Accelerated ageing and lifetime prediction of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) in distilled water

Morgan Deroiné[a], Antoine Le Duigou[a], Yves-Marie Corre[a], Pierre-Yves Le Gac[b], Peter Davies[b], Guy César[c], Stéphane Bruzaud[a, *]

[a] Université Bretagne-Sud, EA 4250, LIMATB, F-56100 Lorient, France
[b] IFREMER, Marine Structures Group, Centre de Bretagne, BP 70, 29280 Plouzané, France
[c] SERPBIO, Université de Bretagne-Sud, Rue de Saint Maudé, 56321 Lorient, France

*: Corresponding author : Stéphane Bruzaud, tel.: +33 2 97 87 45 84 ; fax: +33 2 97 87 45 88 ; email address : stephane.bruzaud@univ-ubs.fr

Abstract:

Accelerated ageing was performed in distilled water at different temperatures (25, 30, 40 and 50°C) on poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), which is a biodegradable biopolymer, in order to estimate its lifetime in aqueous environment. In a first part, degradation mechanisms were followed by gravimetry, tensile tests and steric exclusion chromatography. Both immersion and relative humidity have been examined. In a second part, the strain at break was used as an indicator for lifetime prediction with an Arrhenius extrapolation. The study revealed the presence of only one irreversible degradation mechanism, i.e. hydrolytic degradation, which is temperature dependant. So, within the approach assumptions, the lifetime in distilled water of PHBV following Arrhenius behaviour can be predicted.

Keywords : Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) ; accelerated ageing ; hydrothermal degradation ; lifetime prediction

1. Introduction

Plastic materials were first developed over a century ago and are now used in many areas, especially in the packaging industry [1]. They have many advantages such as light weight, low price and formability, but they are also the cause of current environmental concerns [2]. Indeed, plastics are not only mainly based on non-renewable resources but they also have very long lifetimes, implying high volumes of waste. Despite the efforts undertaken to optimise waste treatment, large amounts of waste are found in nature polluting the world's oceans [3–5]. Progressive fragmentation of non-biodegradable plastics then occurs and their accumulation in the natural ecosystem causes the death of numerous marine animals [6] and increasing dangers for humans, who are at the end of the marine food chain.

In recent years, new bio-based and biodegradable polymers, such as polylactide (PLA), polyhydroxyalkanoates (PHA) or thermoplastic starch (TPS), have received considerable attention as one alternative to conventional petro-based plastics. A well-managed development of these new polymers could reduce plastic waste pollution, but their long term behaviour in an aquatic environment is still unknown. PHA's, which are microbial polyesters [7], are one of biopolymers which have recently received the most attention from the research community. In this work, poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), the most used PHA, has been studied. These polymers exhibit degradability, especially in marine environments [8–10]. Even although the PHBV degradation mechanism has been studied [11–13], the lifetime of PHBV is not clearly established, in spite of its importance for the environmental footprint.

Polymer ageing is a slow process so it is necessary to perform accelerated ageing tests in the laboratory. Water ageing is commonly accelerated using the time-temperature equivalence principle by raising the temperature of water baths. If it can be shown to be valid then

Arrhenius extrapolation can be used to predict the value of a given functional parameter (strain, strength, stiffness…) for lower temperatures and longer times. The Arrhenius relationship is widely used for lifetime prediction of polymer in aqueous environment [14–16] because this approach is relatively easy to perform. Predicting polymer lifetime requires all modes of degradation to be accounted for. This can be difficult in a complex environment such as seawater, where different processes, such as swelling, cracking, creep, hydrolysis, leaching, and even biodegradation, may occur simultaneously or successively. Celina *et al* [17] reviewed many studies where non-Arrhenius behaviour was observed due to at least two competing process, a phenomenon already observed in the PLA case [17].

As seawater is a complex medium which could generate chemical, physical or biological degradation mechanisms, the present study focuses on distilled water and chemical degradation due to a hydrolysis mechanism.

First of all, accelerated ageing was performed in distilled water baths at different temperatures: 25, 30 40 and 50°C. Water uptake, mechanical property evolution and molecular weight variation were studied and the relation between these parameters evaluated. Then, lifetime of PHBV samples immersed in distilled water was estimated for the case of temperate water temperature and the validity of this approach is finally discussed.

