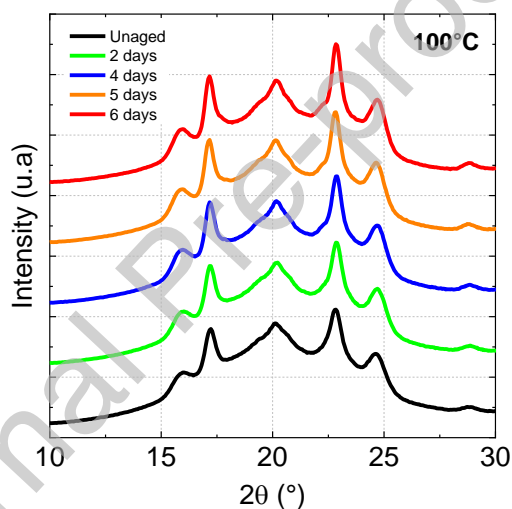

Figure 6 – Effect of ageing on the WAXS pattern at 100°C

Then, the amorphous layer thickness was determined based on SAXS measurements, results are presented in Figure 7. It is observed that l_a remains constant during the early stages of ageing (up to 3 days). For longer ageing durations, l_a decreases with ageing time. This decrease is due to the chemi-crystallization process that occurs during PBAT hydrolysis. As L_p remains roughly constant during the hydrolysis process, the decrease of l_a corresponds to an increase of l_c which can be interpreted as a lamellar thickening.
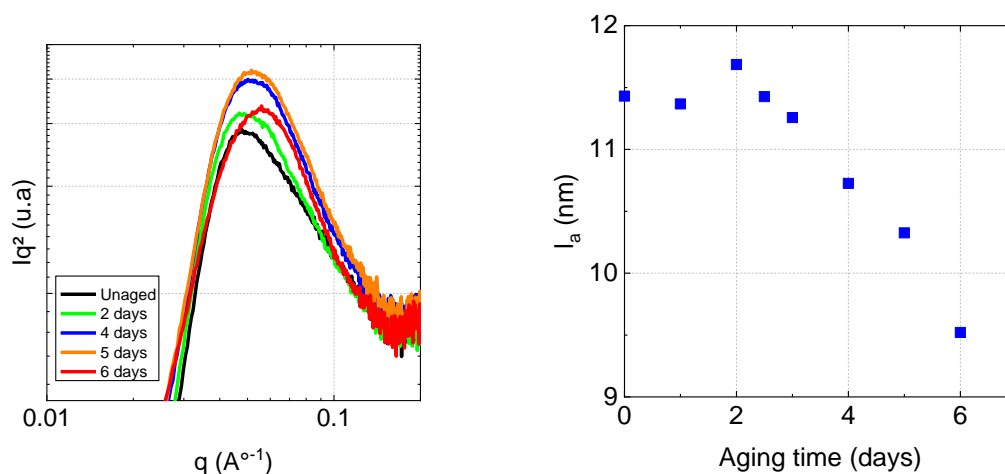
12

Figure 7 – Changes in the amorphous layer thickness at 100°C

3.2.3. Impact of hydrolysis on the mechanical behavior of PBAT

Typical stress/strain curves obtained from uniaxial tensile test are presented in Figure 8, before and after ageing for the three temperatures of interest here (80, 90 and 100°C). First, let us consider the mechanical behaviour of the unaged material. For low strains (i.e. below 10 %) an elastic behaviour is observed. Afterwards, yielding occurs due to the presence of plastic deformation within the sample. Next, hardening of the material occurs and leads to an increase in stress. Final breakage then occurs for a maximum stress of 26 MPa and an elongation close to 800 %. Concerning the tensile behaviour of PBAT after ageing, large changes are observed. A clear decrease in both stress and elongation at break are recorded. To examine the behaviour in more detail, all ultimate properties as well as modulus and yield stress values can be extracted. These are now plotted in Figure 9 for all conditions investigated.
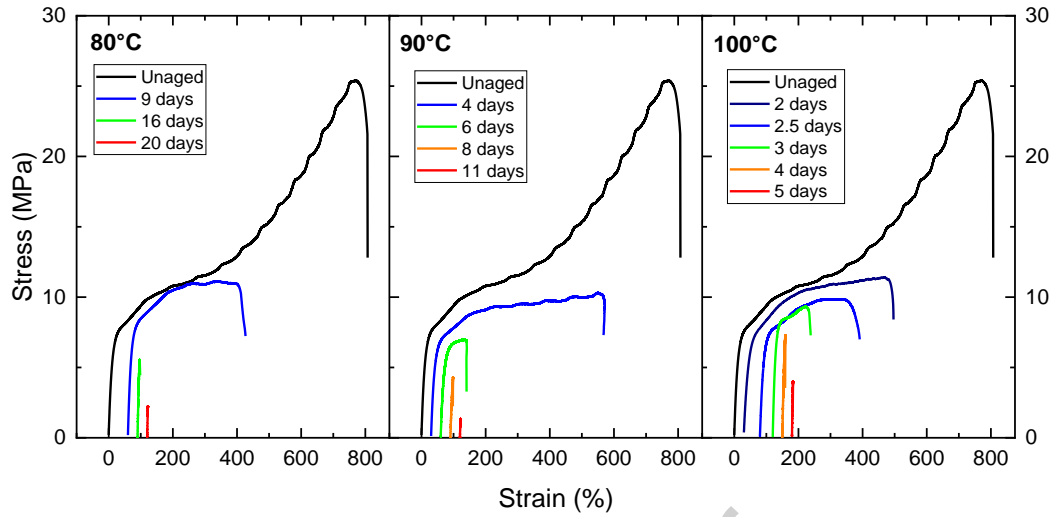
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Figure 8 – Changes in tensile curves as function of ageing duration at 100°C (a) 90°C (b) and 80°C (c)