2. Experimental

2.1. Materials

PHBV (molar ratio of HB to HV of 92:8), commercialized in pellet form under the trade name ENMAT Y1000P, was supplied by Tianan Biological Materials Co. Ltd. (China). According to the manufacturer, PHBV characteristics are as presented on Table 1 and this grade has been previously characterized elsewhere [18].

Table 1

2.2. Tensile specimen manufacture

PHBV pellets were dried at 50°C under vacuum for 24h before processing. Pellets were then injected using a Battenfeld HM 80/120 press. The hopper temperature was 160°C and the profile was the following: 160-165-170-170°C. Injection pressure was 1200 bar and the mould temperature was kept at 35°C. All parameters were kept constant throughout the injection moulding process. PHBV was injected in a mold designed to produce standard specimens with a 180 x 10 x 4 mm geometry (specimen 1A according to NF EN ISO 527).

2.3. Characterization techniques

2.3.1. Water uptake

Dumbbell specimens were immersed in different containers (volume 25L) at 25, 30, 40 and 50°C, in distilled water for up to one year. The distilled water was renewed each week and some drops of bactericide were added in the baths to prevent bacterial growth and biological degradation of PHBV. Ageing test conditions are summarized in Table 2. Ten specimens were removed periodically, washed several times with distilled water, wiped and weighed at room temperature (23°C and RH = 50%) on a balance with a precision of 0.1 mg. The percentage weight gain at any time t, M_t, was determined by Eq. (1):

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

where W_t and W_0 are, respectively, the weight of sample after water exposure and the weight of dry material before immersion. Generally, the maximum moisture absorption, M∞, is calculated as an average value of several consecutive measurements that show very little variation of water absorption. In some cases, the equilibrium plateau is difficult to detect and diffusion coefficient can then be difficult to determine.

Table 2

2.3.2. Dynamic vapour sorption

A Dynamic Vapour Sorption (DVS 5000, TA Instruments) device was used to evaluate water diffusion coefficient on 160 microns thick films cut directly from the dumbbell specimens. This was performed at different relative humidities for temperatures ranging from 20°C to 50°C. Although water diffusion coefficients have been measured under conditions different from those of ageing, these values are still interesting because the water diffusion kinetics in a polymer are not greatly affected by the value of partial pressure of the water in the external environment.

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∞, by Fick's first law Eq. (2):

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

(2)

where e is the thickness of the sample. D can be calculated from the initial linear portion of the absorption curve. For $0.1 \leq M_t/M_\infty \leq 0.5$, the function $M_t/M_\infty = f(\sqrt{t})$ is linear and the Fickian diffusion coefficient D is determined by Eq. (3):

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

(3)

Commonly, the value of D is constant whatever the relative humidity, so extrapolation for immersion in water is then possible.

2.3.3. Mechanical analysis

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 and 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

specimens, which had been dried at room temperature until their weight was constant. At least five specimens were tested for each condition, and the results were averaged arithmetically.

2.3.4. Molecular weight measurement

Steric exclusion chromatography (SEC) was used to determine the evolution of molecular weight induced by hydrolysis. 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 6×10^6 g/mol. The weight-average molecular weight ($\overline{M}_w$) and number-average molecular weight ($\overline{M}_n$) were obtained from the SEC analysis. The polydispersity index (PI) was calculated as $\overline{M}_w/\overline{M}_n$.

2.3.5. Methodology for lifetime prediction

The Arrhenius law is widely used for lifetime prediction of polymer materials, and can be based on different macroscopic indicators such as strain at break [19] or failure stress [20]. In this study, strain at break appears to be a good indicator for lifetime prediction in an aqueous environment, considering that the modification of the sample section has a negligible effect on strain measurement [21].

Nevertheless, there are some basic assumptions to take into account. In order for the approach to be valid, both natural and accelerated ageing should lead to the same microstructural changes, and degradation should involve a single chemical process activated by the temperature.

The Arrhenius approach is based on time-temperature superposition [22] where the activation energy, E_a, must be constant in the temperature range studied. The activation energy is

defined as the minimum energy required to start a chemical reaction, hydrolysis in this case. If the curves obtained at different temperatures all have a similar shape, the normalized data can be plotted against the logarithm of time. Thus, it is possible to overlay all the curves by defining a shift factor a_T, (Eq. 4) in order to plot a master curve:

$$a_T = \exp\left[\frac{E_a}{R}\left(\frac{1}{T_{ref}} - \frac{1}{T}\right)\right]$$

(4)

E_a is the Arrhenius activation energy, R is the gas constant and T is the absolute temperature. By convention, the multiplicative factor a_T for the reference temperature (25°C here) is set to 1. If the empirically derived shift factors lead to superposition of the data from all accelerated temperature, they can be plotted on an Arrhenius plot (log a_T versus 1/T) to examine whether a linear plot results.