There is a significant decrease in stress at break (σ_{break}) from 26 down to 2 MPa along with a decrease in strain at break (ε_{break}) from 800 % down to values close to zero. It is interesting to note that for the strain at break, a change in mechanical behaviour from ductile to brittle occurs once the strain at break reaches a value close to zero (i.e. after 4 days at 100°C, 8 days at 90°C and 16 days at 80°C). Concerning the yield stress (σ_y), it appears that at the early stages of ageing, its value remains constant while for longer ageing durations a decrease is observed. Again, there is a change in behaviour from ductile to brittle. Finally, an increase in Young's modulus (E) is measured during ageing that could be related to the observed increase in crystallinity ratio.
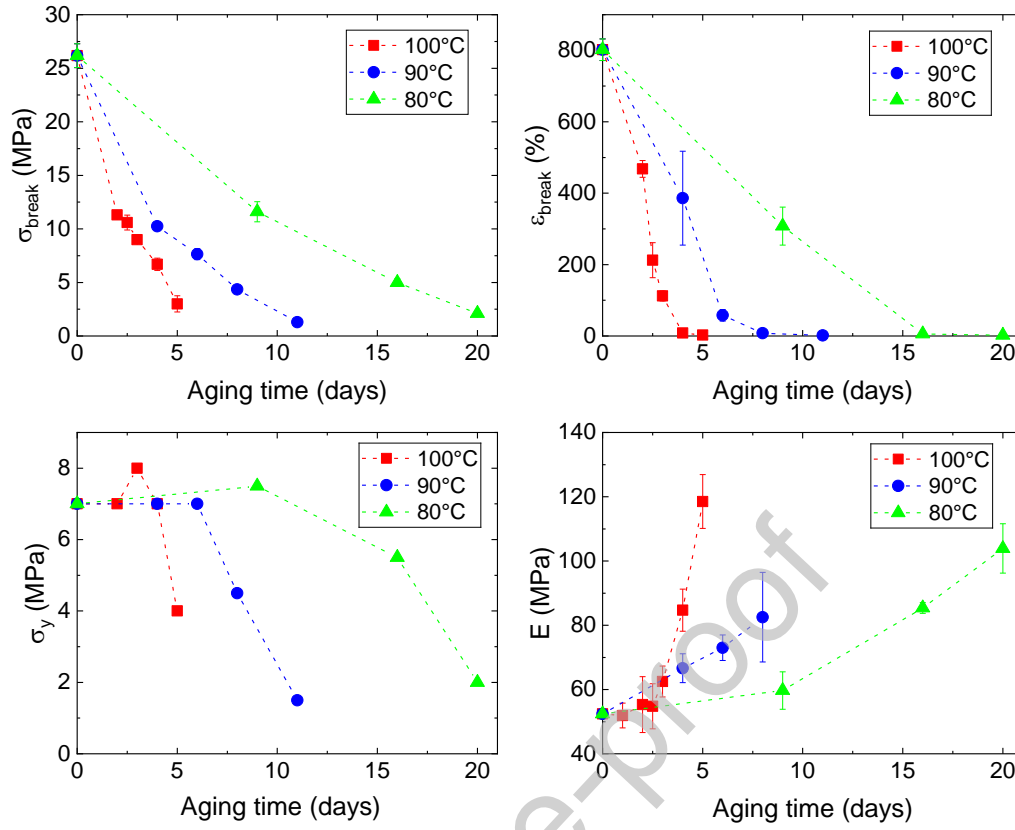
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Figure 9 - Impact of hydrolysis on tensile properties of PBAT as a function of ageing time

4. Discussion

4.1. Impact of ageing temperature on the hydrolysis rate

Based on the results presented above it is possible to assess the chain scission in the amorphous phase as a function of immersion time. Results obtained for the three temperatures considered here are plotted in Figure 10. The chain scission rate is not constant with ageing time, an acceleration occurs. This behavior can be due to an autoaccelerated hydrolysis (as already been shown in polymers with ester group) and/or due to an increase in the water content in the polymer as explained elsewhere. Let us focus here on the activation energy for the hydrolysis in PBAT; using shift factors from time/temperature supperposition it is possible to construct a master curve (not shown here) and the shift factors determined can be described using an Arrhenius behavior, Figure 11. It is thus possible to determine an activation energy for PBAT hydrolysis, a value of 70 kJ/mol is found here. The origin of the embrittlement within the polymer and its mechanical behavior changes during ageing will now be examined.
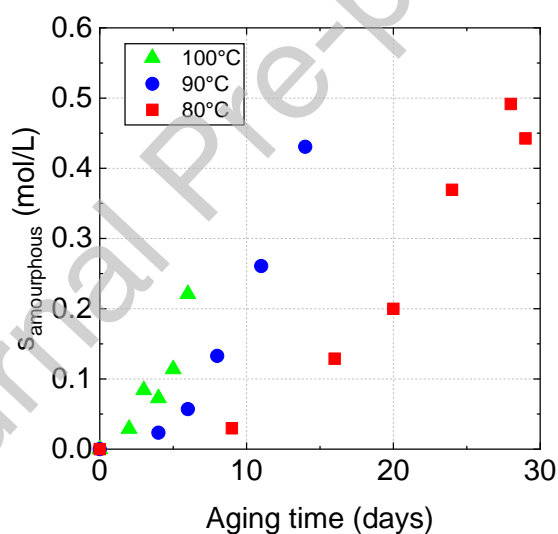

Figure 10 - Effect of temperature on the number of chain scissions in the amorphous phase as a function of ageing time
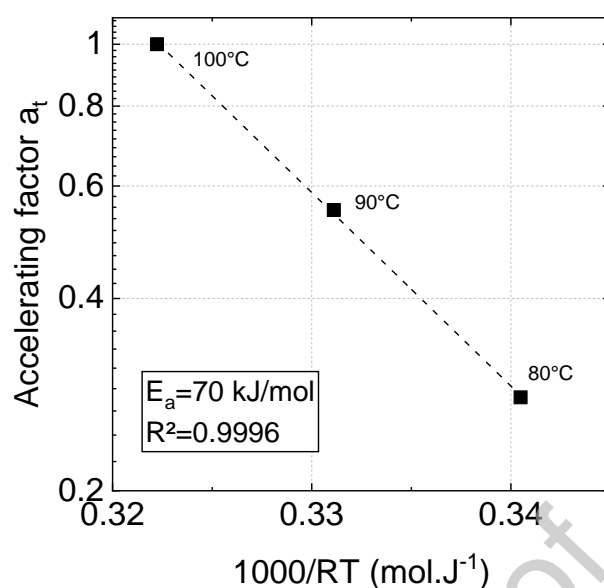
Figure 11 – Determination of the activation energy for PBAT hydrolysis