3. Results and discussion

3.1. Accelerated ageing study

3.1.1. Water uptake

Fig. 1 shows the weight gain of PHBV as a function of $t^{1/2}$ (expressed in hours$^{1/2}$) at different immersion temperatures in distilled water. All the sorption curves follow the same trend and can be divided into three stages. An initial linear relationship between water uptake and square root of time is observed at all ageing temperatures, followed by an intermediate plateau. However, the equilibrium plateau is not easy to detect. Therefore, DVS experiments have been performed on film specimens and the curves, obtained at each relative humidity, indicated a typical Fickian behaviour with a well-defined saturation plateau. Examples of results obtained at a relative humidity of 50% and for the different temperature are presented in Fig. 2.

Figure 1 - Figure 2

The last step, shown on Fig. 1, corresponds to an increase of the water content assigned to a deviation phenomenon from Fickian behavior. Indeed, after the proposed plateau, a continuous increase in water absorption occurs after about 360 days. Moreover, the water content increase is very dependent on the immersion temperature; it is much stronger at higher temperature. This increase, already observed in the literature [23,24], indicates degradation within the polymer and can be attributed to several phenomena such as chain scission due to a hydrolytic mechanism [23]. Moreover, the hydrolysis process products, such as carboxyl groups, have a strong water affinity and may progressively increase the water content [23,24]. Then, the increase is not sudden, as observed in a recent paper in the case of PLA [17], but more progressive with time.

Using Eq. 3 and DVS results where M_t/M_∞ is included between 0.1 and 0.5 (Fig. 2.), Fickian diffusion coefficients were calculated (Table 3). Increasing the temperature has an effect on the diffusion coefficients D. Tang *et al* obtained lower values after immersion in deionized water [25]. Moreover, a linear relation (R²=0.98) is noted between lnD and the inverse of temperature (Fig. 3), suggesting that these coefficients obey an Arrhenius law (Eq. 7):

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

(7)

Table 3 & Figure 3

The activation energy E_a is obtained by DVS from the slope of the linear fitting of lnD vs T^{-1} and is estimated as 70 kJ.mol^{-1}. The relatively high activation energy can be attributed to the highly crystalline and hydrophobic character of the PHBV tested here. Very few published values are available but E_a was found to be slightly lower, around 43.7 kJ.mol^{-1} in deionized water [25] and 56.5 kJ.mol^{-1} in distilled water [26]. Several reasons could explain this difference: the kind of aqueous environment, the grade of PHBV used or the processing conditions which modify the polymer morphology.

DVS results show that water diffusion in this PHBV is Fickian and a thermally activated process following an Arrhenius relationship, and the activation energy is constant over the temperature range. Moreover, the value of D is constant whatever the relative humidity for one temperature. By reverse calculation, it is then possible to find the corresponding saturation mass of immersed specimens from the diffusion coefficients evaluated by DVS and the slope of the sorption curves.

3.1.2. Mechanical properties

Tensile tests were carried out on the aged PHBV specimens in the wet state and after drying, providing information on both reversible and irreversible degradation mechanisms. Fig. 4. presents the evolution of tensile behaviour curves obtained at 40°C for different periods, on wet and dried specimens. The curves obtained in the dry state for the first months allow the plasticization to be revealed. The behaviour evolves towards irreversible degradation, especially considering the curve obtained after immersion for 12 months. Fig. 5 shows the tensile behaviour of PHBV samples after 12 months of immersion in distilled water at different temperatures. At low temperature (25 and 30°C), ductility increases slightly for wet PHBV. After drying, PHBV partially recovers its initial properties, highlighting a plasticization effect of the water. At higher temperature (40 and 50°C), mechanical behaviour of wet samples becomes more brittle than that for the unaged PHBV. This trend is more pronounced at 50°C, with an important decrease of strain and stress at break (Table 4). At these higher temperatures, even after drying, there is no return to the initial state showing, therefore, typical irreversible degradation.