4.2. Origin of the embrittlement

During hydrolysis the mechanical behavior of PBAT undergoes large changes. Here, particular emhphasis will be placed on the elongation and stress at yield. For the first stage of hydrolysis the polymer remains ductile but a decrease in elongation at break is observed. For higher levels of degradation, PBAT becomes brittle. This behavior occurs when entanglements between macromolecular chains are not high enough to allow plastic deformation within the polymer when stretched. A decrease in yield stress is observed, which is very important in the framework of secondary microplastic formation; it means that the polymer can be easily fragmented by mechanical loads such as waves or impacts. Based on all these results, it is interesting to investigate whether it is possible to propose a relationship between the polymer structure and its mechanical properties during ageing that is independent of the ageing conditions. To do so the yield stress and strain at break values obtained after ageing are plotted as a function of the average molar mass in Figure 12.a and Figure 12.b respectively.
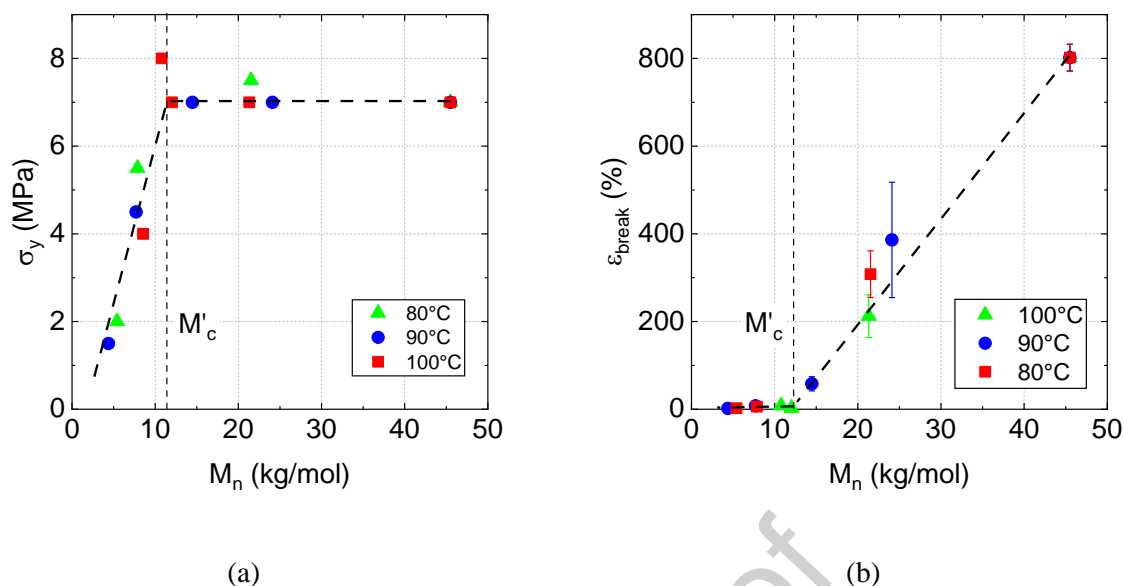
(a)   (b)

Figure 11 – (a) Yield stress and (b) Strain at break as a function of average molar mass

Figure 11 clearly shows that a critical molar mass in PBAT exists despite the fact that chain scission is not random within the polymer. This critical mass is found to be equal to 11 kg/mol and is independent of ageing temperature. Above this value the polymer exibits a ductile behavior and the yield stress is constant but elongation at break decreases. Below this value, the number of entanglements is no longer high enough within the polymer and the PBAT becomes brittle: elongation at break is thus very low and the yield stress starts to decrease. Also, it is interesting to note that two different criteria can be used to identify the critical molar mass. In the literature, the identification of such a value is generally highlighted using a single tensile criterion (usually either the stress or strain at break). A particularly interesting point here is the fact that the decrease in yield stress at very high levels of degradation can be described using a linear relationship with a slope of 0.83 MPa/mol/kg. Such a behavior has already been observed in PET [21] and can be used to investigate polymer fragmentation into microplastics. Indeed, it is believed that polymer fragmentation mostly takes place at extended degradation stages, i.e. at molar mass values below M'$_c$, when the polymer is brittle.

4. Conclusion

In this paper, the long-term behaviour of PBAT was investigated through ageing performed at 80, 90 and 100°C in water. Under these ageing conditions, hydrolysis occurs within the polymer. First, a reaction takes place on the ester located between the terephthalate and adipate groups; then, for higher levels of degradation the ester situated in the adipate group will also react with water. Hydrolysis of PBAT leads to a decrease in molar mass and an increase in crystallinity ratio due to the chemi-crystallization process. No changes in the nature of the crystalline structure are observed during ageing. The chain scissions process in PBAT can be described using an Arrhenian behavior (in the range of temperature considered here) with an activation energy of 70 kJ/mol. A significant change in mechanical properties occurs during ageing, where the polymer exhibits a ductile behaviour at the early stages of ageing and then a brittle behaviour after extensive degradation. It was demonstrated that this change in mechanical behaviour is directly linked with the loss in molar mass induced by ageing. Indeed, the polymer becomes brittle below the critical molar mass when there are no longer sufficient entanglements, identified here for PBAT as $M'_c=11$ kg/mol. The determination of such a value represents a starting point towards the understanding of microplastics formation as it is hypothesised that the fragmentation of polymers into microplastics starts once the polymer becomes brittle.

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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.

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