Figure 4 - Table 4 - Figure 5

Tests on samples both unaged and aged in air for 360 days (in the dark at 23°C and RH=50%) have been performed (Table 4). Mechanical properties are not stable over time. Indeed, after

one year, Young's modulus and stress at break increase while strain at break decreases slightly. These physical ageing phenomena, already observed in the literature [18,27], correspond to a structural relaxation post-crystallization process. After injection, the material was frozen before its crystallization state was completely achieved. A secondary crystallization of the amorphous spherulitic lamellae is one of the hypotheses which could explain this evolution with time [28].

Young's modulus evolutions after immersion in distilled water at different temperatures are also shown on Table 4. Up to 40°C, the stiffness presents a slight increase over ageing time compared to the PHBV specimen aged for 1 year in air, while at 50°C, a 30% increase in Young's modulus is observed.

Fig. 6 and 7 show the evolution of the strain and stress at break with time.

Figure 6 - Figure 7

Water immersion induces an increase of failure strain for short times (< 50 days) followed by a clear drop, especially emphasized at high temperature, i.e. above 30°C, as already described elsewhere [9,29]. After drying, the strain at break tends to decrease whatever the temperature, highlighting the development of irreversible degradation as a function of immersion temperature.

The stress at break remains constant for wet samples immersed at 25 and 30°C (Fig. 7). For samples aged at higher temperatures, there is a sudden increase after 1 month, followed by a constant decrease at 40°C and more accelerated at 50°C. In dry tests, the failure strain continuously decreases over immersion time and similar observations can be made.

The increase of temperature promotes a premature loss of properties, especially at 40 and 50°C with an irreversible degradation of PHBV specimens. Moreover, as expected in the

lifetime prediction methodology, the effect of increasing temperature shifts the property degradation to shorter ageing periods.

3.1.3. Molecular weight analysis

Molecular weight measurement provides a physic-chemical indicator which can clarify the irreversibility of degradation mechanisms. Changes to PHBV specimens during immersion in distilled water are shown in Fig. 8, and values after one year of immersion are presented in Table 5.

Figure 8 – Table 5

Lower temperature immersions (25 and 30°C) result in similar changes over time, with decreases of $\bar{M}_w$ between 30 and 40%, respectively. After immersion at 40°C, the weight average molecular weight decreases quite drastically through the first 4 months, corresponding to a reduction of about 55%, and it continuously decreases up to the end of the study reaching a final $\bar{M}_w$ loss of 70%. At 50°C, there is a sudden drop during the first two months ($\bar{M}_w$ decrease of about 75%) and then $\bar{M}_w$ remains relatively constant until 12 months with a large final reduction of 85%.

The increase of the temperature promotes ester bond cleavage due to accelerated water penetration. This is characteristic of a hydrolysis mechanism. Microstructure of polymers influences their degradation rate. Here, hydrolysis is quite slow because PHBV is highly crystalline (above 60%) while the hydrolysis phenomenon occurs preferentially in amorphous regions [30,31]. Thus, the shape of the curve presented in figure 8 could be attributed to water attack in the amorphous regions and then a very slow water attack on the crystalline regions [32].

3.1.4. Structure/properties relationship

Fig. 9 shows the different relationships between mechanical properties (σ_b and ε_b) and molecular weight ($\overline{M}_w$). A similar bi-linear behaviour is observed for both but with different magnitudes: the curves of the stress and strain at break versus $\overline{M}_w$ both exhibit a change in slope for $\overline{M}_w$ around 110 000 g.mol^{-1}. The decrease of molecular weight, due to extensive chain breakage, results in embrittlement of the PHBV specimens. Moreover, we assume that a molar mass threshold exists above which mechanical properties are not altered. Below this threshold, PHBV degradation occurs faster and the material loses its mechanical performance, corresponding to an "end of use" criterion.

Figure 9

3.2. Lifetime estimation

3.2.1. Validity of assumptions

The first part of this study dealt with the accelerated ageing of PHBV specimens immersed in distilled water at different temperatures, and results showed that PHBV is sensitive to hydrolytic ageing. This part aims to develop a framework which will allow the prediction of the lifetime of PHBV in distilled water.

When exposed to distilled water and considering DVS results, the PHBV water absorption follows Fick's law. These observations suggest that, as long as hydrolytic degradation remains limited, the water absorption in PHBV can be predicted using a Fickian behaviour with a linear Arrhenius law for water diffusion kinetics at different temperatures, using the time/temperature principle. The water presence leads to chain scission hydrolysis which is more and more significant when the water temperature increases. Indeed, when PHBV is immersed in distilled water for longer times or higher temperatures (40 and 50°C), irreversible embrittlement of the polymer is observed with the appearance of chain scission mechanisms due to the ester function hydrolysis.

The ideal case of hydrolysis is one in which the chain scission is non-autocatalytic, non-diffusion controlled and purely random [23]. Indeed, if degradation involves the diffusion of a reactive component from the external environment to the bulk of the material, non-uniform ageing in the polymer thickness can occur. This phenomenon is due to a competition between diffusion and reactive consumption; when diffusion is faster than reaction, then degradation is uniform in the sample thickness whereas, when reaction is faster than diffusion, the resulting degradation is non-uniform [33,34]. However, in this study, degradation is not uniform because the surface is directly in contact with water and the strain at break is governed by surface properties. The strain at break is used as an indicator of aging in order to get around this complication.

3.2.2. Master curve plotting

The evolution of the normalized strain ($\varepsilon_t/\varepsilon_0$) versus the logarithm of time is shown in Fig. 10a, and the curves at each temperature present a similar shape. Then, by successive shifts of the curves established at different temperatures, it is possible to obtain a unique curve (Fig. 10b) associated with the selected reference temperature, i.e. 25°C ($a_{25°C}=1$). An Arrhenius plot of the empirically derived shift factors gives almost linear results with a high correlation coefficient (Fig. 11), suggesting that the Arrhenius approach can be used here. The activation energy value E_a, directly related to the slope, is calculated to be equal to 93 kJ.mol^{-1} for the degradation of PHBV specimens immersed in distilled water.

Figure 10 – Figure 11

Data for long time immersion are necessary to compare with accelerated result predictions. The accelerated ageing of PHBV specimens was performed in distilled water only to study the water effect. Validation of the approach should, therefore, be done with values from specimens immerged at a specific temperature in distilled water, but data are not available. However, considering an end of use criterion, it would then become possible to evaluate a

lifetime prediction, based on the evolution of the failure strain over a time scale appropriate to a desired temperature, as presented in Fig. 12.

Figure 12

3.2.3. Limits of the approach

Some limits to this approach should be highlighted. First, the risk with using increasing temperature to accelerate ageing is that the failure mechanisms which are induced may not be those which would occur naturally when ageing is performed at ambient temperature for longer times. It is clear that, in order to investigate Arrhenius behaviour and thereby to gain confidence in predictions, degradation rates or accelerative shift factors should be available over the largest temperature range possible [35]. Moreover, another factor to consider is specimen geometry. Tests carried out on film specimens provide the simplest information to analyze because in each case, water diffusion is faster than reaction. Considering distilled water as a study parameter to determine lifetime in seawater is also questionable, since the degradation rate could be modified in seawater, which is a complex environment with a large number of mineral salts. Current work is focusing on the other mechanisms which occur in sea water, in order to complete the predictive model.

4. Conclusions

Accelerated ageing of PHBV specimens has been performed in distilled water at different temperatures in order to predict their lifetime in an aqueous environment. Both immersion and relative humidity have been examined. Even if PHBV is well-known to undergo surface erosion with an enzymatic degradation mechanism, only the water effect is studied here, and the aim is to decouple enzymatic mechanisms and hydrolytic mechanisms. Different characterization techniques have been used in order to follow the hydrolytic degradation.

First, the water uptake within PHBV in distilled water is temperature dependant and follows Fickian behaviour. Using the DVS results, a linear relation appears between ln D and the

inverse of temperature. Despite the high crystallinity of PHBV, chain breakage activated by the temperature occurs, caused by hydrolysis of ester bonds as revealed by SEC. The high crystallinity of PHBV may be counterbalanced by the physical state of PHBV at the temperatures studied, which are systematically higher than the glass transition temperature $(T_g(PHBV) = 4°C)$. In all the temperature range studied here, PHBV is in the rubbery state in which the diffusion phenomena are gradually accelerated when the ageing temperature becomes more and more distant from the T_g. Moreover, the loss of linearity between mechanical properties and molecular weight reveals that a threshold in molecular weight exists above which PHBV mechanical properties are not altered by the degradation.

This study also revealed the presence of one dominant degradation mechanism in distilled water, hydrolysis, which is temperature dependant, and experimental data acquired allow a time-temperature superposition principle to be applied with an Arrhenius methodology.

This provides a tool for predicting the long term behaviour of these materials in distilled water. The model is now being extended to include additional degradation mechanisms, notably biodegradation, in order to investigate long term behaviour in sea water.

5. Acknowledgements

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Figure captions

Fig. 1. Evolution of water uptake as a function of the square of root of immersion at different temperatures in distilled water.

Fig. 2. Plots of M_t/M_∞ against $t^{1/2}$/thickness for PHBV at different temperatures obtained by DVS and corresponding at 50% RH.

Fig. 3. Identification of the diffusion coefficient of distilled water in the PHBV for different temperatures by DVS.

Fig. 4. Evolution of tensile behaviour of PHBV specimens aged at 40°C for different periods, before and after drying.

Fig. 5. Evolution of the tensile behaviour of PHBV specimens aged in distilled water at 25, 30, 40 and 50°C after 360 days: before (a) and after drying (b).

Fig. 6. Evolution of the stress at break of PHBV specimens aged in distilled water at 25, 30, 40 and 50°C after 360 days: before (a) and after drying (b).

Fig. 7. Evolution of the strain at break of PHBV specimens aged in distilled water at 25, 30, 40 and 50°C after 360 days: before (a) and after drying (b).

Fig. 8. Evolution of the molecular weight, $\bar{M}_w$, of PHBV specimens aged in distilled water at 25, 30, 40 and 50°C after 360 days.

Fig. 9. Evolution of the stress at break (a) and strain at break (b) as a function of molecular weight.

Fig. 10. Evolution of the normalized strain at break as a function of ageing time for all the temperatures (a) and master curve (b).

Fig. 11. Identification of the activation energy for the strain at break indicator.

Fig. 12. Evolution of different percentage of loss properties and extrapolation to 13°C in order to predict lifetime.

Table 1. Properties of the studied polymer before ageing.

Properties	Values
Density (g.cm^{-3})	1.25
T_g (°C)	4
T_m (°C)	175
$\bar{M}_w$ (kg.mol^{-1})	400

Table 2. Exposure times for samples in distilled water at different temperatures.

Temperature (°C)	Ageing period (days)					
unaged specimen						
23	0					360
distilled water ageing						
25	-	60	120	180	270	360
30	30	-	-	180	-	360
40	30	60	120	180	270	360
50	30	60	120	180	-	360

Table 3. Fickian diffusion coefficients obtained by DVS for PHBV specimens at different temperatures.
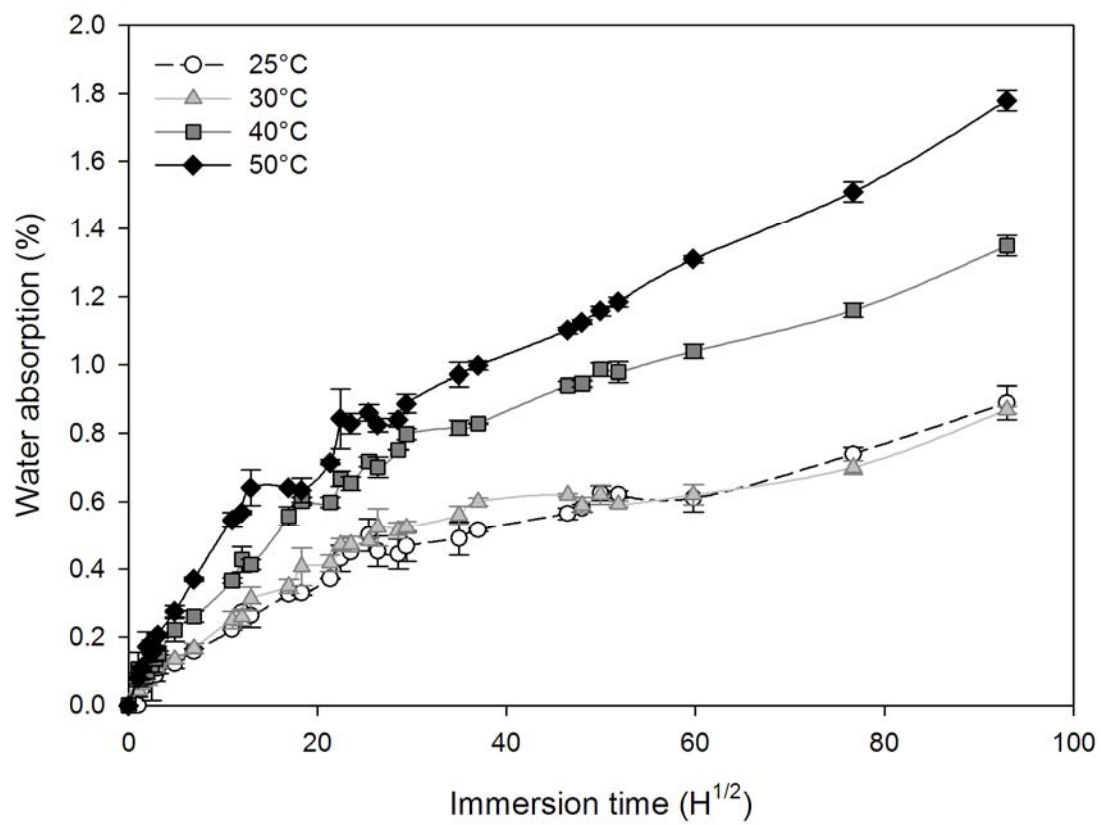
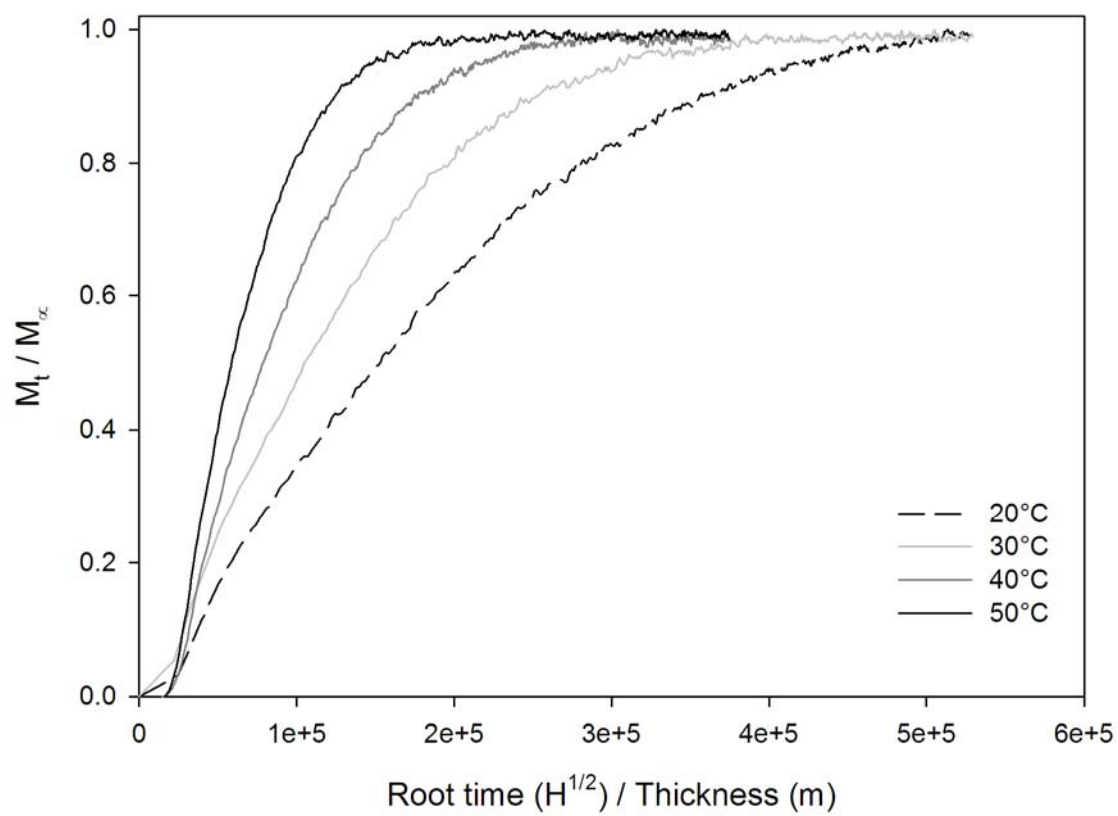| T (°C)	D.10^{-13} (m².s^{-1})
20	19
30	36
40	80
50	281

Table 4. Evolution of PHBV mechanical properties before and after ageing in distilled water at different temperatures.
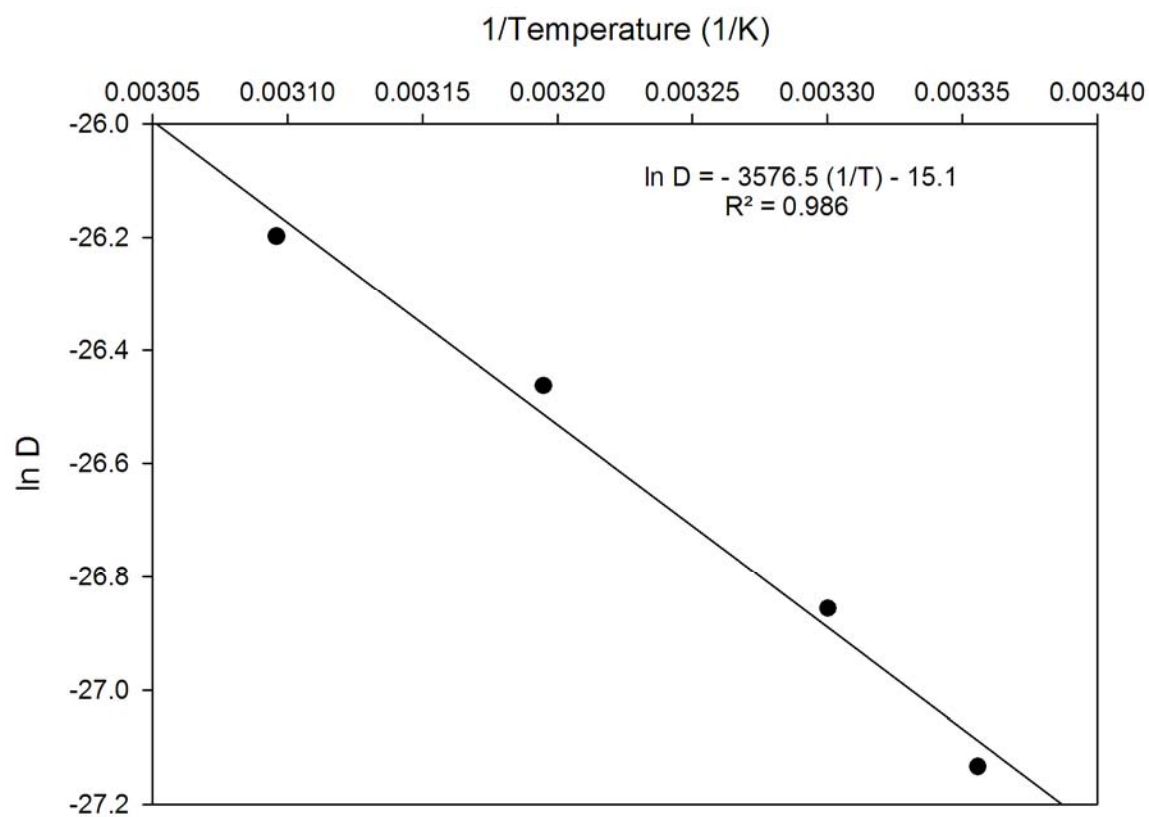
	T (°C)	Ageing time (days)	E (MPa)		σ_b (MPa)		ε_b (%)	
unaged			4390 ± 102		35 ± 1.2		1.4 ± 0,1	
aged in air		360	5005 ± 104	+ 14%	37 ± 0.6	+ 6%	1.1 ± 0.04	- 22%
aged in water	25	360	5065 ± 58	+ 15%	36.5 ± 0.9	+ 4%	1.1 ± 0,1	- 22%
	30	360	4612 ± 269	+ 5%	35.7 ± 1.6	+ 2%	1.0 ± 0,1	- 28%
	40	360	4946 ± 236	+ 13%	26.5 ± 1	- 25%	0.62 ± 0,05	- 55%
	50	360	5686 ± 181	+ 30%	2.5 ± 0.5	- 92%	0.26 ± 0,04	- 82%

Table 5. Evolution of number-average molecular weight ($\overline{M}_n$), weight-average molecular weight ($\overline{M}_w$) and polydispersity index $\overline{M}_w/\overline{M}_n$ of PHBV samples aged 12 months in distilled water at different temperatures.

T (°C)	$\overline{M}_n$ (g.mol^{-1})	$\overline{M}_w$ (g.mol^{-1})	PI
unaged	172 600	398 800	2.3
25	173 000	273 600	1.6
30	141 400	233 900	1.7
40	79 300	112 600	1.4
50	47 600	65 100	1.3

ln D = - 3576.5 (1/T) - 15.1
R² = 0.986

a.

a. wet

b. dry

a. wet

b. dry

a.

b.

$E_a = 93$ kJ / mol
$R^2 = 0.99$

ACCEPTED M